Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality

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Abstract

The purposes of this study were to investigate the removal efficiency of ammonium (NH_4^+) ion from aqueous solution using the natural Turkish (Yıldızeli) zeolite and to characterize equilibrium isotherms. Experiments were carried out using batch method as a function of the solution pH, shaking time, dosage of adsorbent, and temperature. All these factors affected NH_4^+ ion removal from aqueous solution. Equilibrium modelling data were fitted to linear Langmuir and Freundlich models. Dubinin–Redushckevich (D–R) isotherm was applied to describe the nature of ion exchange of NH_4^+ and found that it occurred physically. Thermodynamics parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated. These parameters confirmed that ion exchange of NH_4^+ by the zeolite was feasible, spontaneous and exothermic in nature. Based on the results, it can be concluded that the natural Turkish (Yıldızeli) zeolite is suitable for the removal of NH_4^+ ions in wastewater treatments and agricultural purposes to in terms of sustainability of environmental quality.
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Keywords: Ammonium removal; Natural zeolite; Isotherm; Thermodynamic parameter

1. Introduction

Nitrogen (N) is one of the essential elements for plants, and lack of N in soils often limits agricultural production. The principal forms of N in soil are ammonium (NH_4^+) and nitrate (NO_3^-) and NH_4^+ ions in soils are converted to NO_3^- by microorganisms [1,2]. However, when N compounds are more than needed of plants, parts of the nitrogen compounds (especially NO_3^- ion) leach from soil profile and lead to ground water pollution [1,3]. Therefore, decrease of the transformation and moving of N compounds using adsorbent materials as zeolite and betonite is crucial to save ground water and environmental quality in intensive agricultural production. The presence of excess N compounds also causes the environmental destroy, so N compounds play an important role on water pollution. Therefore, the control of them has vital importance. The ammonia and ammonium ions are the more commonly encountered N compounds in wastewater.

Zeolites have been used as soil conditioners to improve the physical and chemical properties of soil, and the application of zeolite to soils may reduce loses of nutrient and water [4]. Natural zeolite is porous material with high cation exchange capacity (CEC), cation selectivity, higher void volume and great affinity for NH_4^+ [5]. The material has received great interest minimizing ammonia (NH_3) volatilisation in soils with low CEC [6] and NH_3 emission from farm manure [7].

The general formula of a zeolite is follows:

$$(M_x^+, M_y^{2+})(Al_{(x+2y)}Si_{n-(x+2y)}O_{2n})\cdot mH_2O$$
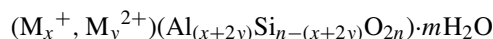
where M^+ and M^{2+} are monovalent and divalent cations such as Na^+, K^+, and Ca^{2+}, Mg^{2+}, Ba^{2+}, respectively. They are called the exchangeable cations. Al^{3+} and Si^{4+} are known as the structural cations, and they make up the framework of the structure with O [5]. In several studies, authors have also reported the use of natural zeolite as a sorbent for trace metals, N compounds, and cations [6–10]. Natural zeolite reserves occur most frequently in Japan, USA, Russia, Hungary, Greece, Croatia, Serbia and Turkey [3,4,11].

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Ion exchange process is used in various fields for ions adsorption in recent years. However, ion exchange processes, which used organic resins, are very expensive. Hence, cheaper materials such as zeolite and sepiolite are needed. The use of zeolite for removal of NH_4^+ ion from aqueous solution and wastewater is especially promising and very competitive compared to other processes such as biological and chemical treatments [3,12,13].

Although the large number of different studies on the removal of ammonium ion from aqueous solutions using zeolite, every special zeolite material requires individual research. Therefore, the results obtained from a study carried out by using zeolite as adsorbent are important with respect of NH_4^+ ion removal from wastewater and farm manure, especially urine of animals, and reducing N losses via NH_3 volatilisation and NO_3^- leaching in soils with increasing soil retention capacity for NH_4^+. In this regard, the objectives of this study were to investigate the effect of the pH, shaking time, dosage of adsorbent, and temperature on ion exchange of NH_4^+ by the natural Turkish (Yıldızeli) zeolite from aqueous solution and to determine the equilibrium isotherms.

