Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite

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Abstract

This paper concerns the removal of ammonium ions from wastewater using a naturally occurring zeolite from Dogantepe region in Turkey. Both batch and continuous (column) experiments were carried out. In batch studies, effects of stirring time (5–120 min) and initial ammonium concentration (8.8–885 mg NH_4^+-Nl^{-1}) on removal efficiency and adsorption isotherms were investigated. In column studies, effects of flowrate, pH, initial ammonium concentration, washing with acid and regeneration on the ammonium adsorption capacity of the zeolite were determined. Increasing initial ammonium nitrogen concentration from 5.0 to 12.0 mgl^{-1}, increased the exchange capacity from 0.70 to 1.08 mg NH_4^+-Ng^{-1}. The flowrate and pH values, at which the highest adsorption capacities were obtained, were found to be 0.5 ml min^{-1} (0.87 mg NH_4^+-Ng^{-1} zeolite) and 4 (mg NH_4-Nl^{-1}), respectively. The corresponding values after washing with acid and regeneration were determined to be 1.32 and 0.73 mg NH_4^+-Ng^{-1}, respectively. The cation exchange capacity of Dogantepe zeolite was found to be 164.62 meq. per 100 g. These findings show that Dogantepe zeolite can be used for the removal of ammonium from wastewater.
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Keywords: Zeolite; Clinoptilolite; Mordenite; Ammonium removal; Exchange capacity; Wastewater

1. Introduction

Nitrogen and phosphorus compounds are very essential elements for living organisms. However, when they are more than needed, they can lead to eutrofication. The main nitrogen removal processes are biological nitrification, denitrification, air stripping, chemical treatment and selective ion exchange [1,2]. Ammonia is usually found as ammonium ion (NH_4^+) in aqueous environments. The conventional method for ammonium and organic removal from municipal and industrial wastewaters are based on biological treatments [3]. Ammonia removal proceeds ion exchange or through nitrification followed by denitrification [4–6]. An alternative to nitrification for removal of ammonia is ion exchange using clinoptilolite. Therefore, several researches have been performed on ion exchange in recent years. It seems that ammonium removal by ion exchange using clinoptilolite is very competitive compared to other processes [4,7–12]. Complete removal of ammonium is required due to its toxicity to most fish species. For fish life, ammonium nitrogen concentration must not be more than 1.5 mg NH_4^+-Nl^{-1} [7,2]. It is stated in Water Pollution Control Regulation in Turkey that the permissible NH_4^+-N (ammonium nitrogen) concentration for first and second class surface water sources should not exceed 0.2 and 1 mg NH_4^+-Nl^{-1}, respectively [13].

The ion exchange method usually employs organic resins, which are very selective. However, they are very expensive. There are, however, cheap alternative materials, such as zeolite, which are abundant in nature. Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment [14]. So far, many different species of this mineral have been identified. Clinoptilolite is the most abundant natural zeolite that occurs in relatively large minerable sedimentary deposits in sufficiently high purity in many parts of the world. Eichorn firstly investigated ion-exchange features of the zeolite minerals in 1858 [15]. One ion exchanger with a high affinity for ammonium ion is clinoptilolite, a naturally occurring zeolite [16,17]. Clinoptilolite is reported to have a classical alumina silicate age-like structure and therefore exhibits significant macroporosity [18]. In nature, the cations present on clinoptilolite are calcium, sodium and potassium. The selectivity order

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of natural zeolite among cations is as follows [6]:

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+$$
$$> Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$$
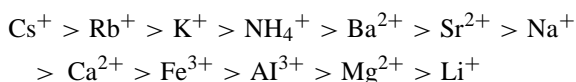
As shown above, one of the cation, on which the natural zeolites have high selectivity, is ammonium ion. The use of a clinoptilolite unit would be a very good tool for compliance with stringent standards of ammonia or alternatively total inorganic nitrogen. Such a unit may be used as an upgrade in existing systems as well as in new treatment plant designs. Among natural zeolites, clinoptilolite occurs most frequently, e.g. in Japan, USA, Russia and Hungary [19]. Turkey is also rich in zeolite reserves. Zeolites are used for several purposes. Natural zeolites, except removing ammonium, are used mostly for removing heavy metal ions from water [20–25]. There are several types of them as natural and synthetic. Both natural and synthetic zeolites have ability for removing several cations from solutions concerning adsorption and ion exchange features [26,27]. The main features of zeolites are high level of ion exchange capacity, adsorption, porous structure, molecular sieve, dehydration and rehydration, low density and silica compounds.

The general chemical formula of a zeolite is:

$$M_xD_y[Al_{x+2y}Si_{n-(x+2y)}O_{2n}]mH_2O$$
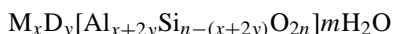
where $M = Na^+$, K^+ or other monovalent cations, and $D = Mg$, Ca, Sr, Ba and other divalent cations [26].

The most suitable form of clinoptilolite for ammonia removal was found to be Na [28]. The use of clinoptilolite for ammonium removal after thermal and/or acid activation was also investigated [29,30].

Several researchers experienced with the usage of zeolite filters for ammonium removal in effluent of wastewater treatment plants [28,31,32]. Considerable research has been conducted to characterize the chemical, surface and ion exchange properties of clinoptilolite [28,31–38]. Cation exchange capacity is dependent on the nature of the cation (size, load, etc.), temperature, concentration of cation in solution and structural characteristics of zeolite. When ion exchange is used as an ammonium removal process in wastewater treatment, a lab-scale or pilot plant testing program is usually required. Lab-scale study allows evaluating the influence of variables, such as pH, contact time, etc. on ammonium performance.

The aim of this study is to investigate ammonium removal from wastewaters by using natural zeolite supplied from Dogantepe (Amasya) region in Turkey.

2. Experimental

2.1. Preparation and measurements of zeolite samples

Zeolite samples used in this study were taken from Dogantepe (Amasya), Turkey. The mineralogical composition of zeolite was determined as 45% clinoptilolite, 35% mordenite, 15% feldspar [(Na, K, Ca)AlSi$_3$O$_8$], and 5% quartz [SiO$_2$] [24]. The theoretical exchange capacities of clinoptilolite and mordenite are 330 and 230 meq. per 100 g, respectively [39]. The theoretical exchange capacity of zeolite used in this study was calculated as 2.29 meq. g^{-1} by using mineralogical composition.

The samples were ground and sieved to $-10 + 20$ mesh (1–2 mm) particle size and then washed with distilled water to remove any non-adhesive impurities and small particles, and then dried at 105 °C for 24 h to remove moisture. Since NH$_4^+$-N ion removal by using natural zeolite was aimed, preconditioning with NaCl, HCl, HNO$_3$, H$_2$SO$_4$, and NaOH, etc. solutions was not considered. A few zeolite samples, however, were treated with HNO$_3$ before usage, just to compare the results obtained from natural and washed samples.

