

# Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite

Ahmet Demir\*, Ahmet Günay and Eyyüp Debik

Yildiz Technical University, Department of Environmental Engineering, 80750, Istanbul, Turkey

## Abstract

Ammonium removal from aqueous solution by a natural ion-exchange resin was investigated by considering the factors affecting the ammonium-exchange capacity including the zeolites' particle size, the loading flow rates and the impact of a number of regenerations upon the ion-exchange capacity. The resin column was exhausted by downflow at 10, 25, 50 and 75 bed volume (BV)/h, until effluent ammonium concentration of more than 10 mg/l  $\text{NH}_4^+$  was achieved. The results indicate that conditioning of the zeolite improves the ion-exchange capacity and that the smaller particle size also causes a higher ion-exchange capacity due to greater available surface area. The actual ion-exchange capacity of the conditioned fine (-1.00+0.125) and coarse (-2.00+1.00) mm clinoptilolite was found to be 0.57 and 0.38 meq/g zeolite, respectively.

## Introduction

Zeolites are aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations (normally  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$ ) in addition to water in their structural framework. The physical structure is porous, containing interconnected cavities in which the metal ions and water molecules are contained. Clinoptilolite is one of the natural zeolites used to remove cations such as heavy metals (Ahmed et al., 1998; Ouki and Kavannah, 1999; Callejas et al., 2001) and ammonium ions from aqueous solutions (Mercer et al., 1970; Koon and Kaufman, 1975; Jorgensen and Barkacs, 1976; Klieve and Semmens, 1980; Schoeman, 1986).

The zeolite-rich tuffs of Bigadiç, in the northwestern part of Turkey, are mainly coarse-grained, glassy, with ash tuffs on top (Sirkeciolu and Senatlar, 1995). The availability of natural zeolites in many countries facilitates low-cost treatment by ion-exchange systems (Mercer et al., 1970). The use of clinoptilolite as a resin has the following advantages:

- good performance of ammonium removal under low temperature;
- compact size and easy maintenance of the full-scale plants; and
- ammonium-ion selectivity (Singh and Prasad, 1997).

The widespread application of ion-exchange processes has led to the development of equipment that functions almost automatically and requires relatively little maintenance. While the total exchange capacity of clinoptilolite is somewhat less than that of synthetic organic resins, its selectivity for the ammonium ion gives it a distinct advantage over conventional exchange resins.

Among the technologies for ammonium control are such processes as air stripping, breakpoint chlorination, nitrification-denitrification and ion-exchange (Metcalf and Eddy, 1991). Ion-exchange seems to be an attractive method especially when low-cost minerals can be used as an exchanger.

Ammonium removal from aqueous solution by ion-exchange has been investigated by many researchers (Koon and Kaufman, 1975; Gaspard et al., 1983; Schoeman, 1986; Haralambous et al., 1992). Koon and Kaufman (1975) were concerned with ammonium removal from municipal wastewater by clinoptilolite. Gaspard et al. (1983) examined the ammonium removal characteristics from drinking water by clinoptilolite. Schoeman (1986) evaluated  $\text{NH}_3\text{-N}$  removal from an underground mine-water by South African clinoptilolite (Pratley) and compared it with Hector clinoptilolite from the USA. Haralambous et al. (1992) compared natural and synthetic zeolites for ammonium removal from aqueous solution.

In the aqueous solution, ammonium can exist in either the non-ionised form ( $\text{NH}_3$ ) and/or ionised form ( $\text{NH}_4^+$ ) depending on the pH and temperature. Of these two forms of ammonium, only the ionised one can be removed by the ion-exchange process. The equilibrium-exchange capacity remains constant up to pH 7. For optimum ion-exchange operation, the pH of the aqueous solution must be at or below 7.

Ion-exchange is an endothermic process. Hence, an increase in temperature tends to increase the exchange capacity of this process (Lin and Wu, 1996).

During the ion-exchange process, the  $\text{Na}^+$  ion is replaced by the  $\text{NH}_4^+$  ion, and hence the  $\text{Na}^+$  ion concentration increases in the liquid phase during the ion-exchange processes. When the ion-exchanger reaches breakthrough, the upflow or downflow regeneration method is applied. Gaspard et al. (1983) reported that the upflow regeneration is more attractive than down-flow regeneration.

The ammonium ion-exchange capacity varies depending on the presence of another cations in the aqueous phase and initial ammonium concentration (Gaspard et al., 1983; Lin and Wu, 1996; Singh and Prasad, 1997; Demir et al., 1998). The ion-exchange capacity is influenced significantly by chemical and physical pretreatment techniques and loading or regeneration of clinoptilolite. The influence of a pretreatment on ion-exchange capacity varied widely depending on the source of clinoptilolite (Klieve and Semmens, 1980).