2. Materials and methods

The natural Turkish zeolite (Yıldızeli town of Sivas) used as an adsorbent in this study was a commercial sample, supplied from Rota A.Ş. Mining Company, Istanbul, Turkey. The mineralogical and chemical composition of the zeolite was determined by using Rigaku D-Max III X-ray diffractometer (Table 1). The natural zeolite samples were crushed in a mortar and sieved using 200-mesh (75 μm) sieve. The crushed samples were dried in an oven at 105 °C for 24 h before used in the experiments.

Preliminary experiments were conducted to optimize general patterns of NH_4^+ ion removal from aqueous solution; pH of solution, shaking time, dosage of adsorbent and temperature. The ion exchange of NH_4^+ ion on the zeolite was carried out using a batch method. The batch experiments were conducted 0.8 g of adsorbent with 40 mL of solutions in the range

Table 1
Chemical and mineralogical composition of natural Turkish (Yıldızeli) zeolite

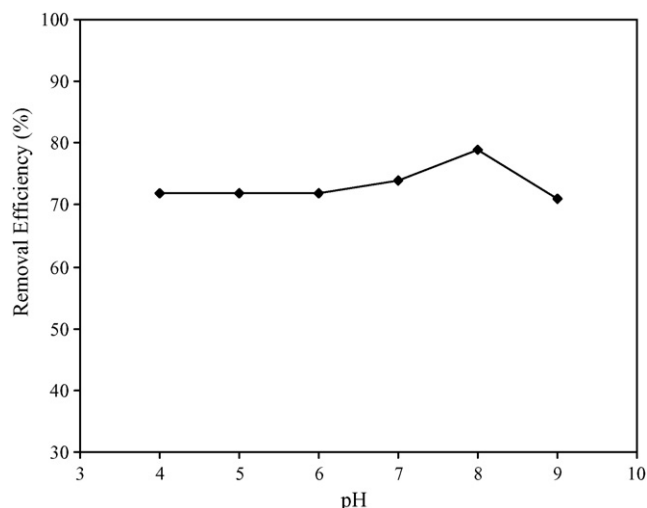| Constituent	Value (%)
SiO_2	64.84
TiO_2	0.32
Al_2O_3	13.69
Fe_2O_3	1.64
MnO	0.04
MgO	1.62
SrO	0.54
BaO	0.12
CaO	5.88
Na_2O	0.95
K_2O	0.50
P_2O_5	0.07
Loss of ignition (at 1000 °C)	10.42
XRD-mineralogical analysis	
Clinoptilolite/heulandite + mordenit	95
Quartz	5

Fig. 1. The effect of pH on NH_4^+ ion removal using the natural zeolite (NH_4^+ ion concentration: 60 mg L^{-1}; adsorbent dosage: 0.4 g; shaking time: 60 min; temperature: 21 °C).

of 20–400 mg L^{-1} initial NH_4^+ concentrations. Analytical grade ammonium chloride salt (NH_4Cl) and deionised water were used in the preparation of the stock NH_4^+ solutions. The stock solutions were diluted to prepare for working solutions.

The screw cap bottles containing sorbate and sorbent were placed in to a shaker (Nüve ST 402) and shaken at 21, 30, 40 and 50 °C at 200 rpm. After equilibrium time, samples were filtered through whatman 42 filter paper. Filtrates were analyzed immediately by steam-distillation method [14]. The removal efficiency (%) and the amounts of exchanged NH_4^+ ion (q_e) by the zeolite were computed using Eqs. (1) and (2), respectively:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q_e is the amount of exchanged ammonium ions (mg g^{-1}), C_0 and C_e are the initial and equilibrium concentrations of ammonium in solution (mg L^{-1}), respectively. V is the solution volume (L) and m is the adsorbent weight (g). The mean value of the duplicate analysis was used to calculate the amount of NH_4^+ in solution, and the limit of error of duplicate samples was lower than 5%.

