Investigation on natural and pretreated Bulgarian clinoptilolite for ammonium ions removal from aqueous solutions

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ABSTRACT

The possibilities for ammonium ions removal from aqueous solutions by natural and NaCl pretreated Bulgarian clinoptilolite from Beli plast deposit were studied. Experiments were carried out using batch method. The adsorption of NH_4^+ was investigated as a function of the solution pH, dosage of adsorbent, initial ammonium concentration and temperature. The results clearly showed that the treatment with NaCl improved both the adsorption capacity and the removal efficiency of natural clinoptilolite. The equilibrium experimental data for adsorbed NH_4^+ ions on clinoptilolite samples were correlated better by the Langmuir isotherm model. The maximum adsorption capacities for ammonium ions shown by natural and pretreated clinoptilolites (CL_Na and CL_Na(t)) were 7.85, 12.29 and 18.40 mg/g, respectively. The results indicated a significant potential of the natural and conditioned clinoptilolites as adsorbents for ammonium removal.

1. Introduction

Nitrogen compounds are very essential elements for living organisms. The presence of excess N compounds causes environmental pollution. Therefore, the control on them is important for the protection of public health. Ammonia and ammonium ions are the more commonly encountered N compounds in waste water and groundwater. There are different methods for removing ammonium ions from wastewaters: air stripping, chemical treatment, selective ion exchange, adsorption and biological nitrification–denitrification [1–7]. Previously we reported that carbon obtained from Bulgarian lignite from Chukurovo deposit by one-step steam pyrolysis-activation followed by oxidative modification gave comparable results despite its worse texture parameters as compared with Norit GAC 1240 oxidized in an analogous way and was a more promising adsorbent as a means of ammonia removal from aqueous solutions [8].

Clinoptilolite, which has a high affinity for the ammonium ion, is one of the most important natural zeolites because it is found in large deposits worldwide. The various aspects of removal from aqueous solutions by clinoptilolite have been investigated by many researchers [6,7,9–15]. It is reported to have a classical alumina silicate age-like structure. The general formula of a zeolite is as follows:

$$(M_x^+, M_y^{2+})(Al_{(x+2y)}Si_{n-(x+2y)}O_{2n})\cdot mH_2O$$
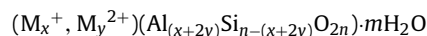
where M^+ and M^{2+} are univalent and divalent cations such as Na^+, K^+, and Ca^{2+}, Mg^{2+}, Ba^{2+}, respectively. They are called exchangeable cations. Al^{3+} and Si^{4+} are known as structural cations. They make the framework of the structure with O [13]. Pretreatment of natural zeolites by acids, bases, surfactants, etc. is an important method to improve their ion-exchange capacity [15–19]. The chemical treatment of clinoptilolite is aimed at removing certain cations from its structure and locating more easily the removable ones, prior to its application. Conditioning with NaCl causes an increase in Na^+ and a decrease in Ca^{2+} concentrations in clinoptilolite, this leading to an increase of the ratios Na^+/Ca^{2+}. Despite the large number of different studies on the removal of ammonium ions from aqueous solutions using clinoptilolite, every special material requires individual research. Therefore, such studies are important for future practical use of this natural material in wastewater treatment. The purpose of this paper is to investigate the removal efficiency of ammonium ions from aqueous solutions using natural and treated Bulgarian clinoptilolite and to characterize equilibrium isotherms.

2. Materials and methods

2.1. Characterization of clinoptilolite

A sample of clinoptilolite was taken from Beli plast deposit in Eastern Rhodopes, Bulgaria. The chosen clinoptilolite was crushed and classified to a size range of 0.2–1.0 mm. Then it was washed

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to remove the water-soluble residues and other undesirable material, and dried in an oven at 378 K for 24 h before its use in the experiments. The clinoptilolite sample was characterized by X-ray diffraction (XRD) and chemical analysis. The chemical composition was determined by analytical methods usual for silicate materials. Characterization of the texture parameters of clinoptilolite was carried out by low-temperature adsorption of nitrogen (77 K) using a conventional volumetric-measuring apparatus. The nitrogen adsorption isotherms were analyzed to evaluate the following parameters: the specific surface areas, the total pore volume and average pore diameter. The clinoptilolite sample was outgassed at 473 K for 6 h under vacuum (10^{-3} Torr) before N_2 adsorption.

