

## Regenerability of Turkish clinoptilolite for use in ammonia removal from drinking water

M. Turan and M. S. Celik

### ABSTRACT

Ion exchange methods using natural clay minerals such as zeolites exhibit a significant potential for the removal of ammonia from contaminated reservoir water or wastewater. The ammonia adsorption capacity of Gördes-Manisa (Turkey) clinoptilolite was studied in bottle adsorption tests and optimum adsorption conditions were established. Synthetic tap water made of  $\text{NH}_4\text{Cl}$  and contaminated reservoir water, along with original and regenerated clinoptilolites, were used in a set of fixed ion exchange columns to identify the ability of clinoptilolite in the removal of ammonia. The breakthrough curves showed that increasing the influent ammonia concentration from 10, 15, and 20 mg/l concomitantly increased the effluent concentration and all the three curves exhibited a rapid rise after 125 bed volumes (BV). When  $C/C_0$  reached 0.1, the BV was approximately 275 and 140 for 1–2 and 2–2.8 mm particle sizes, respectively indicating a larger adsorption capacity of the finer material. After running for 23 h, the  $C/C_0$  values for the untreated, once-regenerated, twice-regenerated and thrice-regenerated clinoptilolites were 0.35, 0.06, 0.02, and 0.14 respectively. Twice-regenerated clinoptilolite showed the best performance compared with the others. The regeneration of clinoptilolite with 30 g/l NaCl solution at pH 11.5 was found to activate the clinoptilolite and increase the ion exchange performance. The breakthrough curves obtained under different conditions reveal that the untreated clinoptilolite adsorbs both the synthetic and reservoir water with the same ammonia concentration in a similar manner. These results indicate the potential of natural clinoptilolite for the removal of ammonia from contaminated reservoir water.

**Key words** | adsorption, ammonia, clinoptilolite, drinking water, ion exchange, zeolite

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### INTRODUCTION

There is a growing interest in the removal of ammonia from contaminated reservoir water or wastewater as it contributes to the life cycle of aquatic species. Wastewater from municipal, agricultural, and industrial operations creates ammonia nitrogen which ends up in lakes, rivers and particularly in drinking water reservoirs. Ammonia nitrogen decreases the dissolved oxygen required for aquatic organisms, and also accelerates the corrosion of metals and construction materials. Elmali-Istanbul (Turkey) reservoir water, though not used presently, contains large amounts of ammonia, as high as 15 mg/l. The maximum limit set by the European Community for drinking water is approximately 0.5 mg/l,

and also a guide level is given as 0.05 mg/l (Train 1979; EC Drinking Water Directive 1980; AWWA 1995). Biological nitrification and denitrification are limited to a minimum concentration of 5 mg/l due to the formation of undesirable chemical compounds. Contrary to this, it is possible to decrease the ammonia level to 1 mg/l using air stripping methods. But the requirement of using water at a temperature of more than 15°C, and carbonate deposition, are disadvantages of this method. The ion exchange method is preferred over other methods since it is stable and easy to maintain, and suits automation and quality control (Mercer *et al.* 1970; Reeves 1972; Lahav & Green 1998).

Considerable research has been conducted to characterize the mechanism of ammonia removal from contaminated reservoir water or wastewater by natural clinoptilolite (McLaren & Farquhar 1973; Jorgensen 1975; Gaspard *et al.* 1983; Ciambelli *et al.* 1985; Booker *et al.* 1996; Celik *et al.* 2001). The ammonium ion is able to exchange with Na, Ca and Mg ions from clinoptilolite more selectively than other inorganic ions. The high selectivity of clinoptilolite for ammonium ions can be explained by the following properties: molecular size, hydration of cations, and anionic corner separation (Si/Al ratio). The ion exchange capacity of zeolites varies over a range of 1.2 to 2.2 meq/g. Clinoptilolites composed of rings of 8 and 10 elements or a 5.6 Å unit window have an ideal molecular size for the ammonium ion (Torii 1978; Mumpton 1988).