3. Results and discussion

3.1. Effect of pH

The removal of NH_4^+ ion from aqueous solution using the natural zeolite was studied at pH values 4–9 and the data obtained were given in Fig. 1. The pH of the aqueous solution was found to be an important factor for the exchange of NH_4^+ ion by zeolite. The removal efficiency increased by raising the pH from 4 to 8 and reached a maximum value at pH 8, and then it decreased at pH 9. The decrease in the NH_4^+ removal efficiency after pH 8 may be due to two factors: (i) in partial dissolution of the

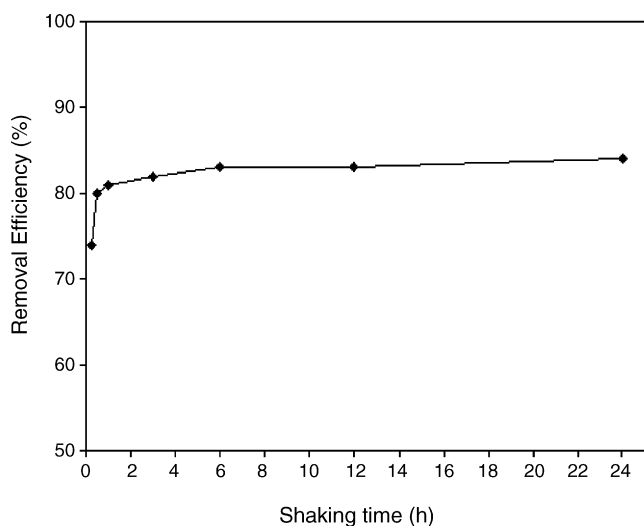Fig. 2. The effect of shaking time on NH_4^+ ion removal using the natural zeolite (NH_4^+ ion concentration: $60\,mg\,L^{-1}$; adsorbent dosage: 0.4 g; pH: 8; temperature: 21 °C).

natural zeolite [5]; (ii) the conversion probability of NH_4^+ into NH_3 specimen [15].

3.2. Effect of shaking time

Fig. 2 shows the effect of shaking time on the removal of NH_4^+ ion using the natural zeolite. Removal efficiency of NH_4^+ ion increased with increasing shaking time and 75% of NH_4^+ ion removal was completed within 15 min. It reached up 80% within 30 min and became very slow with increasing of shaking time. This may be ascribed to the utilization of the most readily available adsorbing sites of the zeolite that leads fast diffusion and rapid equilibrium attain [16]. After, shaking time of 24 h, removal efficiency of NH_4^+ ion was found as 83%. As seen from these values, there is no significant difference between the removal efficiencies determined after 30 min and 24 h. On the basis on these results, a 30 min shaking period was selected for all further studies.

3.3. Effect of adsorbent dosage

The effect of adsorbent dosage on the removal efficiency of NH_4^+ ion was studied using 0.1, 0.2, 0.4, 0.8, 1.2 and 1.6 g zeolite and the results obtained were given in Fig. 3. The removal efficiency of NH_4^+ ions by the zeolite increased with increasing the amount of zeolite, and a plateau occurred at 0.8 g of adsorbent. Fig. 3 also indicates that the NH_4^+ ion removal was negligible at higher amounts of adsorbent dosage than 0.8 g. This may be attributed to the formation of aggregates at higher solid/liquid ratio or precipitation of particles.

3.4. Effect of temperature

Fig. 4 indicates the effect of the temperature (21, 30, 40, and 50 °C) on the removal of NH_4^+ ion. The amount of NH_4^+ ion removed from aqueous solution decreased by rising temperature
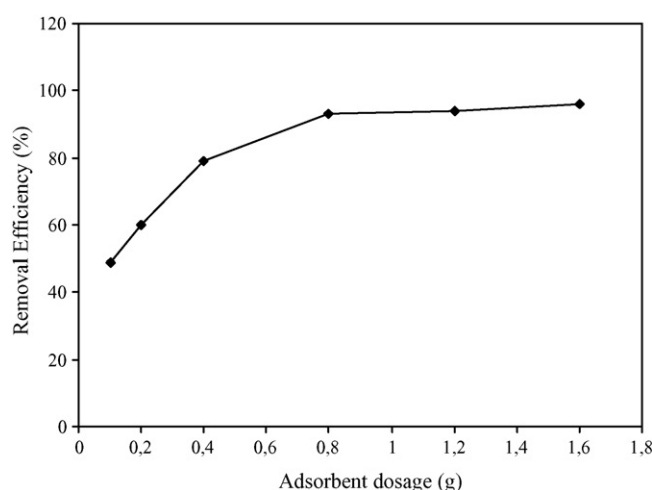

Fig. 3. The effect of adsorbent dosage on NH_4^+ ion removal using the natural zeolite (NH_4^+ ion concentration: $60\,mg\,L^{-1}$; shaking time: 30 min; pH: 8; temperature: 21 °C).

from 21 to 50 °C. The highest removal efficiency was found to be 94% at 21 °C. A decrease in the removal efficiency of NH_4^+ ion with the rise in temperature was due to the increasing tendency to desorb from the interface to the solution. This result also indicated that the adsorption process of NH_4^+ onto natural zeolite was exothermic in nature.