2.2. Pretreatment procedure of clinoptilolite

Ammonium ions adsorption studies were carried out using three different clinoptilolite forms, natural and treated samples:

- Sample 1 (CL): natural clinoptilolite.
- Sample 2 (CL_Na): natural clinoptilolite treated with 2 mol/L NaCl solution at 293 K. An aliquot of 10 g was transferred to a conical flask containing 100 mL of 2 mol/L NaCl solution. The suspension was magnetically stirred over a period of 24 h and was separated from the supernatant by filtration. The clinoptilolite sample was then washed with deionized water until no more Cl^- was detected in the washing water. The pretreated sample was dried at 378 K for 6 h and stored in a desiccator until further use.
- Sample 3 (CL_Na(t)): the third sample of clinoptilolite was prepared by treating clinoptilolite with 2 mol/L NaCl solution (clinoptilolite/solution ratio of 100 g/L) at 363 K over a period of 7 h in thermostat. After a cool-down period, the sample was filtered and washed with distilled water. After washing, the Na-modified clinoptilolite was dried at 378 K for 6 h.

2.3. Adsorption studies

Batch experiments were performed in a stirred system at 293 K except for the experiment on the effect of temperature. The experiments were carried out in plugged 50-mL Erlenmeyer flasks containing 0.25 g clinoptilolite sample and 25 mL NH_4Cl solution. On reaching equilibrium the adsorbent was eliminated by filtering through a Millipore filter (0.2 μm). Initial and equilibrium concentrations of ammonium ions were determined spectrophotometrically with a Berthelot reactive using a Spekol 11 apparatus. The amount of NH_4^+ ions adsorbed by the clinoptilolite sample at equilibrium (Q_e, mg/g) was calculated using the expressions:

$$Q_e = (C_0 - C_e) \times \frac{V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentration of NH_4^+ (mg/L), respectively. V is the solution volume (L) and m is the adsorbent weight (g).

Analytical grade ammonium chloride (NH_4Cl) and deionised water were used for the preparation of the stock NH_4^+ solutions. The working solutions containing different concentrations of NH_4^+ in the range 50–250 mg/L were prepared by stepwise dilution of the stock solutions. The initial pH value was adjusted by addition of NaOH or HCl to the designed value.

3. Results and discussion

3.1. Characterization of clinoptilolite

The chemical and mineralogical composition and the main texture parameters of the natural clinoptilolite are presented in Table 1.

Table 1
Chemical, mineralogical and structural characteristics of natural Bulgarian clinoptilolite.

Parameter	Value
Chemical analysis	
SiO_2, %	70.43
Al_2O_3, %	11.11
Fe_2O_3, %	1.89
Na_2O, %	1.35
K_2O, %	3.62
CaO, %	2.36
MgO, %	0.38
H_2O, %	6.92
Other, %	1.94
Si/Al	5.3
XRD analysis	
Clinoptilolite, %	83
Cristobalite, %	5
Heulandite, %	7
Quartz, %	2
Albite, %	2
Microcline, %	1
Surface area, m^2/g	26.0
Total pore volume, cm^3/g	0.082
Average pore radius, nm	20.4