The objective of this research is to investigate the effectiveness of using clinoptilolite columns to treat ammonia in drinking water. In this study, batch adsorption tests, followed by column studies with clinoptilolite using synthetic or contaminated reservoir water, are performed along with a study of the effectiveness of clinoptilolite regeneration on column performance.

## EXPERIMENTAL

### Materials

The clinoptilolite sample used in the experiments was received from Incal Company which operates in the Manisa-Gördes region of Turkey. The sample was classified into two different particle size groups: 2–2.8 mm (6–8 mesh), and 1–2 mm (8–16 mesh). The chemical analysis of the clinoptilolite sample is given in Table 1. The sample was identified as Ca-clinoptilolite, because it is rich in  $\text{Ca}^{++}$  and  $\text{K}^+$ . Other relevant properties are listed in Table 2.

### Batch adsorption experiments

Adsorption experiments were conducted in 20 ml vials using particles in the size range of 1–2 mm. Conditioning

**Table 1** | Chemical analysis of Gördes clinoptilolite

| Constituent                    | % by wt |
|--------------------------------|---------|
| SiO <sub>2</sub>               | 67.87   |
| CaO                            | 2.17    |
| K <sub>2</sub> O               | 2.74    |
| SO <sub>3</sub>                | 0.01    |
| Al <sub>2</sub> O <sub>3</sub> | 11.18   |
| MgO                            | 0.93    |
| TiO <sub>2</sub>               | 0.08    |
| P <sub>2</sub> O <sub>5</sub>  | 0.03    |
| Fe <sub>2</sub> O <sub>3</sub> | 0.98    |
| Na <sub>2</sub> O              | 0.92    |
| LOI*                           | 13.12   |

\*Loss on ignition.

**Table 2** | Some of the properties of Gördes clinoptilolite (Sirkecioğlu & Erdem-Şenatalar 1995; Cicek *et al.* 2000)

| Property                            | Value   |
|-------------------------------------|---------|
| Cation exchange capacity, meq/g     | 1.9–2.2 |
| Pore diameter, Å                    | 4       |
| Purity, %                           | 92      |
| Bed porosity, %                     | 40      |
| Density, g/cm <sup>3</sup>          | 2.15    |
| Apparent density, g/cm <sup>3</sup> | 1.30    |
| Suspension pH                       | 7.5–7.8 |

speed in a shaker was kept constant at 400 rpm throughout the experiments. Ammonia analysis was performed by the Nessler method utilizing a UV spectrophotometer. The

adsorption isotherm was fitted to the Langmuir model in the following form:

$$x/m = (abC_r)/(1 + bC_r) \quad (1)$$

By multiplying both sides of Equation (1) and rearranging, the following formula could be evaluated:

$$C_r/(x/m) = (1/ab) + (1/a)C_r \quad (2)$$

where  $x/m$  is the adsorption density as amount of ammonia adsorbed by the adsorbent (mg/g),  $a$  and  $b$  are the Langmuir constants, and  $C_r$  is the equilibrium concentration of ammonia left in the solution after ion exchange.

### Column preparation and operation

The laboratory scale experimental set-up consists of fibre-glass ion exchange columns, raw water and regeneration solution tanks, feed pumps, valves and a treated water tank. The cylindrical column has a diameter of 3 cm and a height of 100 cm. The clinoptilolite sample of 1–2 mm in size, filling the 50 cm bed height, weighed 370 g. A peristaltic pump, Masterflex 100, was used to feed ammonia-containing solutions to the column at a rate of  $1.17 \text{ cm}^3/\text{s}$ . The empty bed contact time ( $EBCT$ ) was obtained as:

$$EBCT = V_R/Q_F \quad (3)$$

Because bed volume and flow rate were measured as  $350 \text{ cm}^3$  and  $1.17 \text{ cm}^3/\text{s}$ , respectively,  $EBCT$  was found to be 5 min. During the adsorption process, the samples were taken in 2-h periods and analysed using the Nessler method. The breakthrough curves were obtained by plotting the normalized effluent ammonia concentration ( $C/C_o$ ) versus bed volume ( $BV$ ). When the  $C/C_o$  value approached 1, the process was terminated and regeneration started. The  $BV$  is defined as:

$$BV = V_F/V_R \quad (4)$$

The regeneration solution consisted of 30 g/l of NaCl and 1.5 g/l of NaOH with a pH value of approximately 11.5;

this value was close to that used elsewhere (Turan *et al.* 1999). The regeneration solution was pumped to the bottom of bed using a pump that maintains both mixing and expansion of the bed. Thus, the upflow in the bed accelerated the desorption of ammonia from clinoptilolite particles.

## RESULTS AND DISCUSSION

### Batch adsorption studies

The previous tests indicated that the adsorption density (mg/g) of clinoptilolite decreases quickly with an increasing solid/liquid ratio up to 1 g/20 ml (5%), and above this ratio the rate of adsorption density decrease slows down. Similarly, tests conducted as a function of conditioning time indicated that the adsorption density remained constant after 60 min. In order to determine the optimum pH, experiments were carried out in the pH range of 6.5–12 using 10 mg/l initial ammonia concentration, 60 min of conditioning time and 5% of solids concentration. Increasing pH resulted in a marginal decrease in adsorption and natural pH was found to yield an optimum (Cicek *et al.* 2000). Therefore, the subsequent tests were performed at 5% solids concentration (solid to liquid ratio of 0.05), 60 min of conditioning time, and at natural pH. Adsorption data performed at 5% solids concentration and 60 min of conditioning time are presented in Figure 1. The initial ammonia concentration varied between 1 and 1400 ppm. The adsorption isotherm in Figure 1 illustrates that adsorption of ammonia ( $C_r/C_o$ ) yields a slope higher at lower ammonia concentrations and decreases with increasing ammonia concentration until it reaches a plateau.

The clinoptilolite/ammonia adsorption isotherm can be divided into three regions. The sharp increase in the first region can be ascribed to the ion exchange of ammonia with ions such as Na, Ca, and K in relatively larger quantities. In the second region, other multivalent ions such as Mg and Al undergo the ion exchange process (Ersoy 2000). The ion exchange is completed in the third region. The adsorption value of 7.4 mg/g, which is reached

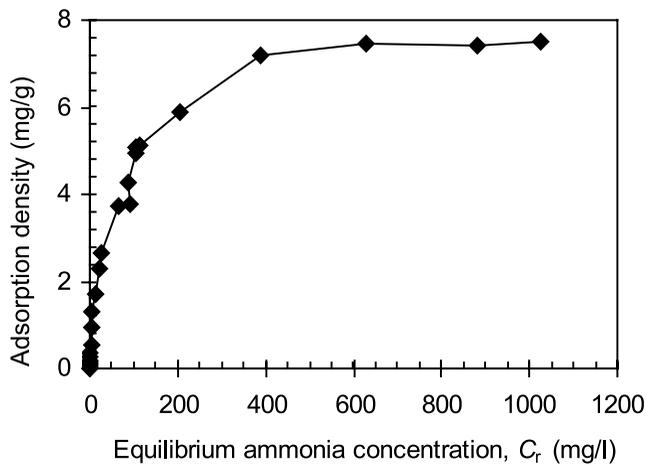


Figure 1 | Adsorption isotherm of clinoptilolite-ammonia system.