Chemical composition of zeolitic sample is given in Table 1. The mineral from Dogantepe is a mixture of clinoptilolite, mordenite, and other phases. This mixture is referred to as zeolite in the following sections. The mineralogical features of samples were determined using Rigaku D Max IIIC X-ray diffractometer in Cumhuriyet University. The mineralogical compositions of original and treated samples were determined by using JCPDS (1990) files [40]. Semi-quantitative weight percentages of samples were calculated by using mineral intensity factors based on an external standard method [41]. In the experimental studies, the ammonium ion concentration in the solution was determined by using Nessler method according to standard methods [42]. Absorbance values were read using a Shimadzu UV-1201V spectrophotometer. In acidic conditions, X-ray diffraction analyses were done to find out the structural stability of samples for pH 4, 4.5, and natural one. The experiments were studied by the batch and continuous (column) processes.

Table 1
Chemical composition of Dogantepe (Amasya) zeolite

Oxide	(wt.%)	Elements	ppm
SiO$_2$	70.27	Cr	8
TiO$_2$	0.19	Ni	1
Al$_2$O$_3$	12.90	Co	4
ΣFe$_2$O$_3$[a]	1.38	Cu	13
MnO	0.02	Pb	26
MgO	1.71	Zn	54
CaO	2.05	Rb	106
Na$_2$O	3.21	Ba	137
K$_2$O	1.49	Sr	1470
P$_2$O$_5$	0.04	Ga	15
LOI[b]	6.57	Nb	7
Total	99.43	Zr	182
		Y	16
		Th	25

[a] Total Fe.
[b] Loss on ignition (1000 °C).

2.2. Batch experiments

In the batch studies, the effects of stirring time and ammonium concentrations on ammonium removal efficiency by zeolite were examined by using synthetic NH_4^+-N solutions.

2.2.1. Effects of stirring time and ammonium concentration

In order to find out the optimum stirring time, 1 g zeolite samples (1–2 mm) were added into 100 ml of 88 mg l^{-1} ammonium solutions in 250 ml beaker and stirred for 5–120 min at a fixed temperature (20 °C) and 150 rpm rate. Then the effect of initial ammonium concentrations (8.8–885 mg NH_4^+-N l^{-1}) on the removal efficiency was investigated at the same working conditions ($T = 20$ °C; 150 rpm).

2.2.2. Adsorption isotherms

The ion exchange reaction is a stoichiometric process, where one equivalent of an ion in the solid phase is replaced by equivalent of an ion from solution. The reaction may be written as

$$Na_{(z)}^+ + NH_{4(s)}^+ \Leftrightarrow Na_{(s)}^+ + NH_{4(z)}^+$$
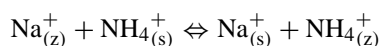
The subscripts z and s refer to the zeolite and solution phases, respectively.

The ion exchange isotherms characterize the equilibrium of an ion in solid phase with the concentration of the ion in solution.

Graphical representation usually shows all possible experimental conditions at a given temperature. Ammonium removal capacities for zeolite were studied with ion exchange isotherms. For the effective utilization of a natural zeolite as an ion exchanger, it is essential to have chemical models that help to describe accurately NH_4^+-N equilibrium. Empirical equations such as the Freundlich and the Langmuir were fitted to experimental data. Freundlich and Langmuir isotherms were formulated at 20 min stirring time, 10 g l^{-1} zeolite per solution ratio and 8.8–885 mg NH_4^+-N l^{-1} concentrations at room temperature (20 °C) and 150 rpm stirring speed to main zeolite particles in suspension. Total amount of adsorbed ammonioum was divided by the dry weight of zeolite to find out the average amount adsorbed, which was plotted against effluent ammonium concentrations to show an isotherm test.

2.3. Column (continuous) experiments

The column loading capacity was determined from the breakthrough curve by using samples taken from Cumhuriyet University wastewater treatment plants. The composition of wastewater taken from wastewater treatment plant effluent is as follows (mg l^{-1}): NH_4-N = 5–12; chemical oxygen demand (COD) = 18; biological oxygen demand (BOD) = 10; suspended solids (SS) = 8 mg l^{-1}; PO_4 = 0.03; Na = 12; K = 0.5; Ca = 161; Mg = 16.5. Generally, breakthrough curve is illustrated as "S" shape for most adsorption processes in water and wastewater treatment. Some parameters, such as initial pollutant concentration, pH, flowrate, adsorption mechanism, equilibrium conditions and particle size, conditioning, and column diameter affect the real shape of breakthrough curve [28,43–46]. The main point in column design is breakthrough analysis.

Therefore, in this paper; effects of some factors (flowrate, pH, washing with acid, and regeneration) on breakthrough capacities were investigated. However, the effect of particle size on breakthrough capacity was not considered. Based on literature, studies with ammonia removal, particle size was selected in the range 1–2 mm. Hlavay et al. [45] found that 0.5–1 mm particle size gave the highest performance. Semmens et al. [43] concluded that small particle sizes increased the removal efficiency. Milan et al. [47] studied ammonia removal by ion exchange in columns packed with homionic zeolite with a particle size of 5 mm. Ratanatamskul et al. [48] used a natural clinoptilolite with a size of 7–15 mm for residual ammonia and phosphorus removal from domestic wastewater. Baykal and Güven [10] used clinoptilolite with a size of 1–2 mm to remove ammonia from domestic wastewater. As expected, as the particle size decreases, the surface area and adsorption capacities increase.
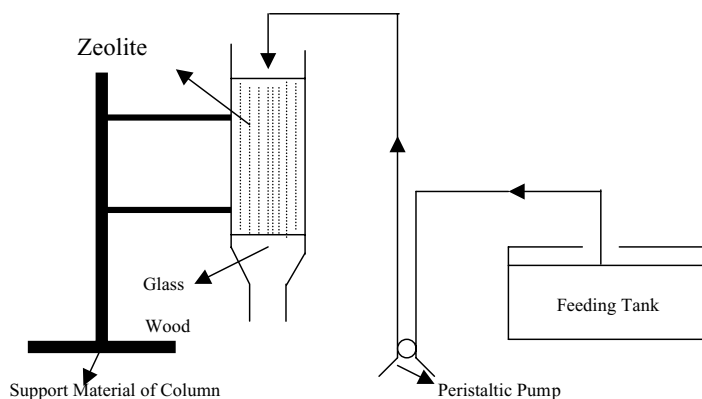

Fig. 1. The experimental setup.

Experiments were all performed in a column of 1.20 cm in diameter and 55 cm height and operated in the upflow mode. The column experiments were conducted at 5 and approximately 12 mg NH_4^+-$N1^{-1}$. The sample was filtrated with a filter paper (0.45 µm) in order to eliminate inert materials. The experimental setup is illustrated in Fig. 1. The features of setup are given in Table 2.

2.3.1. Effect of flowrate

Flowrates determined contact times were controlled with a pump. Wastewater was fed into the column system at 4, 2, 1, and 0.5 ml min^{-1} flowrates (5, 10, 20, and 40 min contact times) with constant influent pH value as 4.5. This process continued until zeolite reached saturation ($C/Co = 1$). For the flowrates of concern, the breakthrough curves of the system were drawn and compared with each other.