As can be seen from Table 1, it contained significant amounts of SiO_2 (70.4%) and Al_2O_3 (11.1%), while the contents of other metal oxides were less than 11%. Cristobalite, heulandite, quartz, albite and microcline are the main mineral admixtures (17%). The low-temperature nitrogen adsorption on natural clinoptilolite (Fig. 1) is expressed by IV-type isotherm with a hysteresis loop of the type H3 by IUPAC classification [20]. This type isotherm is typical for micro-mesoporous materials. The average pore diameter is 20.4 nm, corresponding to mesopores. It is established that the type H3 of hysteresis loop is usually given by the aggregates of particles or adsorbent containing slit-like pores [21]. The sharp rise of the isotherm under the lowest relative pressures may be caused by the presence of free micropores in the clinoptilolite sample. The specific surface area of Bulgarian clinoptilolite is 26.0 m^2/g. The relatively low values of specific surface area and pore volume found for CL (26.0 m^2/g and 0.082 cm^3/g, respectively) are due to the fact that N_2 cannot enter into the pores of the natural clinoptilolite and it is mainly adsorbed on the external surface of the solid.
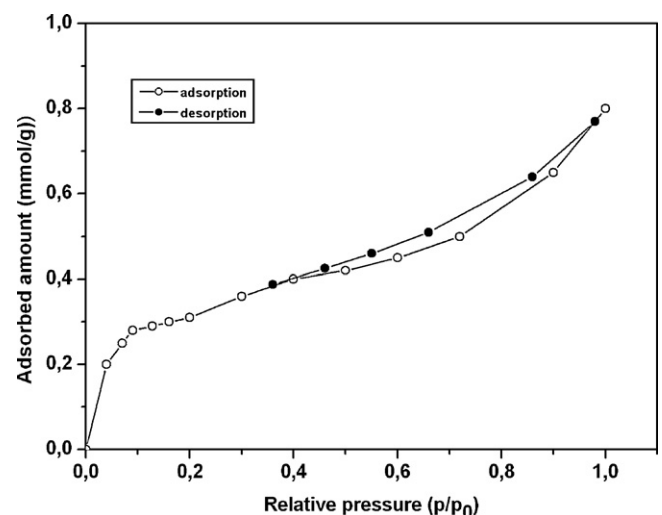

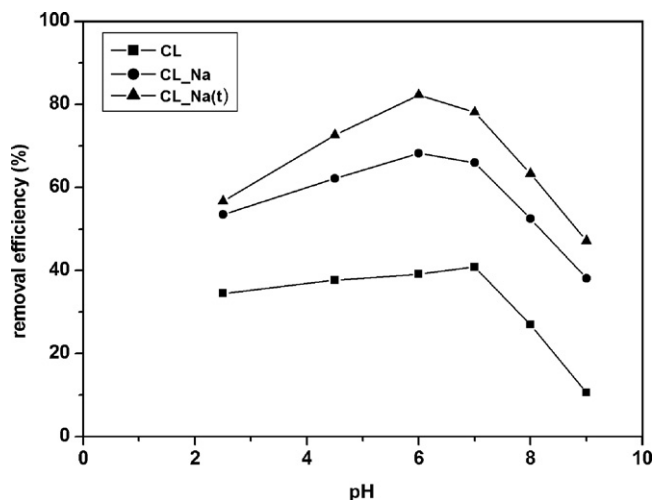**Fig. 1.** Nitrogen adsorption/ desorption isotherms for initial clinoptilolite.

Fig. 2. Effect of pH on removal efficiency of NH_4^+ ions (C_0 175 mg/L, stirring time 1 h, clinoptilolite amount 10 g/L).

Fig. 3. Effect of clinoptilolite amount on sorption capacity of ammonium ions (C_0 175 mg/L, stirring time 1 h, pH 6.0).

3.2. Effect of pH

The optimum time to establish adsorption equilibrium between the clinoptilolite samples and the ammonium ions of different concentrations is determined experimentally and is found to be 1 h. The adsorption studies are performed taking into account these preliminary experiments.