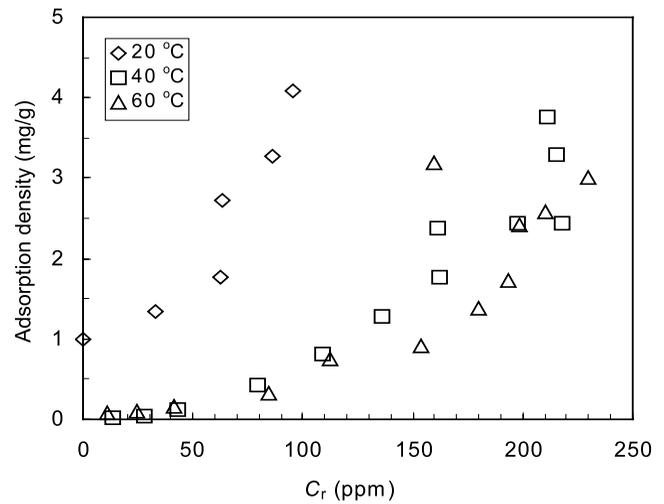


Figure 3 | Temperature dependence of ammonia adsorption onto clinoptilolite.

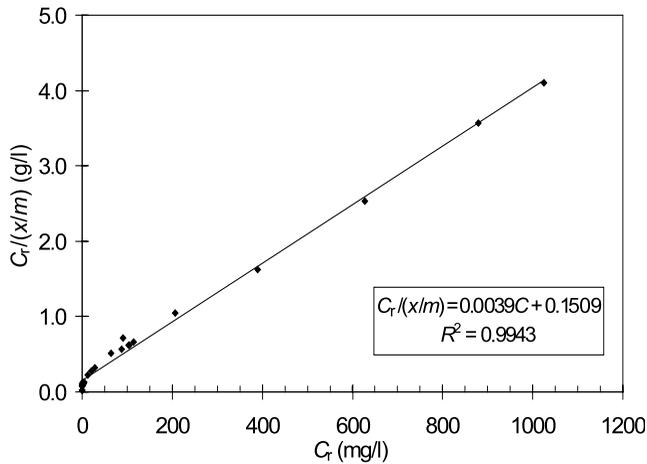


Figure 2 | Application of the Langmuir model to the adsorption of clinoptilolite.

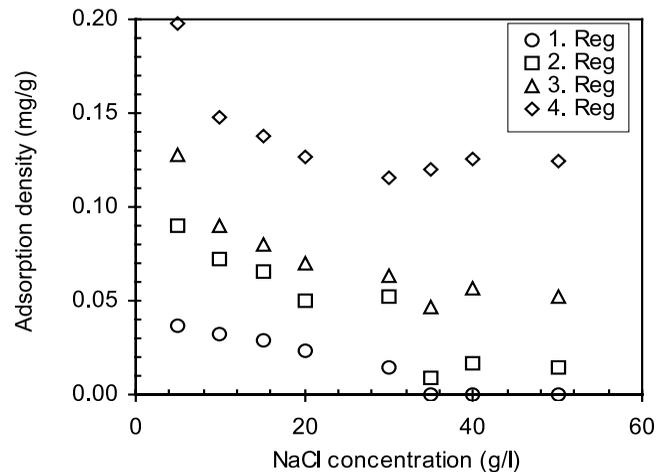
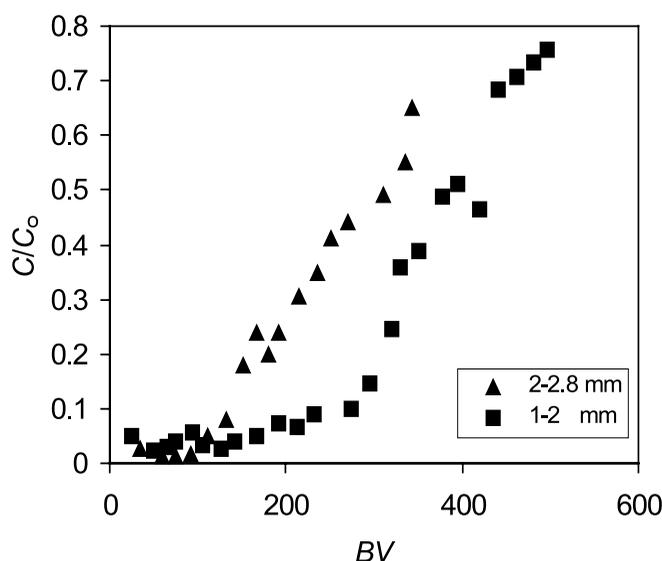


Figure 4 | Effect of NaCl concentration during the regeneration of clinoptilolite.