2.3.2. Effect of pH

The effect of different pH values ranging between 4 and 7.5 at optimum flowrate (0.5 ml min^{-1}) was investigated. It was observed that the highest removal efficiency was achieved at pH 4, based on the results of breakthrough curves. Since complete removal of NH_4^+-N was not possible to achieve at an initial concentration about 12 mg NH_4^+-$N1^{-1}$ in column experiments, initial NH_4^+-N concentration was decreased to 5 mg NH_4^+-$N1^{-1}$ and the experiment was repeated to observe if 100% removal efficiency could be reached.

2.4. Washing samples with acid

The effect of washing the zeolite sample with acid (0.005 M HNO_3) at 150 rpm stirring rate was also considered. Following treatment with acid, it was washed out with distilled water and dried at 105 °C for 24 h before using it in column experiments to create breakthrough curves.

2.5. Regeneration experiments

NaCl solution (1 M) was used for regeneration. The NaCl solution was passed through the column at three different flowrates (0.3, 0.2, and 0.1 ml min^{-1}) and a constant pH of 10 to determine the effect of contact time on regeneration, and thus, on ammonium removal efficiency. The ammonium removal efficiencies obtained using regenerated samples were compared with those obtained using natural ones.

2.6. Cation exchange capacity

Cation exchange capacity was measured with a Jenway Model Flame Photometer through analyzing sodium concentration in the effluent. The details of the method used for the determination of cation exchange capacity of sample are described by Semmens and Martin [37]. Ten grams of sample was given into column and 2 M NaCl solution was added in order to convert the zeolite to Na^+ form. Residual NaCl solution on zeolite surface was washed with distilled water. Then 100 ml 1 M KCl solution was given into column.

Since the K^+ selectivity of clinoptilolite is higher with respect to its Na^+ selectivity, saturation with Na^+ was first performed. Then, Na^+ ion concentration in KCl solution was measured with flame photometer and cation exchange capacity was calculated.

3. Results and discussion

3.1. Batch experiments

3.1.1. Effect of stirring time and initial ammonium concentration

NH_4^+-N removal, depending on stirring time, is given in Fig. 2. As shown in Fig. 2, after 20 min stirring time, the removal efficiency did not change considerably. Therefore, the optimum value of stirring time was found to be 20 min.

Concentrations in the range 8.8–885 mg NH_4^+-$N1^{-1}$ were studied to investigate effects of NH_4^+-N concentrations
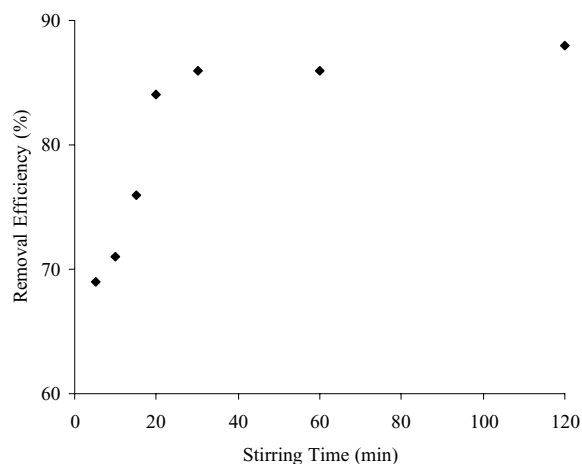
Table 2
Characteristics of the experimental system

Water flow rate	0.5, 1, 2, 4 ml min^{-1}
Column height	55 cm
External diameter	1.20 cm
Internal diameter	1.06 cm
Area	0.88 cm^2
Column material	Glass
Packet height	20 cm
Bed volume	19 cm3
Ion exchanger	
Type	Clinoptilolite
Mass	15 g
Size range	1–2 mm
Type of pump	Peristaltic pump, Master flex, 100

Fig. 2. The change of NH_4^+-N removal efficiency vs. stirring time (NH_4^+-N: 88 g l^{-1}; clinoptilolit/solution amount: 10 g l^{-1}; particle size: 1–2 mm, T: 20 °C).
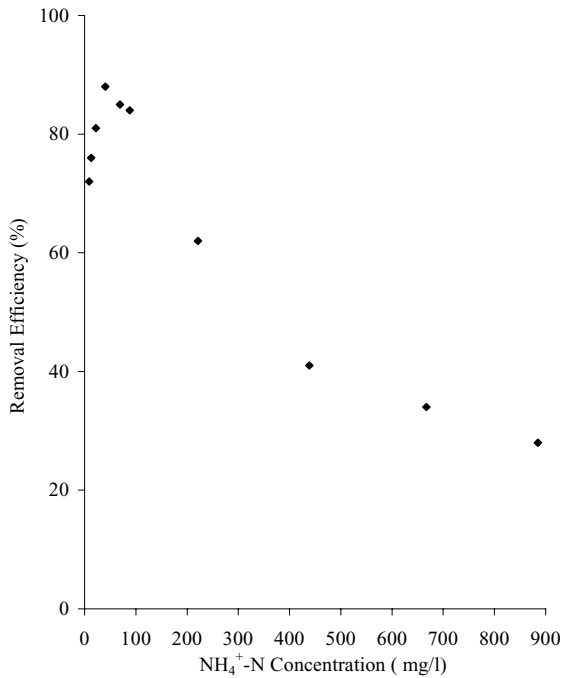
Fig. 3. Different NH_4-N^+ concentrations vs. removal efficiencies (T: 20 °C).

on removal efficiency. The increase at removal efficiency was achieved in the range of 8.8–40.3 mg NH_4^+-$N l^{-1}$ concentrations as shown in Fig. 3. After 40.3 mg NH_4^+-$N l^{-1}$ concentration, removal efficiency of NH_4^+-N decreased. Increase at removal efficiency in range between 8.8 and 40.3 mg NH_4^+-$N l^{-1}$ could be attributed to the weak binding between ion exchanger material (zeolite) and NH_4^+. This result can be generally expected from clinoptilolite having micropores and macropores [49].