The pH of the aqueous solution is an important controlling parameter in adsorption processes. The removal of NH_4^+ ions from aqueous solutions by different clinoptilolite samples was studied at pH values from 2.5 to 9.0 and the data obtained are given in Fig. 2. As can be seen the removal of ammonium with all samples increases when raising the pH from 2.5 to about 6 and then decreases again because clinoptilolite is highly selective for H_3O^+ ions when the H_3O^+ ions concentration is high. Thus, at lower pH values, H_3O^+ ions compete with NH_4^+ ions for the exchange sites in clinoptilolite samples [6,19]. The decrease in the NH_4^+ removal efficiency above pH 7 may be due to two factors: (1) partial dissolution of the natural clinoptilolite [13] and (2) possible conversion of NH_4^+ into NH_3 [6,13,19]. The removal of the NH_4^+ ions on samples CL, CL_Na and CL_Na (t) is compared. It is established that over the whole studied pH range (2.5–9.0) pretreated clinoptilolite samples adsorb NH_4^+ ions better than natural clinoptilolite.

3.3. Effect of amount of clinoptilolite

Fig. 3 shows the effect of the amount of natural and pretreated clinoptilolites on the adsorption capacity of ammonium ions. These results evidence that the adsorbed amount of NH_4^+ decreases with the increasing clinoptilolite doses from 2.5 to 30 g/L. This decrease of adsorption capacity is due to the increasing interface area when the suspension is diluted [22]. The decrease continues to 10 g/L clinoptilolite concentration and beyond this value there is not a significant change in amount of the adsorbed NH_4^+ ions.

3.4. Effect of initial ammonium ions concentration

The dependence of the initial concentrations on the amount of adsorbed NH_4^+ ions by natural and pretreated clinoptilolites is shown in Fig. 4. In all cases an increase of ammonium adsorption with increasing of the initial concentration is observed. This increase continues up to 175 mg/L and it is negligible beyond this
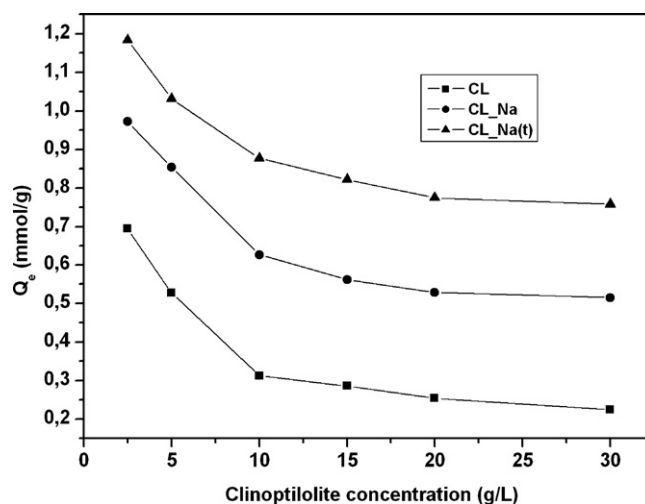
value. The plateau represents saturation of the active sites available on the clinoptilolite samples for interaction with ammonium ions. It can be concluded that the amount of NH_4^+ adsorbed onto unit mass of the adsorbent at equilibrium rapidly increases at a low initial concentration and then begins to slightly increase with the NH_4^+ concentration from 175 to 250 mg/L. These results indicate that energetically less favorable sites become involved with increasing ammonium concentrations in the aqueous solution [23]. According to the data from Fig. 4, the amount of NH_4^+ adsorbed by CL_Na(t) and CL_Na samples is higher when compares to CL. It has been found that the highest adsorption capacity belongs to the CL_Na (t) sample. The exposure of the natural clinoptilolite to a NaCl solution leads to the production of the sodium-rich sample. Na-rich forms of clinoptilolite are known to have an enhanced exchange capacity, because also a part of the more tightly bound K and Ca cations are exchanged when treated with Na solutions [17,24]. It is clear that as the temperature of treatment with NaCl increases, the sodium content of the clinoptilolite increases in parallel and this increase is mainly attributed to the exchange of K^+ and Ca^{2+} [24].
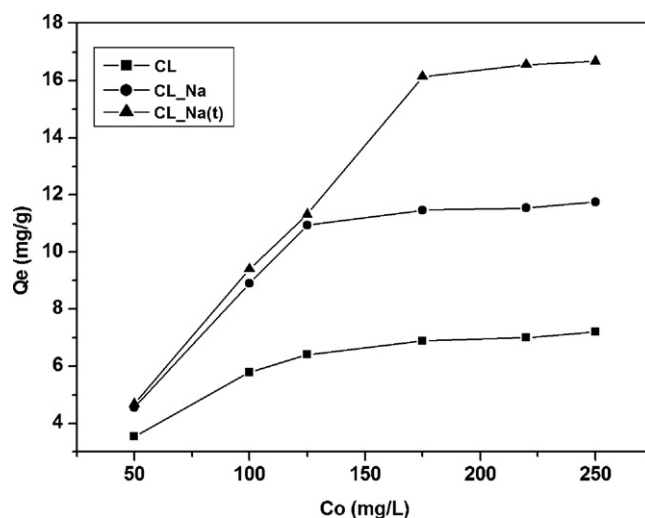