3.5. Ion exchange isotherms

Langmuir and Freundlich models are used to describe the equilibrium isotherm data [17]. In this study, both models were employed to describe the relationships between the amounts of exchanged NH_4^+ ion by zeolite and its equilibrium concentration in the solution. The experimental data conformed to the linear
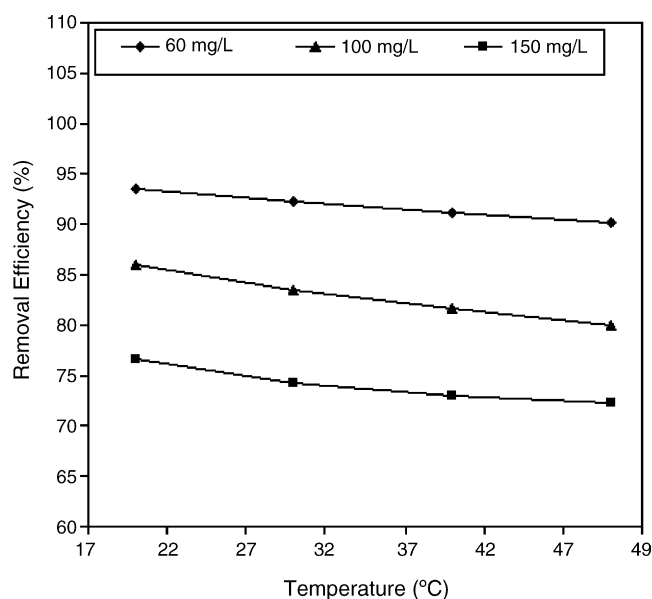

Fig. 4. The effect of temperature on NH_4^+ ion removal using the natural zeolite (NH_4^+ ion concentration: $60\,mg\,L^{-1}$; optimum adsorbent dosage: 0.8 g; shaking time: 30 min; pH: 8).
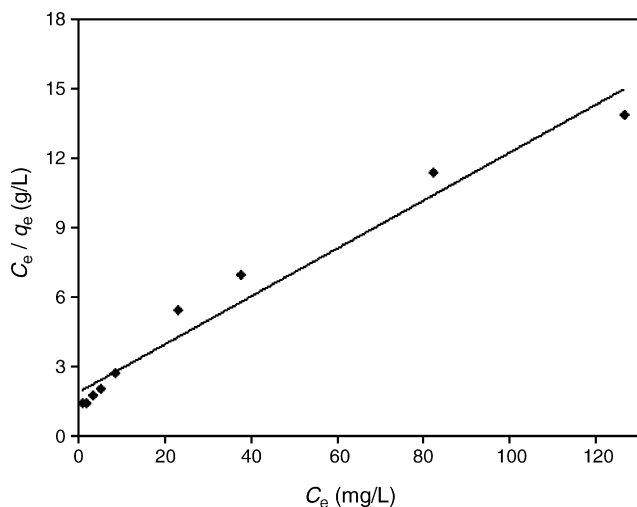
Fig. 5. Linear plot of Langmuir isotherm of NH_4^+ ion adsorption on the natural zeolite (optimum adsorbent dosage: 0.8 g; shaking time: 30 min; pH: 8; temperature: 21 °C).

form of Langmuir model expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{kb} + \frac{C_e}{b} \tag{3}$$

where C_e is the concentration of NH_4^+ ion in equilibrium solution (mg L^{-1}), q_e is the amount of NH_4^+ adsorbed (mg) by per unit mass of adsorbent (g), and the value of b (mg g^{-1}) and k (L mg^{-1}) are maximum adsorption capacity of adsorbent and the adsorption energy coefficient, respectively. The determination coefficient value of the linear plot of Langmuir isotherm was found satisfying ($r^2 = 0.965$) (Fig. 5). The calculated from the slope and intercept of the linear plot, the maximum amount of exchanged NH_4^+ (b) and the Langmuir constant (k) were 9.64 mg g^{-1} and 0.0548 L mg^{-1} at 21 °C, respectively. Lebedynets et al. [18] and Karadag et al. [16] reported that the maximum amount of exchanged NH_4^+ using the transcarpathian clinoptilolite and natural Turkish clinoptilolite were 11.5 and 8.12 mg g^{-1} at 25 °C, respectively. Weatherley and Miladinovic [19] found the ion exchange capacity of New Zealand clinoptilolite for NH_4^+ ion as 6.588 mg g^{-1}.