3.1.2. Adsorption isotherms

Adsorption isotherms are essential for the description of how NH_4^+-N concentration will interact with zeolite (clinoptilolite) and are useful to optimize the use of zeolite as an adsorbent. Therefore, empirical equations (Freundlich or Langmuir isotherm model) are important for adsorption data interpretation and predictions. Both Freundlich and Langmuir models were used for the evaluation of experimental results. The Freundlich model is as follows [50]:

$$q_e = K_f C_e^{1/n}$$

where K_f and $1/n$ are constants.

$$K_f = 2.23, \quad 1/n = 0.38 \quad \text{and} \quad R^2 = 0.9847$$

For 20 °C isotherm equilibrium of NH_4-N^+ ion exchange:

$$q_e = 2.23 C_e^{0.38}$$

Maximum amount of NH_4^+-N adsorbed on zeolite (q_e) was 25.93 mg g^{-1}.
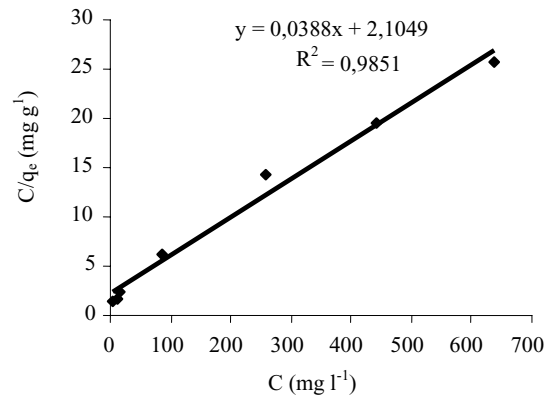

Fig. 4. Langmuir adsorption isotherm curve (T: 20 °C).

The Langmuir model which is given below assumes a uniform distribution of energetic adsorption sites [51]:

$$q_e = \frac{q_m K C_e}{1 + K C_e}$$

where q_e is the amount adsorbed, C_e is equilibrium concentration of adsorbate, q_m is the amount of adsorbate adsorbed per unit mass of zeolite corresponding to complete monolayer coverage, and K is the Langmuir constant.

$$q_m = 25.77 \, \text{mg/g}, \quad K = 0.018, \quad R^2 = 0.9851.$$

For 20 °C, isotherm equilibrium of NH_4-N^+ ion exchange was found to be as follows:

$$q_e = \frac{0.46 C_e}{1 + 0.018 C_e}$$

The maximum amount of NH_4^+-N adsorbed on zeolite (q_e) was 23.70 mg g^{-1}.

As shown in Figs. 4 and 5 and above equations, both isotherms could be used. However, when the amount of the ammonium ion adsorbed (q_e) was considered, the Freundlich
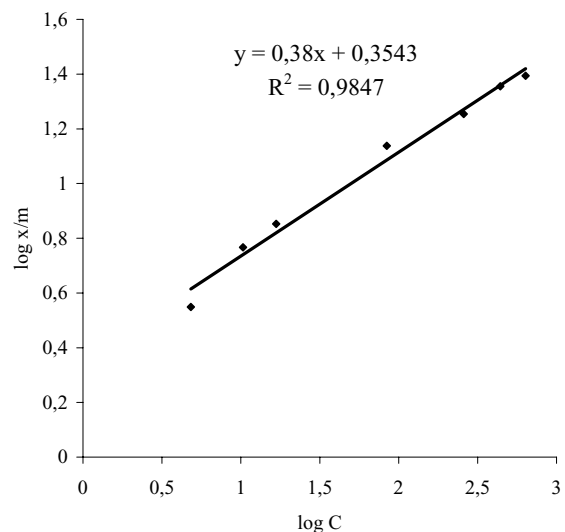

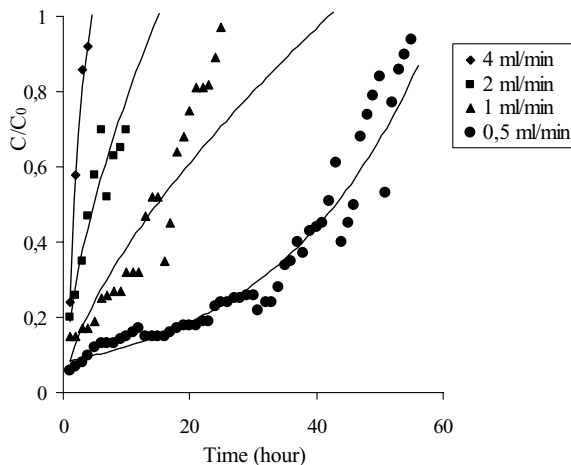Fig. 5. Freundlich adsorption isotherm curve (T: 20 °C).

Fig. 6. Breakthrough curves for wastewater containing NH_4^+-N ions (T: 20 °C; pH 4.5; Q: 4, 2, 1, 0.5 ml min^{-1}).

isotherm of NH_4^+-N on zeolite gave a q_e higher than that of Langmuir isotherm. Therefore, the Freundlich isotherm model should be employed for the experimental data.

3.2. Column experiments (breakthrough analysis)

3.2.1. Effect of flowrate

Influent NH_4^+-N concentration of wastewater was approximately 12 mg NH_4^+-N l^{-1}. For each contact time and flowrate employed, the breakthrough curves are given in Fig. 6. The column, when operated at flowrates of 4, 2, 1, and 0.5 ml min^{-1}, reached saturation value in very short time periods. Corresponding time periods to reach saturation values for the above flowrates were found to be 4th, 11th, 25th, and 56th hours, respectively. As can also be derived from the above given values, the time required to reach saturation increases with decreasing flowrate, or, in other words, increasing contact time. Based on experimental results, the adsorption capacities determined for NH_4^+-N ions at saturation values for 4, 2, 1, and 0.5 ml min^{-1} flowrates (pH 4.5) were found to be 0.25, 0.46, 0.63, and 0.87 mg NH_4^+-N g^{-1}, respectively.

The flowrate is one of the important parameters in column design. When compared with the one achieved at 4 ml min^{-1}, it was observed that the adsorption capacities increased by 84, 152, and 248% when the flowrate was decreased to 2, 1, and 0.5 ml min^{-1}, respectively. The optimum flowrate was determined to be 0.5 ml min^{-1}.

3.2.2. Effect of pH

Breakthrough curves were determined for various pH values. They are illustrated in Figs. 7 and 8 for 0.5 ml min^{-1}. As can be seen from the figures, the time required to reach saturation for pH 7.5 and 4 were 41 and 67 h, respectively.

Adsorption capacities determined at pH 7.5, 6.0, 5.5, 5.0, 4.5, 4.0, and 0.5 ml min^{-1} flowrate were calculated to be 0.67, 0.87, 0.71, 0.78, 0.87, and 1.08 mg NH_4^+-N g^{-1}, re-
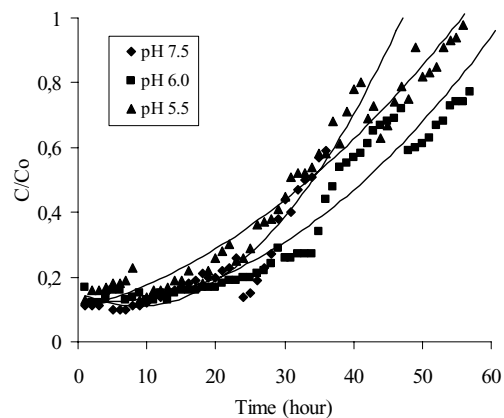

Fig. 7. Breakthrough curve for wastewater containing NH_4^+-N ions (T: 20 °C; pH 7.5, 6.0, 5.5; Q: 0.5 ml min^{-1}).

spectively. Thus, it was considered that the optimum pH was 4 for ammonium removal from wastewater. As can be seen from diffraction patterns of the samples, two of them obtained at pH 4 and 4.5 were almost same and not much different from the original one (Fig. 9). However, Koon and Kaufman [28] studied the effect of pH (4, 6, 8, and 10) on ammonia removal and reported that the highest adsorption capacity of the sample was reached at pH 6. The adsorption capacity decreased a little bit at pH 4. Vaughan [52] reported that a structural degradation was detectable at pH < 2.