The present work considers ammonium removal by a natural ion-exchange resin. This investigation concentrates on defining various operational parameters necessary to remove ammonium efficiently through ion-exchange by using the zeolite, clinoptilolite. The main objective of this study is to evaluate the capacity of

\* To whom all correspondence should be addressed.

☎ +90 212 259 7070 (2865); fax: +90 212 261 9041;

e-mail: ahmetd@yildiz.edu.tr

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Component (%)	Yücel and Çulfaz, 1985	Çelenli et al., 1994	Sirkecioglu and Senatlar, 1995
SiO <sub>4</sub>	-	67.96	-
SiO <sub>2</sub>	67.6	-	64.99
Al <sub>2</sub> O <sub>3</sub>	11.3	10.74	9.99
K <sub>2</sub> O	2.17	3.01	1.95
CaO	3.26	0.74	3.51
Na <sub>2</sub> O	-	0.81	0.18
MgO	1.18	1.49	1.01
Si	-	15.36	-
Fe <sub>2</sub> O <sub>3</sub>	0.77	-	3.99
MnO	0.02	-	-
TiO <sub>2</sub>	0.07	-	-
NaO <sub>2</sub>	0.3	-	-
H <sub>2</sub> O	13.4	-	14.47

Sieve opening, mm	1.00	0.60	0.50	0.30	0.25	0.125
% Passing sieve	100	64	54	28	20	0

Bigadiç clinoptilolite for removing ammonium ions from aqueous solutions under varying conditions.

## Materials and methods

In this study, two different clinoptilolite forms were used. One of them was raw clinoptilolite and the other a conditioned clinoptilolite which was used after the first regeneration. The experiments were conducted in two phases with investigations using batch sorption and column studies.

### Chemical and physical properties of the zeolite clinoptilolite

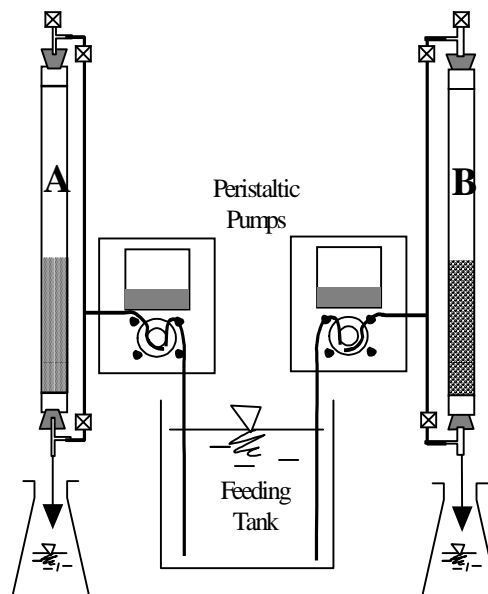
The ion-exchanger used in the experiments was obtained from Bigadiç, in the north-western part of Turkey. The natural zeolite was chosen on the basis of its good ammonium-ion selectivity and potentially low cost. The chemical properties of the clinoptilolite used in this study are given in Table 1.

The effective particle size was 0.18 mm with a uniformity coefficient of 2.98 for the fine particles. The sieve analysis is provided in Table 2.

Zeolite was broken into pieces and sieved into a diameter of (-1.00+0.125) and (-2.00+1.00) mm (numbers in the parentheses indicate sieve size in mm through which particles passed and were retained, respectively). The zeolite was then washed with distilled water to remove turbidity and after drying in an oven for over an hour at 70°C, was put in a desiccator.

### Test chemicals and analysis

Ammonium chloride stock solution (1 000 mg/l NH<sub>4</sub><sup>+</sup>) was prepared by dissolving NH<sub>4</sub>Cl in deionised water. The solution was further



**Figure 1**  
The experimental set-up

diluted before use. The ammonium chloride and other chemicals used were of analytical grade. Synthetic samples were prepared to give ammonium concentrations of 10, 20, 40 and 80 mg/l by adding appropriate amounts of ammonium chloride stock solution to distilled water.

The ammonium concentration of the samples was determined by the standard Nesslerisation method using Pharmacia LKB-Nowaspec-spectrophotometer (*Standard Methods*, 1983). It should be noted that no more than 10 ml of sample was taken for measurement of ammonium, and hence the total volume of the aqueous solution was affected insignificantly by sampling.