On the other hand, the dimensionless equilibrium parameter or separation factor, R_L, based on the further analysis of Langmuir equation can be given by

$$R_L = \frac{1}{1 + kC_0} \tag{4}$$

where C_0 (mg L^{-1}) is the initial amounts of adsorbate and k is Langmuir constant. The R_L parameter is considered as more reliable indicator of the adsorption. There are four probabilities for the R_L value; for favorable adsorption, $0 < R_L < 1$, (ii) for unfavorable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$, (iv) for irreversible adsorption, $R_L = 0$ [20–23].

Fig. 6 shows the variation of R_L with initial concentration of the NH_4^+ ion. As could be seen from the curve, the R_L parameters lied between 0 and 1 represent that the removal of NH_4^+ ion by natural zeolite is propitious. Fig. 6 also indicates that the R_L value approaches zero as the C_0 value is increased, and it means that
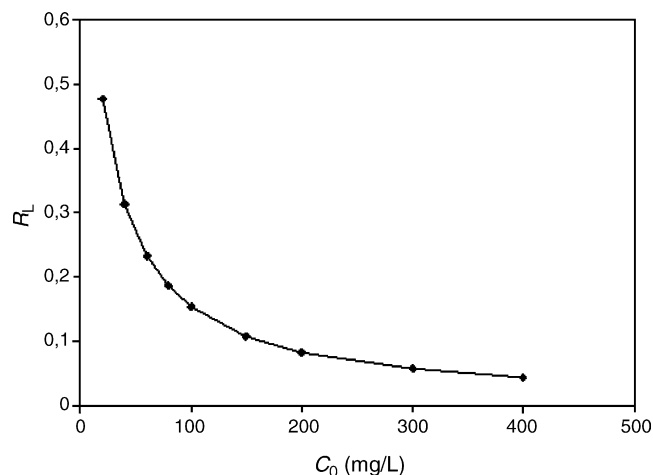

Fig. 6. Variation of separation factor (R_L) as a function of initial NH_4^+ ion concentration (optimum adsorbent dosage: 0.8 g; shaking time: 30 min; pH: 8; temperature: 21 °C).

the adsorption of NH_4^+ ion onto natural zeolite is less favorable at high concentration of the solution. In addition, the values of separation factor (R_L) prove that the natural zeolite is a potential adsorbent for NH_4^+ ion removal from aqueous solution. Similar results have been reported for removal of NH_4^+ ion by zeolite [16].

The ion exchange data were also applied to Freundlich model in logarithmic form [24] expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

where K_f (mg g^{-1}) is the measure of the adsorption capacity of the adsorbent, $1/n$ (L g^{-1}) is a constant relating to adsorption intensity or surface heterogeneity. The determination coefficient (r^2) value of the linear plot of Freundlich isotherm (Fig. 7) was found to be 0.965. The values of K_f and $1/n$ were found to be 0.93 and 0.488, respectively. The magnitude of $1/n$ value generally ranges from 0 to 1 and it is a measure of exchange intensity
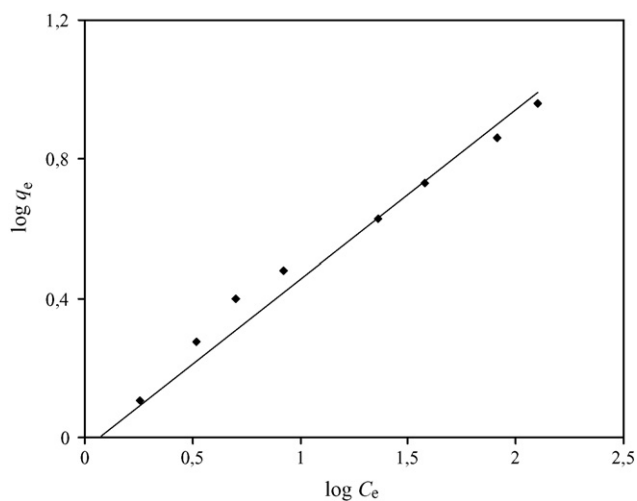