In this study; as shown above, adsorption capacities of samples were same for pH 4.5 and 6 (adsorption capacity 0.87 mg NH_4^+-N g^{-1}). The highest capacity of sample was 1.08 mg NH_4^+-N g^{-1} at pH 4. Zeolite sample is mixture of clinoptilolite and mordenite. Therefore, it could not fully compare with clinoptilolite studies. In this study; complete NH_4^+-N removal was not possible to achieve. Therefore, influent ammonium concentration (approximately 12 mg NH_4^+-N l^{-1}) was decreased to 5 mg NH_4^+-N l^{-1}. The system was operated at a flowrate of 0.5 ml min^{-1} and pH 4 at which, formerly, the highest adsorption capacities were obtained. As shown in Fig. 10, 100% removal efficiency
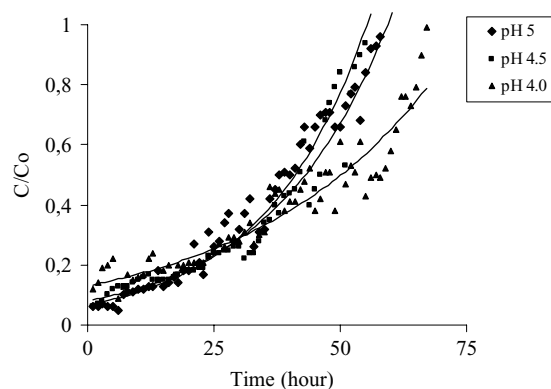

Fig. 8. Breakthrough curve for wastewater containing NH_4^+-N ions (T: 20 °C; pH 5, 4.5, 4.0; Q: 0.5 ml min^{-1}).
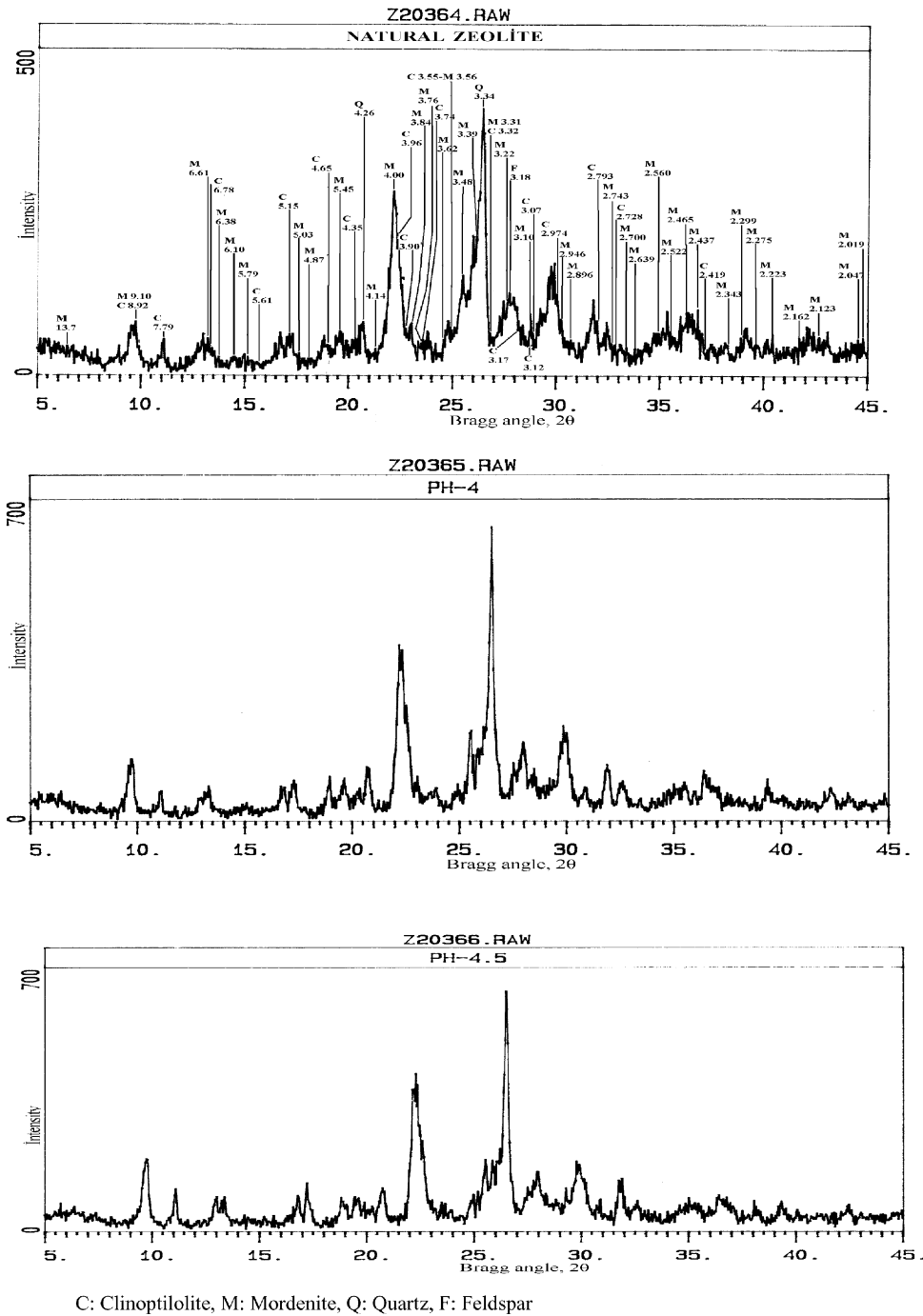
C: Clinoptilolite, M: Mordenite, Q: Quartz, F: Feldspar

Fig. 9. The results of X-ray diffraction analysis.

was obtained. However, the adsorption capacity was found to be 0.70 mg NH_4^+-N g^{-1}.