### Batch studies

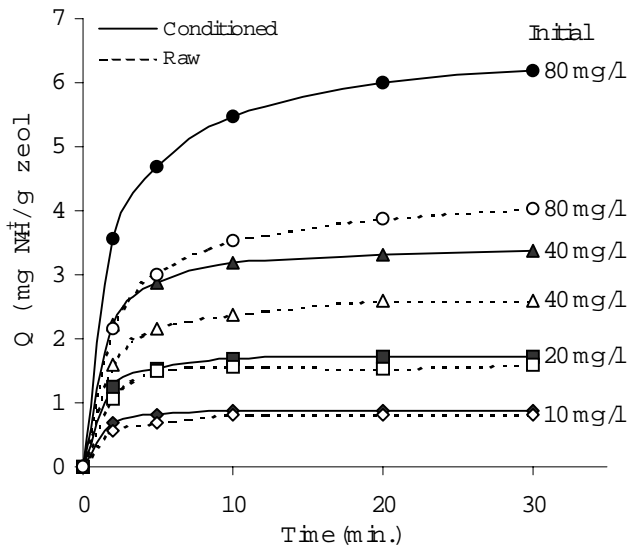
In the first phase of runs, batch sorption isotherms for the removal of ammonium were investigated. Batch sorption isotherms were determined in 500 ml conical flasks. Weighed amounts (0.4 g) of clinoptilolite were introduced into four conical flasks, to which 400 ml of ammonium solution concentrations of between 10 and 80 mg/l were added.

The flasks were shaken for 30 min and samples were taken periodically for measurement of aqueous-phase ammonium concentration. Preliminary tests confirmed that a 30 min contact time was enough to reach a steady-state ammonium concentration.

### Column studies

In this study, two columns (A and B) each with an inner diameter of 15 mm were used. The bed height and volume of the columns were 140 mm and 25 cm<sup>3</sup>, respectively. Column A was filled with fine zeolite (-1.00+0.125) mm and Column B was filled with a coarse zeolite (-2.00+1.00) mm.

In the column studies, operation and regeneration parameters, and ion-exchange capacity of clinoptilolite were investigated. Two peristaltic pumps (Watson Marlow 505L) were employed to feed the stock solution to the ion-exchange column at the desired flow rate. The ammonium concentration of the samples collected from the column exit was monitored. No stratification in the combined



**Figure 2**

Effect of initial ammonium concentration in the aqueous solution on the exchange capacity at 20 °C and pH 7-7.5

scheme was observed under the flow rates employed. The basic experimental setup is shown in Fig. 1.

The resin column was exhausted by downflow at three different superficial velocities of 25, 50 and 75 bed volume (BV)/h, until an ammonium breakthrough of more than 2 mg/l  $\text{NH}_4^+\text{-N}$  was achieved. The columns were then regenerated with two different NaCl solutions (10 g NaCl/l and 20 g NaCl/l) and at two different superficial velocities, namely, 16 BV/h and 25 BV/h. The regenerant was passed through the column in the upflow mode. The absence of ammonium in the effluent indicated the completion of regeneration. Another loading cycle was then carried out.

## Results and discussion

### Sorption isotherms

The Langmuir and Freundlich parameters were determined by the following procedures. The amount of ammonium accumulated on the clinoptilolite was calculated by the following expression as the difference between the amount present in the initial ammonium concentration and that remaining in solution after equilibrium with the clinoptilolite.

$$Q = \frac{(C_o - C_e)V}{M} \quad (1)$$

where:

- Q (mg/g) is the amount of ammonium adsorbed
- $C_o$  (mg/l) represents initial ammonium concentration
- $C_e$  (mg/l) represents equilibrium ammonium concentration
- V (l) is the volume of solution
- M (g) is the mass of zeolite.

Results determined by using Eq. (1) are plotted vs. time and shown in Fig. 2 for the fine (-1.00+0.125) mm clinoptilolite.

The initial ammonium concentration provides the necessary driving force to overcome all mass-transfer resistances of ammonium between the aqueous and solid phases. The removal of ammonium is high in the initial 5 min, but thereafter the rate significantly levels off and eventually approaches zero, i.e. when equilibrium is attained. These changes in the rate of removal might be due to the

TABLE 3 Langmuir and Freundlich models parameters for best fit and corresponding correlation coefficients		
	Raw zeolite	Conditioned
<b>Freundlich model</b>		
$K_f$	0.608	0.806
$1/n$	0.537	0.727
$r^2$	0.956	0.989
<b>Langmuir model</b>		
$K_L$	0.440	0.770
$A$	0.085	0.069
$r^2$	0.992	0.999

fact that, initially, all adsorbent sites were vacant and the solute concentration gradient was high. Afterwards, the ammonium uptake rate by the zeolite decreased significantly, due to decrease in adsorption sites. A decreasing removal rate, particularly towards the end of the experiment, indicated a possible monolayer of ammonium ions on the outer surface and pores of the zeolite and pore diffusion onto the inner surface of zeolite particles through the film due to continuous agitation maintained during the experiment.