Fig. 7. Linear plot of Freundlich isotherm of NH_4^+ ion adsorption on the natural zeolite (optimum adsorbent dosage: 0.8 g; shaking time: 30 min; pH: 8; temperature: 21 °C).
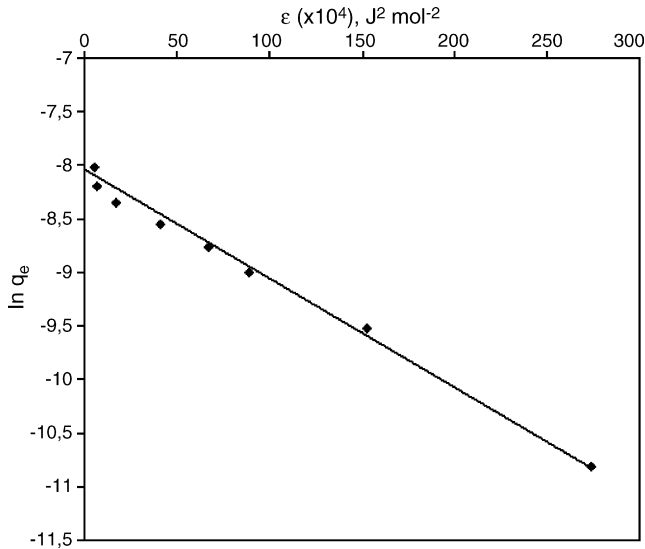
Fig. 8. D–R isotherm plot of NH$_4^+$ ion adsorption on the natural zeolite (optimum adsorbent dosage: 0.8 g; shaking time: 30 min; pH: 8; temperature: 21 °C).

Fig. 9. Variation of the distribution coefficient (K_d) in NH$_4^+$ ion removal using the natural zeolite as a function of temperature (optimum adsorbent dosage: 0.8 g; shaking time: 30 min; pH: 8).

or surface heterogeneity, and the value of $1/n$ smaller than 1 pointed out the favorable removal conditions [16,25–27]. Freundlich constant for natural Turkish clinoptilolite was found to be K_f: 0.612 and $1/n$: 0.517 for NH$_4^+$ ions [16]. Sarioglu [3] estimated K_f as 2.23 and $1/n$ as 0.38 for NH$_4^+$-N ions. Weatherley and Miladinovic [19] determined K_f as 2.27 and $1/n$ as 0.336 for the adsorption of NH$_4^+$ ion onto New Zealand clinoptilolite.

The data were also modelled by D–R isotherm to determine the type of adsorption (physical or chemical) [26,28,29]. The linear form of D–R isotherm is represented as the following equation:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{6}$$

where q_e is the amount of NH$_4^+$ ions adsorbed onto per unit dosage of the natural zeolite (mol L^{-1}), q_m the theoretical monolayer adsorption capacity (mol g^{-1}), β is the constant of the adsorption energy (mol^2 J^{-2}), which is related to the average energy of adsorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution [26,28,29], the ε is Polanyi potential, which described as

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \tag{7}$$

where R is the gas constant (J mol^{-1} K^{-1}), T the temperature (K), C_e is the equilibrium concentration of the NH$_4^+$ (mol L^{-1}).

The value of mean energy of sorption (E; kJ mol^{-1}) can be calculated from D–R parameter β as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