3.2.3. Effect of acidification on NH_4^+-N ion removal

The breakthrough curve for the acid-washed sample is given (0.005 M HNO_3) in Fig. 11. In literature, for removal of ions, conditioning generally is preferred to increase adsorption capacity. The suitable form was found to be the Na form [28,45]. Inel [29] also considered ammonium ion adsorption with acid-activated zeolite samples. As mentioned before, especially conditioning with NaCl increases the adsorption capacity in a range between 25 and 100% [53,37]. There are amorphous materials in pores of zeolite rocks which prevent ion passage when they contact with solution. It was determined that these materials can be removed from these pores by washing with 0.1–0.25 M diluted acid. It was concluded that small amounts of cations could also be removed [44]. As shown in Fig. 11, the NH_4^+-N removal

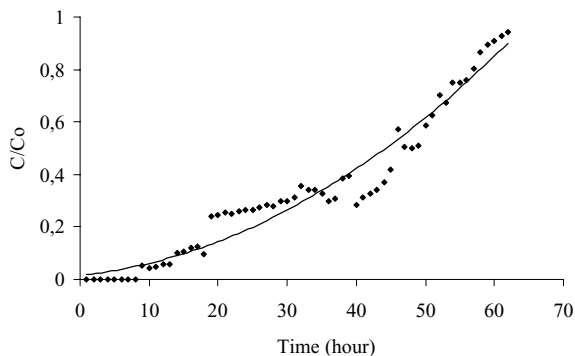Fig. 10. Breakthrough curve for wastewater containing initial NH_4^+-N ion $5 \, mg \, l^{-1}$ (*T*: $20\,^{\circ}C$; pH 4.0; *Q*: $0.5 \, ml \, min^{-1}$).

efficiency increased by 22% when compared with the efficiency obtained using natural sample. Adsorption capacity of the acid-activated sample was calculated to be 1.32 mg NH_4^+-N g^{-1}.

3.3. Regeneration studies

Zeolite saturated with NH_4^+-N ions was regenerated with 1 M NaCl solution. The system was operated at three different contact times (10, 20, and 40 min, corresponding flowrates are 0.3, 0.2, and 0.1 ml min^{-1}, respectively) based on the batch experimental results. 50-ml samples were taken from the effluent during regeneration and analyzed for NH_4-N. The results are illustrated in Fig. 12. Then, regenerated zeolite samples were used for ammonium removal. Fig. 13 illustrates the breakthrough curves of the natural and regenerated zeolite samples. As can be seen from the figure, there is a 31.52% loss of adsorption capacity after regeneration at pH 10. The adsorption capacities for natural zeolite and regenerated zeolite were found to be 1.08 and 0.73 mg NH_4^+-N g^{-1}, respectively under the same operational conditions (*Q*: $0.5 \, ml \, min^{-1}$, pH 4).

Fig. 12. The change of amount of NH_4-N^+ ions in solution released from clinoptilolite depending on regenerated volume (*T*: $20\,^{\circ}C$).

3.4. Determination of cation exchange capacity of sample (CEC)

Cation exchange capacities were calculated using the following equation:

$$CEC \, (meq. \, g^{-1}) = (V_{KCl}) \times (C)/m_z$$

where V_{KCl} is the volume of the KCl solution (l); *C* is the Na^+ ion concentration in KCl solution (meq. l^{-1}); and m_z is the mass of the clinoptilolite in column (g).

The cation exchange capacity of different clinoptilolite samples in Turkey are reported to change between
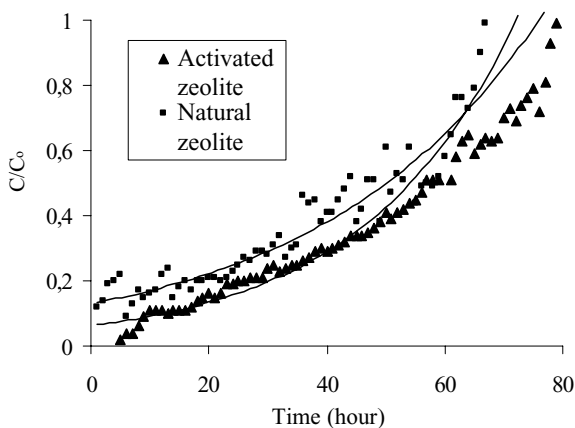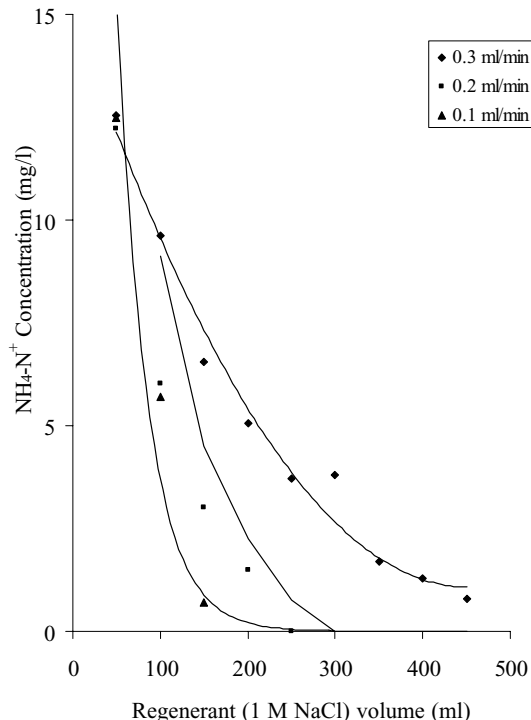

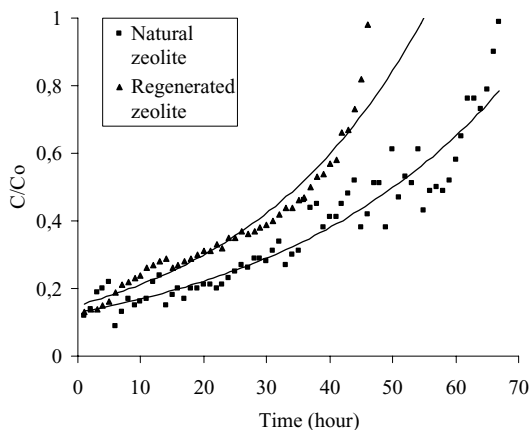Fig. 11. Comparison of activated sample with acid and natural clinoptilolite (*T*: $20\,^{\circ}C$; pH 4; *Q*: $0.5 \, ml \, min^{-1}$).

Fig. 13. The effect of regeneration on the performance of clinoptilolite (*T*: $20\,^{\circ}C$; pH 4; *Q*: $0.5 \, mg \, l^{-1}$).

Table 3
Comparison of zeolite sample studies with some literature values

Reference	Sample	Theoretical exchange capacity (meq. g^{-1})	Cation exchange capacity (meq. g^{-1})	Breakthrough capacity (mg NH$_4$-N g^{-1})	Influent ammonium nitrogen values (mg NH$_4$-N l^{-1})
White and Bursey [56]	[a]Na-clinoptilolite	–	1.37	–	–
Metropolous et al. [57]	Na-clinoptilolite	2.25	–	–	–
	Na-mordenite	2.114			
	Na-ferrierite	1.795			
Baykal and Guven [10]	Na-clinoptilolite	–	–	2	15–17
Dryden and Weatherley [58]	Na-clinoptilolite	–	2.1	–	1–5
Haralambous [59]	Na-clinoptilolite	2.27	–	1.09 meq. NH$_4$ g^{-1}[b]	–
Roman and Warchol [60]	Na-clinoptilolite1	–	1.17	–	–
	Na-clinoptilolite2	–	1.63	–	
Hlavay et al. [45]	Na-clinoptilolite	–	–	4.05, 4.07, 4.47	17, 27,45
Booker et al. [61]	Na-clinoptilolite	–	–	1.78	34.3
Present study	Natural zeolite (clinoptilolite + mordenite)	2.29	1.65	1.08	11–13

[a] Na-form clinoptilolite.
[b] Batch study.