The adsorption rate of ammonium by both raw and conditioned clinoptilolite was initially fast, during the first 5 to 10 min, depending on the initial ammonium concentration, and then gradually decreased with increase in contact time. With the increase of ammonium concentration in solution, the adsorption capacity of the ammonium ion also increases. Singh and Prasad (1997) observed that with high concentrations of ammonium (98.76 mg  $\text{NH}_4^+$  /100 ml), adsorption by 13X molecular sieve synthetic zeolites becomes constant, possibly because of complete removal of  $\text{Na}^+$  by  $\text{NH}_4^+$  cations.

The equilibrium removal of the ammonium ion considered can be mathematically expressed in terms of adsorption isotherms. Adsorption isotherm data are commonly fitted to the Freundlich or the Langmuir models as:

$$Q = K_f C_e^{1/n} \quad (2)$$

or

$$Q = \frac{K_L C_e}{1 + a C_e} \quad (3)$$

respectively, where:

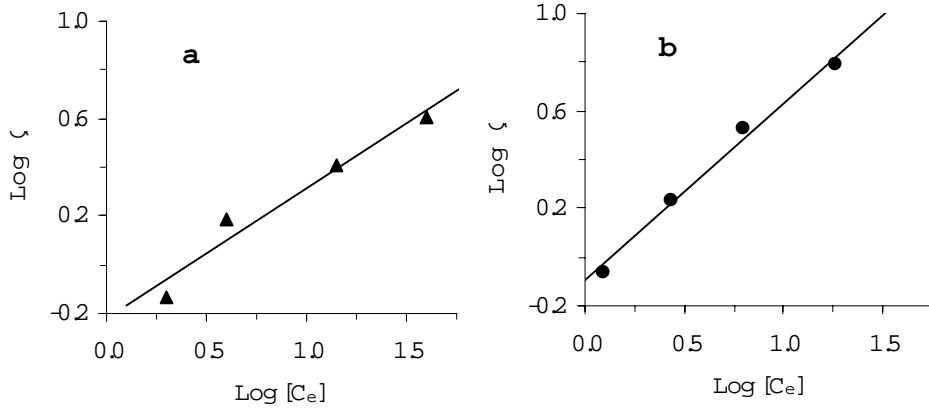
- $(K_f)$ , and  $(1/n)$  are indicative isotherm parameters of sorption capacity and intensity, respectively
- $(K_L)$  and  $(a)$  are Langmuir model parameters.

These models are rearranged to the linear form by taking logarithms on both sides.

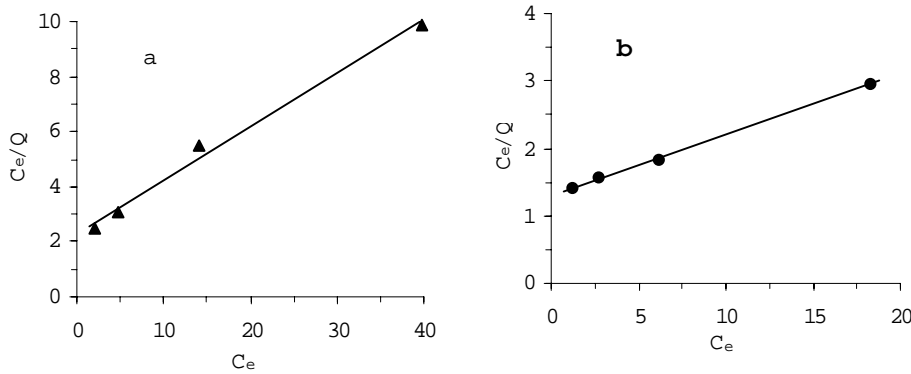
$$\log Q = \log K_f + n \log C_e \quad (4)$$

$$C_e/Q = 1/K_L + (a/K_L) C_e \quad (5)$$

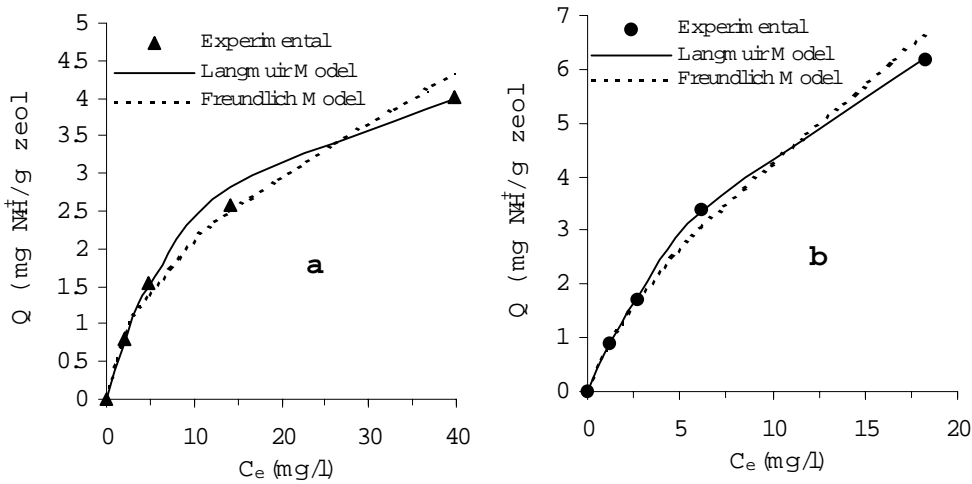
Plotting the experimental data using Eqs. (4) and (5) in Figs. 3 and 4 indicates that both models give good fit for the data. The values of  $(K_L)$ ,  $(a)$ ,  $(K_f)$  and  $(1/n)$  that best fitted the data as well as the corresponding correlation coefficients are presented in Table 3.