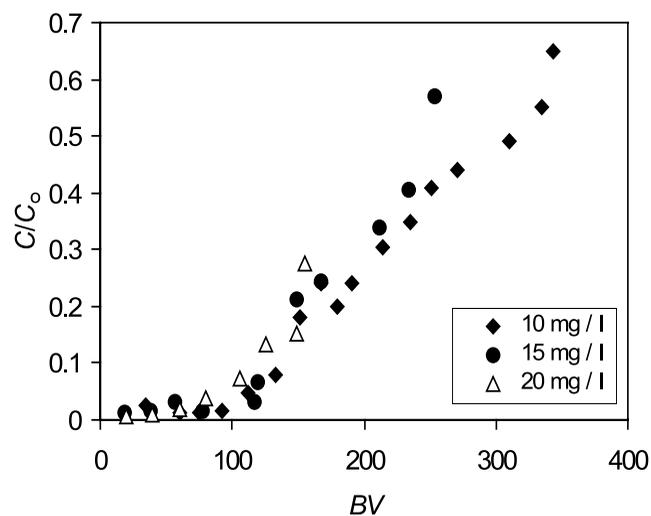
at the plateau, can be used in the calculation of cation exchange capacity. Fitting of the Langmuir model to the experimental data is shown in Figure 2. When  $C_r/(x/m)$  is plotted against  $C_r$ , the Langmuir model fits the data very well. Also,  $a$  and  $b$  values can be graphically calculated as  $a = 256.41$  mg/g and  $b = 25.845 \times 10^{-3}$  l/mg. Figure 3 shows the temperature dependence of ammonia adsorption onto clinoptilolite. Increasing temperature from 40 to 60°C caused a large increase in adsorption density.

The adsorption process depends on the ion exchange between  $\text{NH}_4^+$  in the solution and  $\text{Na}^+$  present in the

structure of clinoptilolite. When the clinoptilolite is saturated with ammonia, it should be converted to the  $\text{Na}^+$  form for further use. The effect of  $\text{Na}^+$  concentration on ammonia adsorption for different regeneration steps is shown in Figure 4. NaCl concentration shifted adsorption densities of regenerated clinoptilolite to the higher values with increasing regeneration steps. Also, adsorption densities become nearly constant for concentrations higher than 30 mg/l of NaCl.



**Figure 5** | Breakthrough curves as a function of particle size using clinoptilolite and synthetic water at an ammonia concentration of 10 mg/l.



**Figure 6** | Breakthrough curves obtained for the 1–2 mm particle size of the clinoptilolite bed using synthetic water with ammonia concentrations of 10, 15 and 20 mg/l.

### Column studies with clinoptilolite

The breakthrough curves were plotted as bed volume ( $BV$ ) versus normalized effluent ammonia concentration ( $C/C_0$ ). In Figure 5, the breakthrough curves were plotted as a function of particle size using clinoptilolite and synthetic water with an initial ammonia concentration of 10 mg/l. At a  $C/C_0$  value of 0.1, the bed volume ( $BV$ ) reaches approximately 275 and 140 for 1–2 mm and 2–2.8 mm particle sizes, respectively. Similarly, the value of  $C/C_0$  after a 30 h running period was 0.24 and 0.55 for 1–2 mm and 2–2.8 mm size groups, respectively. Consequently, as expected, the finer material yields a higher adsorption capacity than the coarse one due to the higher specific surface area of the former.