140 and 200 meq. per 100 g [54]. In this study, cation exchange capacity of the zeolite sample was determined to be 164.62 meq. per 100 g for the particle size of concern. It was difficult to discuss ammonium removal studies from literature, since so various parameters (such as initial ammonium concentration, particle size, flowrate, structure of zeolite, etc.) were studied in literature, especially with Na-form clinoptilolite. The zeolite used in this study was used as natural without Na conditioning. In literature, effective or breakthrough capacities for a number of western clinoptilolite samples showed a considerable range. Samples from Owyhee Country, Idaho, have the highest capacities, 0.14 meq. g^{-1}, whereas samples from Washoe Country, Nevada, exhibit the lowest capacities, 0.06 meq. g^{-1} [55]. It was considered a few quantitative comparision of the behavior and performance of the Dogantepe zeolite with other clinoptilolites. Therefore, comparison of present study with others is given in Table 3.

As shown from Table 3, capacities found in column studies are very low compared to literature values. The cation exchange capacity of sample was found to be approximately 1.65 meq. g^{-1}. Theoretical capacity of zeolites was found to be 2.29 meq. g^{-1}. Impurities such as quartz and feldspar do not affect the results because of their absence of adsorption abilities. Thus, non-zeolitic minerals should be ignored.

Despite the theoretical high exchange capacity of zeolite, low ammonium quantities are retained. One of the reasons for low breakthrough capacities is the high percentage of non-zeolitic impurities (20%) and the relative low capacity of mordenite which forms the 35% of the zeolite. Another reason is relatively large size of particles (1–2 mm). Depending on the textural properties of zeolite samples, smaller sizes may be needed to decrease the diffusional resistance which is usually the controlling resistance for most zeolite particle–cation systems. The shape of the breakthrough curves and immediate breakthrough of ammonium ions may

be taken as an indication of this. Furthermore, column studies were carried out with feeds obtained from conventional activated sludge wastewater plant effluent. Presence of other cations in wastewater might decrease the capacity for ammonium. Briefly, in applications of ammonium removal from wastewater, other cations (Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}) will be present. These other cations will compete for sites on the zeolite, hence lowering the effective capacity for the ammonium ion. For the current study, especially high Ca^{2+} ion concentration (161 mg l^{-1}) could decrease the capacity for ammonium. Since NH$_4^+$-N ion removal by using natural zeolite was aimed, preconditioning with NaCl, HCl, HNO$_3$, H$_2$SO$_4$, and NaOH, etc. solutions was not considered. This also significantly decreases the capacity of zeolite. However, in batch studies, amount of NH$_4^+$-N adsorption was high because of using synthetic feeding.

The influence of pretreatment upon the cation exchange capacity and selectivity of zeolites for ammonia ions was investigated by a number of researchers. It was demonstrated that the CEC of clinoptilolite depends on the pretreatment method and that conditioning improves its ion exchange ability and removal efficiency.

4. Conclusion

In this study, NH$_4^+$-N removal from wastewater by using zeolite was investigated. The column system was operated at different flowrates. Then the breakthrough curves were drawn for each contact time. The system saturated very fast, within 5 min. The highest adsorption capacity was obtained at a contact time of 40 min (Q: 0.5 ml min^{-1}). It was observed that the pH value, at which the highest adsorption capacity (1.08 mg NH$_4^+$-N g^{-1}) was obtained, was 4. 100% NH$_4^+$-N removal efficiency was not possible to achieve for an initial ammonium concentration of 12 mg l^{-1}. Therefore,

influent NH_4^+-N concentration was decreased to $5\,\mathrm{mg\,l^{-1}}$ and the experiments were repeated. It was found that 100% removal efficiency could be achieved in the system. It can be concluded that this method can be used for low influent NH_4^+-N concentrations.

The highest adsorption capacity obtained with acid-washed sample was determined to be $1.32\,\mathrm{mg\ NH_4^+}$-N$\,\mathrm{g^{-1}}$ and the cation exchange capacity of Dogantepe zeolite was found to be $164.62\,\mathrm{meq.}$ per $100\,\mathrm{g}$. However, the efficiency of the natural or acid washed zeolite can be further increased through conditioning with Na.

As a summary, NH_4^+-N ions can be removed from wastewater by using Dogantepe (Amasya), Turkey clinoptilolite. Perhaps, it can be concluded that the selectivity of the natural zeolites for a particular ion, such as NH_4, is very much dependent on its origin as well as on the type of ions already present in the structure. Comparing the results of this study with literature values, it is very hard to give general conclusions for the ammonium exchange capacities of these types of minerals (mixture of clinoptilolite and mordenite).

Acknowledgements

References

[1] R. Sedlack, Phosporus and Nitrogen Removal from Municipal Wastewater: Principles and Pratice, second ed., Lewis Publisher, New York, 1991.

[2] Metcalf and Eddy, revised by G. Tchobanoglous, F.L. Burton, Wastewater Engineering: Treatment, Disposal, Reuse, third ed., McGraw-Hill International Editions, USA, 1991.

[3] G. Kelly, Environmental Engineering, Mc-Graw Hill Publishing Company, Maidenhead, England, 1996.

[4] M.A. Jama, H. Yücel, Sep. Sci. Technol. 24 (15) (1990) 1393–1416.

[5] Water Treatment Handbook, fifth ed., Degremont, 1979, pp. 1186.

[6] L.L. Ames, The cation sieve properties of clinoptilolite, Am. Miner. 45 (1960) 689–700.

[7] B.W. Mercer, L.L. Ames, C.J. Touhill, W.J. Van Slyke, R.B. Dean, J. Water Pollut. Control Fed. 42 (1970) 95–107.

[8] J.R. McLaren, G.J. Farquhar, J. Environ. Eng. Div., ASCE 99 (1973) 429–446.

[9] L. Liberti, G. Boari, D. Petruzzeli, R. Passino, Water Res. 15 (1981) 337–342.

[10] B. Beler Baykal, D. Akça Güven, Water Sci. Technol. 41 (9) (1997) 107–114.

[11] M.L. Nguyen, C.C. Tanner, N. Z. J. Agric. Res. 41 (1998) 427–446.

[12] R. McVeigh, L. Weatherley, Water Sci. Technol. 40 (2) (1999) 143–149.

[13] Water Pollution Control Regulation, National Newspaper, 04.09.1988.

[14] S.K. Ouki, M. Kevannagh, Water Sci. Technol. 39 (10–11) (1999) 115–122.

[15] F.A. Mumpton, Natural zeolites: a new industrial mineral commodity, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites, Occurrence, Properties, Use, Pergamon Press, New York, 1978, pp. 285–302.