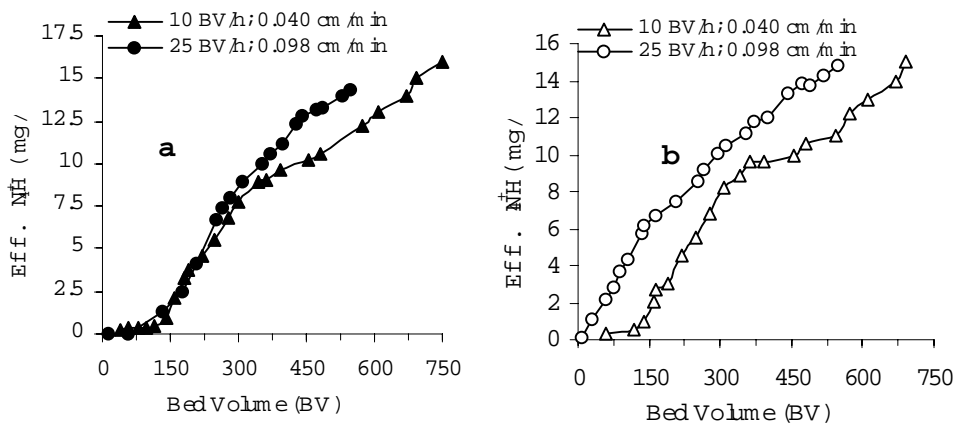
**Figure 3**  
Linearised Freundlich isotherm for ammonium removal by zeolite (10 g zeolite/l and 20 °C); a: Raw; b: Conditioned



**Figure 4**  
Linearised Langmuir isotherm for ammonium removal by zeolite (10 g zeolite/l and 20 °C); a: Raw; b: Conditioned



**Figure 5**  
Comparison of the Freundlich and Langmuir adsorption isotherms for ammonium ion removal; a: Raw; b: Conditioned.



**Figure 6**  
Effect of the superficial velocity on the breakthrough curve of ammonium removal at 20 mg/l  $\text{NH}_4^+$  initial ammonium concentration for raw zeolite; a: (-1.00+0.125) mm; b: (-2.0+1.0) mm

TABLE 4 Ion-exchange capacities of clinoptilolite					
NH <sub>3</sub> -N	Load BV/h	Ion-exchange capacity, meq/g	Break- point, BV	Natural zeolite	Reference
18.8 mg/l NH <sub>3</sub> -N municipal wastewater	16.6	0.68	200	Hector clinoptilolite (-0.84+0.30) mm	Koon and Kaufman (1975)
20 mg/l NH <sub>3</sub> -N	20	1.69 (total)	190	Conditioned zeolite	Klieve and Semmens (1980)
20.5 NH <sub>3</sub> -N underground mine- water	5 10 15	0.348 0.270 0.206	200 170 120	Pratley clinoptilolite (-0.70+0.25) mm	Schoeman (1986)
15 mg/l NH <sub>3</sub> -N synthetic tap water	11 17 25	0.53*	186 150 90	Bigadiç clinoptilolite (-0.84+0.297) mm	Sirkeciolu and Senatlar (1995)
20 mg/l NH <sub>3</sub> -N synthetic tap water	11 17 25	0.53*	185.0 167.5 85.0	Bigadiç clinoptilolite (-0.84+0.297)	
20 mg/l NH <sub>4</sub> <sup>+</sup> synthetic	25-50	0.57 **	450	Bigadiç clinoptilolite (-1.00+0.125)	
20 mg/l NH <sub>4</sub> <sup>+</sup> synthetic	75	0.57 **	350	Bigadiç clinoptilolite (-1.00+0.125)	
20 mg/l NH <sub>4</sub> <sup>+</sup> synthetic	25	0.38 **	300	Bigadiç clinoptilolite (-2.0+1.0)	
* Maximum total ion-exchange capacity ** ion-exchange capacities according to breakthrough point					

The comparisons of each of the models with the data are presented in Fig. 5.