Fig. 4. Dependence of initial ammonium concentrations on the amount of adsorbed NH_4 ions by clinoptilolite samples (stirring time 1 h, clinoptilolite amount 10 g/L, pH 6.0).

3.5. Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. There are several isotherm equations available for analyzing experimental adsorption equilibrium data. In this study, the equilibrium experimental data for adsorbed NH_4^+ on clinoptilolite samples were analyzed using the Langmuir (2), Freundlich (3) and Dubinin–Radushkevich (4) isotherm models. The linear forms of these isotherms are as follows:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \tag{2}$$

where C_e is the concentration of NH_4^+ ions in the equilibrium solution (mg/L), Q_e is the amount of NH_4^+ adsorbed (mg) by per unit mass of adsorbent (g), Q_0, the maximum adsorption capacity (mg/g); K_L, the constant of the Langmuir equation related to the enthalpy of the process.

$$\ln Q_e = \ln k_F + (1/n)\ln C_e \tag{3}$$

where k_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

$$\ln Q_e = \ln Q_0 - \beta\varepsilon^2 \tag{4}$$

where β is the constant of the adsorption energy (mol^2/J^2), and ε is the Polanyi potential, described as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{5}$$

where R is the gas constant (J/mol K) and T is the temperature (K). The mean adsorption energy E (kJ/mol) can be calculated from parameter β as follows:

$$E = \frac{1}{(-2\beta)^{1/2}} \tag{6}$$

The corresponding correlation coefficients and the isotherm constants are calculated and presented in Table 2. The Langmuir model yielded a much better ($R^2 = 0.990–0.998$) fit than that of the Freundlich ($R^2 = 0.899–0.948$) and Dubinin–Radushkevich models ($R^2 = 0.804–0.986$). This result is in agreement with various researchers who used Langmuir equation to represent ammonium removal by clinoptilolite [12,19,26]. The greatest equilibrium adsorption capacity Q_0 for ammonium ions obtained for CL_Na(t), is 18.40 mg/g, which decreases to 12.29 mg/g for CL_Na and 7.85 mg/g for natural clinoptilolite. The Langmuir isotherms are shown in Fig. 5. The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation factor R_L, which is defined as:

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{7}$$

The values of R_L for adsorption of NH_4^+ on the natural and pretreated clinoptilolites are shown in Fig. 6. The R_L values are found to vary within the ranges, 0.24–0.06, 0.13–0.03 and 0.11–0.02 for CL, CL_Na and CL_Na(t), respectively, the initial NH_4^+ concentration values being 50–250 mg/L (Fig. 6). All values are in the range of 0–1 which indicates a favorable adsorption. In addition, the values of the separation factor (R_L) prove that natural and NaCl pretreated clinoptilolites are potential adsorbents for NH_4^+ ion removal from aqueous solutions.
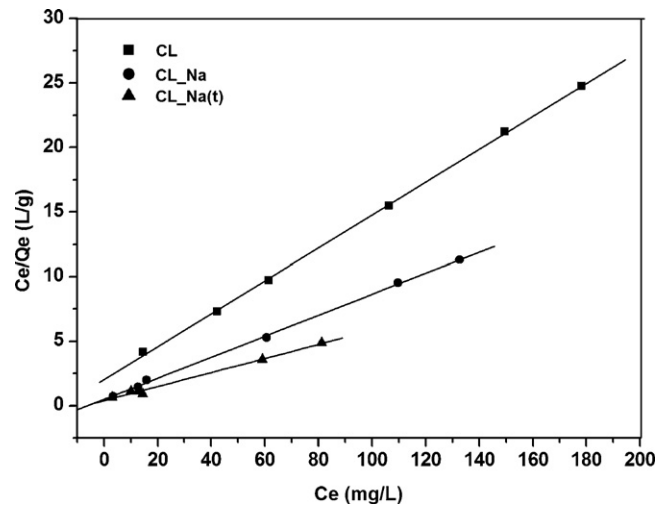

Fig. 5. Linear plots of Langmuir isotherm of NH_4^+ ions sorption on the clinoptilolite samples (C_0 175 mg/L, stirring time 1 h, clinoptilolite amount 10 g/L, pH 6.0).

3.6. Thermodynamic parameters

The adsorption of NH_4^+ ions on CL_Na(t) as a function of temperature was studied by varying the mixing temperature from 293 to 333 K, while keeping all other parameters constant. The results are shown in Fig. 7. The amount of NH_4^+ ions removed from aqueous solution decreases with increasing temperature. A decrease in the removal efficiency of NH_4^+ ion with the raise in temperature is due to the increasing tendency to desorb from the interface to the solution. This result indicates that the adsorption process of NH_4^+ ions onto CL_Na(t) is exothermic in nature. Changes in the adsorption standard free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) are calculated using the following equations:

$$K_d = \frac{Q_e}{C_e} \tag{8}$$

$$\Delta G^\circ = -RT \ln K_d \tag{9}$$

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

where K_d is the equilibrium constant, R is the gas conctant (J/mol K) and T is the temperature (K). The enthalpy change, ΔH°, and the entropy change, ΔS°, are determined from the slope and intercept
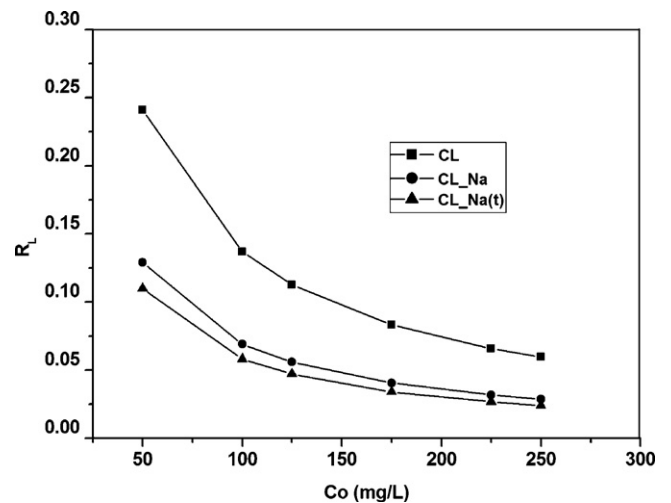

Fig. 6. Variation of separation factor (R_L) as a function of initial NH_4^+ concentrations (stirring time 1 h, clinoptilolite amount 10 g/L, pH 6.0).

Table 2
Isotherm constants for the ammonium adsorption by clinoptilolite samples.