[16] R.J. McVeigh, The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria, Ph.D. thesis, The Queen's University of Belfast, Northern Ireland, UK, 1999.

[17] L.L. Ames, Zeolite removal of ammonium ions from agricultural wastewaters, in: Proceedings of the 13th Pacific Northwest Industrial Waste Conference, Washington State Universitiy, Pullman, Washington, 1967, p. 135.

[18] G.V. Tsitsishvili, T.G. Andronikashivili, in: P.A., Williams (Ed.), Natural Zeolites, Ellis Harwood Ltd., 1992, p. 290.

[19] Y. Murakami, A. Iijima, J.W. Ward (Eds.), Elsevier Scientific Publ. Co., Amsterdam, 1986.

[20] G. Ataman, Batı Anadolu Zeolit Olusumları, Hacettepe Üniversitesi, Yer Bilimleri Enstitüsü, Ankara, 1977.

[21] R.L. Hay, R.A. Sheppard, Rev. Miner. 4 (1981) 93.

[22] B.W. Mercer, L. Ames, Zeolite Ion Exchange in Radioactive and Municipal Waste Water Treatment, 1978, pp. 451–462.

[23] F.A. Mumpton, P.H. Fischman, J. Anim. Sci. 45 (1977) 1188–1203.

[24] H. Yalçın, Cumhuriyet Üniversitesi Mühendislik Fakültesi Dergisi, Seri A. Yerbilimleri Cilt. 14, Sayı 1, 1997, pp. 43–56.

[25] F. Macasek, D. Keltos, L. Matel, Solvent Extract. Ion Exchange 9 (5) (1991) 865–874.

[26] G. Gottardi, Minerology and crystal chemistry of zeolites, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites, Pergamon Press Ltd., 1978, p. 537.

[27] M.J. Zamzow, B.R. Eichebaum, Sep. Sci. Technol. 25 (13–15) (1990) 1555–1569.

[28] J.H. Koon, W.J. Kaufman, J. WPCF 47 (3) (1975) 448–465.

[29] O. İnel, Tr. J. Chem. 19 (1995) 323–330.

[30] N. Aral, A. Günay, O. Sevimoğlu, M. Çalı, E. Debik, Fres. Environ. Bull. 8 (5–6) (1999) 344–349.

[31] US-EPA, Optimisation of ammonia removal by ion exchange using clinoptilolite, EPA-Report, Project #17080 DAR, 1971.

[32] H. Witte, M. Keding, Korrespondenz Abwasser 11 (1992) 1612–1620.

[33] D.W. Ming, F.A. Mumpton, Zeolites in soil. in: J.B. Dixon, S.B. Weed (Eds.), Minerals in Soil Environments, second ed., Soil Science Society of America, Madison, WI, 1989, p. 873.

[34] M.W. Ackley, R.T. Yang, AIChE J. 37 (1991) 1645.

[35] K.D. Mondale, R.M. Carland, F.F. Aplan, Miner. Eng. 8 (1995) 535.

[36] R.M. Carland, F.F. Aplan, Miner. Metallurg. Process. 12 (1995) 210.

[37] M.J. Semmens, W.P. Martin, Water Res. 22 (5) (1988) 537–542.

[38] M.J. Zamzow, J.E. Murphy, Sep. Sci. Technol. 27 (1992) 1969–1984.

[39] M.R. Barrer, Cation-exchange equilibria in zeolites and feldspathoids, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites Occurrence, Properties, Use, 1978, pp. 385–395.

[40] JCPDS, Powder Diffraction File. Alphabetical Indexes Inorganic Phases. Swarthmore, PA, 1990, p. 871.

[41] G.W. Brindley, Quantitative X-ray mineral analysis of clays, in: G.W. Brindley, G. Brown (Eds.), Crystal Structures of Clay Minerals and their X-ray Identification, Mineralogical Society, London, 1980, pp. 411–438.

[42] APHA, Standard Methods for the Examination of Water and Wastewater, nineteenth ed., Washington, DC, USA, 1995.

[43] M.J. Semmens, A.C. Booth, G.W. Tauxe, J. Environ. Eng. Div., ASCE 104 (2) (1978) 231–244.

[44] M.J. Semmens, S.R. Linne, Studies on the ammonium removal and filtration performance and regeneration of clinoptilolite, in: Proceedings of the 39th Industrial Waste Conference, Purdue University, 1985.

[45] J. Hlavay, Gy. Vigh Olaszıv, J. Inczdy, Water Res. 16 (4) (1982) 417–420.

[46] R.C. Polta, A demonstration of ammonia removal by ion exchange. in: Proceedings of the 33rd Industrial Waste Conference, Purdue University, May 9, 10 and 11, 1978.

[47] Z. Milan, E. Sanchez, P. Weiland, C. de Las Pozas, R. Borja, R. Mayari, N. Rovirosa, Chem. Eng. J. 66 (1997) 65–71.

[48] C. Ratanatamskul, C. Chiemchaisri, K. Yamamoto, Water Sci. Technol. 31 (9) (1995) 145–152.

[49] T.C. Jorgensen, L.R. Weatherley, Water Res. 37 (2003) 1723–1728.

[50] A. Mellah, S. Chegrouche, Water Res. 31 (1997) 621.

[51] C.D. Holland, R.G. Anthony, Fundamentals of Chemical Reaction Engineering, second ed., Prentice Hall, Englewood Cliffs, NY, 1989.

[52] D.E.W. Vaughan, Properties of natural zeolites, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites, Occurrence, Properties, Use, Pergamon Press, New York, 1978, pp. 353–371.

[53] L. Curkovic, S. Stefanovic, T. Filipan, Water Res. 31 (6) (1997) 1379.

[54] A. Kuleyin, Doğal Klinoptilolite ile Sızıntı Suyu ve Atıksudan Ağır metal ve Amonyak Giderimi, Doktora Tezi, Ph.D. thesis, OMÜ Fen Bilimleri Enstitüsü, Samsun, 1999.

[55] C.B. Murphy, O. Hrycykm, W.T. Gleason, Natural zeolites: novel uses and regeneration in wastewater treatment, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites, Occurrence, Properties, Use, Pergamon Press, New York, 1978, pp. 471–478.

[56] D.A. White, R.L. Bussey, Sep. Purif. Technol. 11 (1997) 137–141.

[57] K. Metropoulos, E. Maliou, M. Loizidou, N. Spyrellis, J. Environ. Sci. Health A28 (7) (1993) 1507–1518.

[58] H.T. Dryden, L.R. Weatherley, Aquacultural Eng. 8 (1989) 109–126.

[59] A. Haralambous, E. Maliou, M. Malamis, Water Sci. Technol. 25 (1992) 139–145.

[60] R. Petrus, J. Warchol, Microporous Mesoporous Mater. 61 (1–3) (2003) 137–146.

[61] N.A. Booker, E.L. Cooney, A.J. Priestley, Water Sci. Technol. 34 (9) (1996) 17–24.