As a consequence, the Freundlich and Langmuir isotherms for ammonium removal, on the raw clinoptilolite can be represented by the following empirical formula:

$$Q = 0.608 C_e^{0.537} \quad (6)$$

and

$$Q = \frac{0.44 C_e}{1 + 0.085 C_e} \quad (7)$$

respectively. For the conditioned clinoptilolite, the Freundlich and Langmuir isotherms are obtained as follows:

$$Q = 0.806 C_e^{0.727} \quad (8)$$

and

$$Q = \frac{0.77 C_e}{1 + 0.069 C_e} \quad (9)$$

respectively.

### Column studies

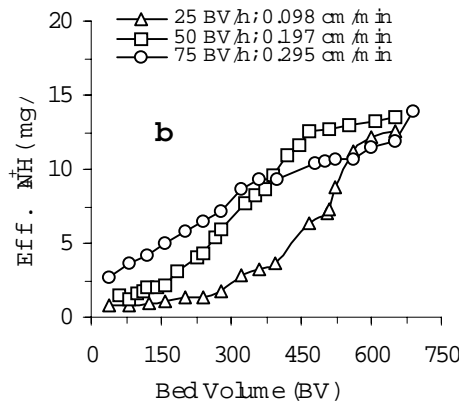
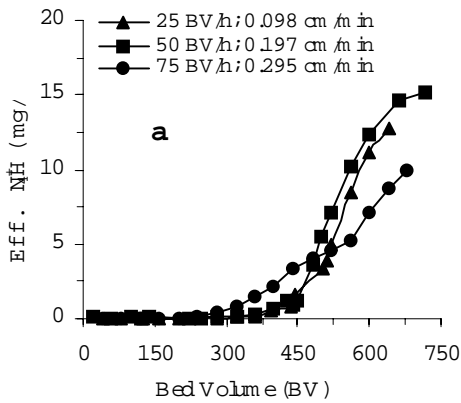
The concentrations of the solution for column studies were prepared synthetically at the level of 20 mg/l of NH<sub>4</sub><sup>+</sup>. The breakthrough curves of ammonium removal by clinoptilolite are shown in Figs. 6 and 7 for various superficial velocities of the aqueous solution.

The average ammonium leakage before breakthrough was less than 0.5 mg/l for Column-A after the first regeneration (Fig. 7 a). Changing the flow rate from 10 to 25 BV/h resulted in no significant decrease in ammonium adsorption capacity for the fine and the coarse raw clinoptilolite (Fig. 6).

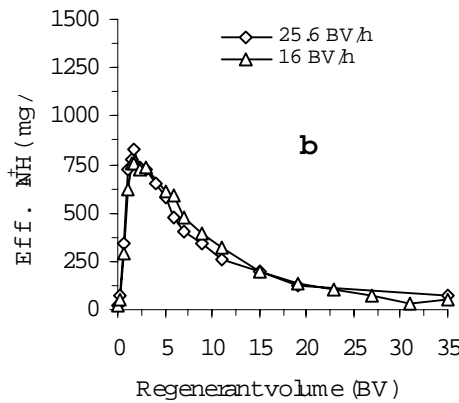
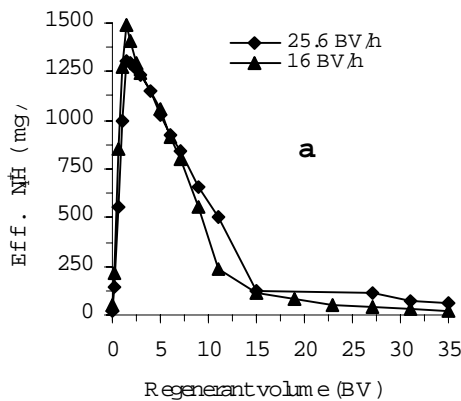
The capacity to 1 mg/l NH<sub>4</sub><sup>+</sup> breakthrough was reached in 450 BV for the fine clinoptilolite (-1.00+0.125) column with superficial velocities of both 25 and 50 BV/h. On the other hand, the capacity of 1 mg/l NH<sub>4</sub><sup>+</sup> breakthrough was reached in 350 BV for the fine zeolite column with superficial velocity of 75 BV/h. As the superficial velocity of the aqueous solution decreases, the hydraulic residence time increases, resulting in more NH<sub>4</sub><sup>+</sup> being removed by the ion-exchange resin. Ion-exchange capacities of clinoptilolite are given in Table 4.