Clinoptilolite samples	Langmuir parameters			Freundlich parameters			Dubinin–Radushkevich parameters		
	Q_0 (mg/g)	K_L (L/mg)	R^2	k_F	n (L/mg)	R^2	Q_m (mg/g)	E (kJ/mol)	R^2
CL	7.85	0.063	0.998	1.88	3.66	0.899	6.62	0.82	0.804
CL_Na	12.29	0.162	0.998	4.01	4.51	0.909	11.35	0.63	0.986
CL_Na(t)	18.40	0.135	0.990	4.45	2.75	0.948	16.12	0.57	0.974
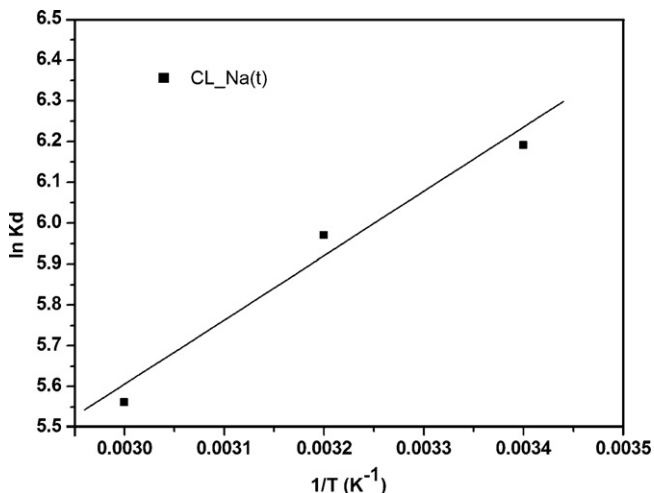
Fig. 7. Variation of equilibrium constant as a function of temperature (C_0 175 mg/L, stirring time 1 h, CL_Na(t) 10 g/L, pH 6.0).

Table 3
Values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ at different temperatures for CL_Na(t).

Temperature (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
293	−15.07	−12.94	7.21
313	−15.39		
333	−15.53		

of the plot of $\ln K_d$ versus $1/T$, respectively (Fig. 7). The determination coefficient value (R^2) of the linear plot is found to be 0.998. The values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ parameters are presented in Table 3. Change in the standard free energy has negative values −15.07 kJ/mol at 293 K, −15.39 kJ/mol at 313 K and −15.53 kJ/mol at 333 K. This negative values indicate that adsorption of NH_4^+ ions on CL_Na(t) is feasible and spontaneous. The increase in negative values of $\Delta G°$ with increasing temperature shows that adsorption of ammonium ions becomes more spontaneous at higher temperatures. In addition, the process has physical characteristic since $\Delta G°$ values are between 0 and −20 kJ/mol [12,13,25]. The enthalpy change, $\Delta H°$, has a negative value of −12.94 kJ/mol. Therefore, ammonium removal by CL_Na(t) is an exothermic process. The low $\Delta H°$ values showed weak interactions between the NH_4^+ ions and the negatively charged sites on the surface of the CL_Na(t). The change in entropy, $\Delta S°$, is found to be 7.21 J/mol K. This result implies that ammonium ions in solid phase (surface of adsorbent) are in a much more chaotic distribution compared to the relatively ordered state of bulk phase (aqueous solution).

4. Conclusions

The experimental parameters such as solution pH, adsorbent dosage, initial concentration and temperature influenced the NH_4^+ ions removal from aqueous solutions by the natural and treated with NaCl clinoptilolites. Comparison of the data with Langmuir, Freundlich and Dubinin–Radushkevich isotherm models show the Langmuir model describes the process more accurately. The treat-

ment with NaCl improved both the adsorption capacity and the removal efficiency of natural clinoptilolite. The maximum adsorption capacities for NH_4^+ ions shown by CL, CL_Na and CL_Na(t) were 7.85, 12.29 and 18.40 mg/g, respectively. The values of $\Delta S°$, $\Delta H°$ and $\Delta G°$ for the ammonium removal by CL_Na(t) were determined. The negative values of change in Gibbs free energy and enthalpy change indicate that adsorption of NH_4^+ on CL_Na(t) is spontaneous and exothermic.

Based on the experimental results, it can be concluded that ammonium ions can be effectively removed from aqueous solutions using natural and NaCl treated Bulgarian clinoptilolite from Beli plast deposit. Hence, Bulgarian clinoptilolite may be used as a low cost source for the removal of NH_4^+ and it may be an alternative to more expensive materials such as synthetic resins.

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