The value of mean energy of sorption gives information about chemical and physical sorption. Therefore, interpretation of NH$_4^+$ ion sorption, whether chemical or physical, can be made for adsorbents. As seen in Fig. 8, the slope of the D–R plot (ln q_e versus ε^2; r^2: 0.985) gives β constant and, q_m value was calculated from intercept of the plot. The β and q_m values were found
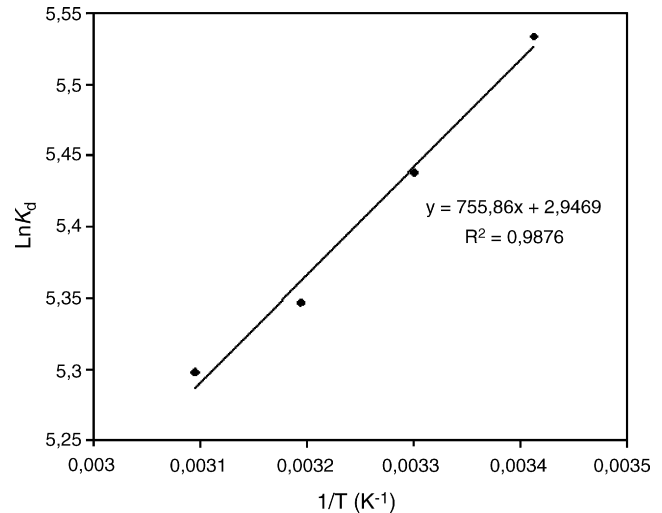
to be -1.01×10^{-6} mol^2 J^{-2} and 3.22×10^{-4} mol g^{-1}, respectively. The E value was calculated as 0.7 kJ mol^{-1} by using Eq. (8). The E value ranges from 1 to 8 kJ mol^{-1} for physical sorption and from 9 to 16 kJ mol^{-1} for chemical sorption [26,28,29]. The mean value of E (0.7 kJ mol^{-1}) was found in the range of 1–8 kJ mol^{-1}, indicating that the type of sorption of NH$_4^+$ ions onto the natural zeolite was essentially physical.

3.6. Thermodynamic parameters

In order to investigate the effect of temperature on the NH$_4^+$ ion exchange by the zeolite, the distribution coefficient, K_d (mL g^{-1}), was calculated at the temperature of 294, 303, 313 and 323 K by using Eq. (9) [23,26]:

$$K_d = \frac{q_e}{C_e} \tag{9}$$

The K_d values were calculated as 253, 230, 210 and 200 mL g^{-1} for the temperature of 294, 303, 313 and 323 K, respectively. It can be noteworthy that the distribution coefficient decreases with increasing temperature (from 294 to 323 K) and it reveals the process to be exothermic.

Thermodynamic parameters, the enthalpy change, $\Delta H°$, and the entropy change, $\Delta S°$, were calculated from the slope and intercept of the plot of ln K_d against $1/T$, respectively [26,29,30], as shown in Fig. 9:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

The other thermodynamic parameter, Gibbs free energy change, $\Delta G°$, was calculated by

$$\Delta G° = -RT \ln K_d \tag{11}$$

The enthalpy change, $\Delta H°$, had a value of -6.284 kJ mol^{-1}. The negative $\Delta H°$ exhibited that the NH$_4^+$ ion exchange by the zeolite was exothermic. The low $\Delta H°$ values showed weak interactions between the NH$_4^+$ ions and the negatively charged sites

on the surface of the zeolite. Change in the entropy, ΔS° was found to be 24.5 J mol^{-1} K^{-1} for NH$_4^+$ ion removal from aqueous solution. This result implied that NH$_4^+$ ion in solid phase (surface of adsorbent) were in a much more chaotic distribution compared to the relatively ordered state of bulk phase (aqueous solution). Moreover, Gibbs free energy change, ΔG°, was calculated to be -13.48, -13.70, -13.92 and -14.23 kJ mol^{-1} for the NH$_4^+$ ion exchange at the temperature range of 294–323 K. The negative value of ΔG° confirmed the feasibility and spontaneous nature of the NH$_4^+$ ion exchange by the zeolite. In addition, the process proceeded physically because ΔG° values had lower value than -20 kJ mol^{-1} [31]. This result was in well agreement with that obtained from the D–R isotherm.

4. Conclusions

The experimental parameters such as solution pH, shaking time, the adsorbent dosage, and temperature influenced NH$_4^+$ ion removal from aqueous system by the zeolite. The NH$_4^+$ ion exchange data fitted to linear Langmuir and Freundlich models. Moreover, the D–R isotherm indicated that the ion exchange of NH$_4^+$ by the zeolite was physical in nature. The negative ΔG° values confirmed the feasibility and spontaneous nature of the NH$_4^+$ ion exchange at studied temperatures. The negative ΔH° value also depicted that the ion exchange process was an exothermic in nature.

Based on the results, it can be concluded that the natural Turkish (Yıldızeli) zeolite is suitable adsorbent for NH$_4^+$ ion removal from aqueous solution. Moreover, it can be recommended for wastewater treatments and agricultural purposes in terms of sustainability of environmental quality.

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