The particle size of (-1.0+0.125) mm zeolite gives a higher ammonium adsorption capacity than that of the (-2.0+1.0) mm zeolite particle size. The adsorption capacities calculated by graphical integration of the area above the breakthrough curves are about 0.57 and 0.38 meq/g NH<sub>4</sub><sup>+</sup> for particle sizes ranging between (-1.0+0.125) and (-2.0+1.0) mm, respectively. This indicates that the smaller particle size has a higher ion-exchange capacity due to greater available surface area.

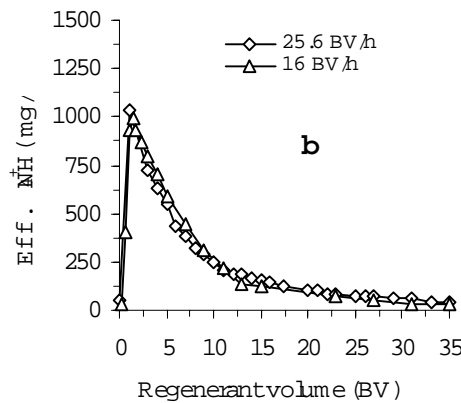
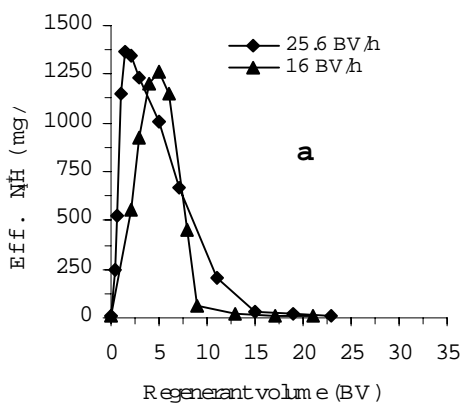
Five loading and four regeneration cycles were carried out without loss of NH<sub>4</sub><sup>+</sup> adsorption capacity. It is further observed that after the 1st regeneration, ammonium adsorption capacity of zeolite was increased. This shows that on regeneration of the zeolite column with NaCl solution, the Na ions have activated the zeolite column. After the 2nd and 3rd regenerations, the loading process was repeated and it was found that the ammonium adsorption



**Figure 7**  
Effect of the superficial velocity on the breakthrough curve of ammonium removal at 20 mg/l  $\text{NH}_4^+$  initial ammonium concentration for conditioned zeolite;  
**a:** (-1.00+0.125) mm;  
**b:** (-2.0+1.0) mm



**Figure 8**  
Ammonium elution (10 gr NaCl/l, pH 12.3);  
**a:** (-1.00+0.125) mm;  
**b:** (-2.0+1.0) mm



**Figure 9**  
Ammonium elution (20 gr NaCl/l, pH 12.3);  
**a:** (-1.00+0.125) mm;  
**b:** (-2.0+1.0) mm

capacity of the clinoptilolite remained constant. This indicates that using NaCl solution, the regeneration of the column could be done repeatedly without loss of ammonium adsorption capacity.

### Regeneration

Columns were prepared by complete regeneration with 35 BV of regenerant containing 10 and 20 g NaCl/l and a pH of 12.3 adjusted by using NaOH. Ammonium elution by 10 and 20 g NaCl/l regenerant solutions is shown in Figs. 8 and 9, respectively. 15 BV of regenerant, corresponding to the use of 20 g NaCl/l were sufficient to reduce the effluent ammonium concentration in the regenerant to less than 20 mg/l for the fine zeolite column (Fig. 9a). On the other hand, after feeding 15 BV of regenerant to the coarse zeolite column containing 10 and 20 g NaCl/l, effluent ammonium concentrations were about 200 and 150 mg/l, respectively. The

coarse zeolite column needs more regenerant solution than the fine zeolite column for complete regeneration.

It is concluded from Figs. 8 and 9 that a volume of 15 BV-0.35 M NaCl solution is sufficient for nearly complete regeneration of the zeolite column of (-1.00+0.125) mm particle size. The coarse zeolite needs more regenerant solution than the fine zeolite for complete regeneration and regeneration seems to be completed when 25 to 35 bed volumes of regenerant solution pass the ion-exchanger bed for both of the columns.

Results of the experimental investigation are used to develop optimum operational conditions for clinoptilolite exchangers.