Figure 6 shows the breakthrough curves obtained for the 1–2 mm particle size of the clinoptilolite bed using synthetic water with ammonia concentrations of 10, 15 and 20 mg/l. The value of  $C/C_0$  after 12 h of running was found to be 0.04, 0.06 and 0.13 for ammonia concentrations of 10, 15 and 20 mg/l, respectively. Increasing the influent concentration increased the effluent concentration. On the other hand, all the three curves exhibited a rapid rise after 125  $BV$ .

### Effect of clinoptilolite regeneration on column performance

When the normalized effluent ammonia concentration ( $C/C_0$ ) approached 1, the adsorption process was terminated and regeneration started. A good adsorbent, in addition to its high adsorption capacity, must also exhibit good regeneration for multiple uses. Regenerability of clinoptilolite with 30 g/l NaCl solution at pH 11.5 in a fixed bed column against time is presented in Figure 7. The regeneration curve reveals that the amount of ammonia in clinoptilolite increases in the first 10 min up to an ammonia concentration of 20 mg/l, followed by a decrease at the same rate, and then becomes practically nil at the end of 20 min.

The ion exchange capacities of the original (untreated) and regenerated clinoptilolites for the 1–2 mm size fraction are given as a function of bed volume ( $BV$ ) in Figure 8. Twice-regenerated clinoptilolite showed the best performance compared with the others; the  $C/C_0$  value after 23 h of running was 0.02. After a 23-h running period, the  $C/C_0$  values for the original, once-regenerated, twice-regenerated and thrice-regenerated clinoptilolites were 0.35, 0.06, 0.02, and 0.14, respectively.

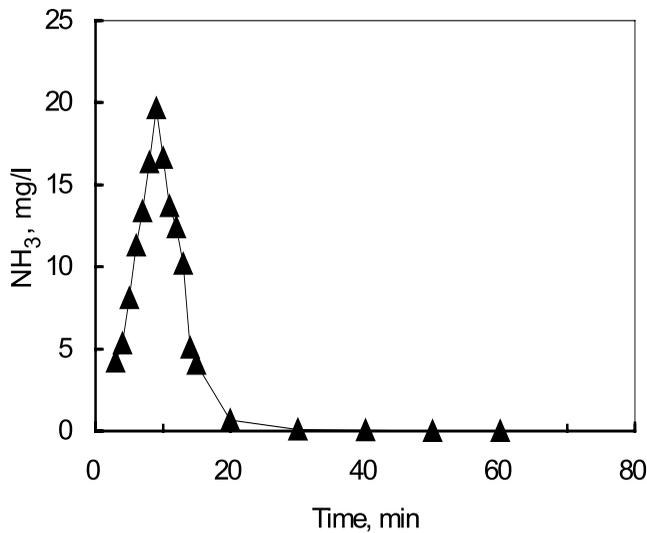


Figure 7 | Regeneration of ammonia from clinoptilolite in a fixed bed.

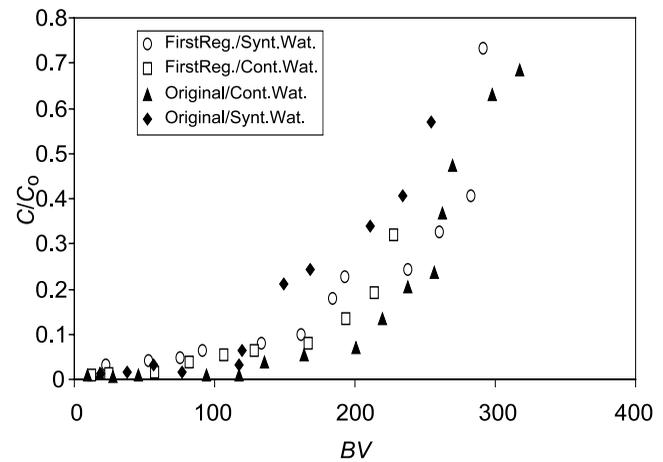


Figure 9 | Breakthrough curves using synthetic and contaminated reservoir water, both with an ammonia concentration of 15 mg/l, for the original (untreated) and regenerated clinoptilolites using particle sizes of 1–2 mm.