### Conclusion

The removal of ammonium from synthetic solution was demonstrated successfully on a laboratory scale with a selective



ion-exchange process. The following conclusions can be drawn from this study:

- The data obtained from batch studies were applied to Langmuir and Freundlich isotherms. The Langmuir isotherm gives an adequate correlation coefficient value compared to the Freundlich isotherm correlation isotherm.
- The particle size of (-1.00+0.125) mm zeolites gives higher ammonium adsorption capacity than that of (-2.0+1.0) mm particle size of zeolites. The adsorption capacities calculated by graphical integration of the area above the breakthrough curves are about 0.57 and 0.38 meq/g  $\text{NH}_4^+$  for particle sizes ranging between (-1.0+0.125) and (-2.0+1.0) mm, respectively.
- The capacity to 1 mg/l  $\text{NH}_4^+$  breakthrough was reached in 450 BV for the fine clinoptilolite (-1.00+0.125) column with superficial velocities of both 25 and 50 BV/h. On the other hand, the capacity of 1 mg/l  $\text{NH}_4^+$  breakthrough was reached in 350 BV for the fine zeolite column with superficial velocity of 75 BV/h. A flow rate of 25 to 50 BV/h loading is advocated. It is a reasonable velocity and has no negative effect on adsorption capacity.
- The capacity increases considerably with the first regeneration. It seems that the clinoptilolite has been activated by the regenerant containing 10 and 20 g/l NaCl and a pH of 12.3 adjusted by using NaOH. Regeneration can be accomplished with about 10 BV of regenerant containing 20 g/l NaCl applied at a rate of 16 BV/h for fine clinoptilolite. After the 2nd and 3rd regenerations ammonium adsorption capacity of zeolite remained constant. The columns could be regenerated a number of times without loss of ammonium adsorption capacity.

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### References

- AHMED S, CHUGHTAI S and KEANE MA (1998) The removal of cadmium and lead from aqueous solution by ion-exchange with Na-Y zeolite. *Separation and Purification Technol.* **13** (1) 57-64.
- CALLEJAS RL, GEHR R, JOMÉNEZ BE and ALVAREZ PJJ (2001) Heavy metal removal with mexican clinoptilolite: multi-component ionic exchange. *Water Res.* **35** (2) 373-378.
- ÇELENLİ A, BÜRTÜK Y and SURNER F (1994) Industrial usage of heavy metal ions, an example from Turkey. Paper presented at Int. Segmite 2<sup>nd</sup> Conf., April 4-7, Karaci.
- DEMİR A, DEBİK E and GÜNAY A (1998) Eysel atıksulardan amonyum gideriminde iyon degistirici olarak dogal zeolit kullaniminin arastirilmesi. *ISKI Profesi Yildiz*, Istanbul.
- GASPARD M, NEVEU A and MARTIN G (1983) Clinoptilolite in drinking water treatment for  $\text{NH}_4^+$  removal. *Water Res.* **17** (3) 279-288.
- HARALAMBOUS A, MALIOU E and MALAMIS M (1992) The use of zeolite for ammonium uptake. *Water Sci. Technol.* **25** (1) 139-145.
- JORGENSEN SE and BARKACSK K (1976) Ammonium removal by use of clinoptilolite. *Water Res.* **10** 213-224.
- KLIEVE JR and SEMMENS MJ (1980) An evaluation of pretreated natural zeolites for ammonium removal. *Water Res.* **14** 161-168.
- KOON JH and KAUFMAN WJ (1975) Ammonium removal from municipal wastewaters by ion-exchange. *J. WPCF* **47** (3) 448-465.
- LIN SH and WU CL (1996) Ammonium removal from aqueous solution by ion-exchange. *Ind. Eng. Chem. Res.* **35** 553-558.
- MERCER BW, AMES LL, TOUHILL JC, VAN SLYKE WJ and DEAN RB (1970) Ammonium removal from secondary effluents by selective ion-exchange. *J. WPCF.* **42** (2) R95-R107.
- METCALF and EDDY INC. (1991) *Wastewater Engineering: Treatment, Disposal and Reuse* (3<sup>rd</sup> edn.) Mc Graw Hill Co., New York.
- OUKISK and KAVANNAGHM (1999) Treatment of metals-contaminated wastewaters by use of natural zeolites. *Water Sci. Technol.* **39** (10-11) 115-122.
- SCHOEMAN JJ (1986) Evaluation of a South African clinoptilolite for ammonium-nitrogen removal from an underground mine water. *Water SA* **12** (2) 73-82
- SINGH G and PRASAD B (1997) Removal of ammonium from coke-plant wastewater by using synthetic zeolite. *Water Environ. Res.* **69** (2) 157-161.
- SIRKECIOGLU A and SENATLAR A (1995) Removal of ammonium ions from wastewaters by Bigadiç clinoptilolite. *Tr. J. of Eng. and Environ. Sci.* **19** 399-405.
- STANDARD METHODS (1989) *Standard Methods for the Examination of Water and Wastewater* (17<sup>th</sup> edn.). American Public Health Association, Washington DC.
- YÜCEL H and ÇULFAZ A (1985) Yerel ve dogal klinoptilolit zeolitinin fiziksel ve kimyasal özellikleri. *Doga Bilim Dergisi* **9** (3) 288-296.