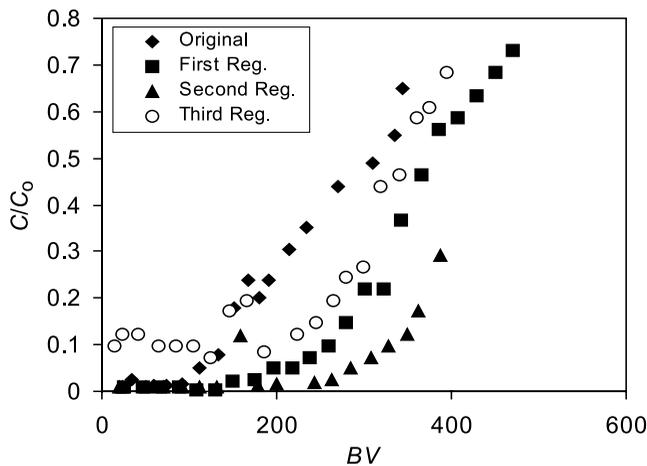


Figure 8 | Ion exchange capacities of the original (untreated) and regenerated clinoptilolite zeolites of 1–2 mm particle size at 10 mg/l influent concentration.

Twice-regenerated clinoptilolite showed the best performance compared with the others while the thrice-regenerated clinoptilolite still performs better than the original clinoptilolite. The regeneration of clinoptilolite, similar to sepiolite, is expected to activate the clinoptilolite by expanding the size of micropores and thus enabling the penetration of ammonium ions with the resultant increase in ion exchange. It is predicted that first and second regeneration may cause amenability of ammonium

ions to micropores with a concomitant increase in the surface area, but the third regeneration appears to decrease the specific surface area and ion exchange capacity due to the appearance of macropores. It should be noted that because the clinoptilolite waste contains ammonia upon regeneration, it can be conveniently used as fertilizer and also in soil remediation. The price of sized clinoptilolite is 90 US\$/t excluding freight charges to the destination and other taxes, customs clearance etc. at the destination—Istanbul (Turkey).

### Column tests with contaminated reservoir water

The breakthrough curves using synthetic water and contaminated reservoir water, both with an ammonia concentration of 15 mg/l, for the original and the regenerated clinoptilolites are presented in Figure 9. Since the influent concentrations of the reservoir water and the synthetic water are similar, the differences are ascribed to the ionic compositions of the waters. The breakthrough curves obtained with the synthetic and reservoir waters for the original clinoptilolite increase at a rate higher than those for the regenerated one. After 23 h of running, the  $C/C_0$  value reached 0.32 and 0.23 for the regenerated clinoptilolite with the reservoir and synthetic waters, respectively.

## CONCLUSIONS

Batch tests indicated that a solid/liquid ratio of 0.05 and 60 min of conditioning time was sufficient for adsorption. The effect of pH on adsorption was almost negligible, whereas temperature had a pronounced effect on the adsorption of ammonia. The Langmuir model fitted to the experimental data showed a good agreement. Addition of NaCl as a regenerant shifted adsorption densities of regenerated clinoptilolite to the higher values with increasing regeneration steps, and adsorption densities become nearly constant for concentrations higher than 30 mg/l NaCl.

The removal of ammonia from the clinoptilolite column, within the concentration range of ammonia used in this study, usually decreases after about 200 BV where the  $C/C_o$  is maintained below 0.1. The ion exchange process for the coarse particle size exhibits a lower capacity than for the finer particle size. This can be attributed to the higher specific surface area of fine particles. Increasing the influent concentration of ammonia increased the effluent concentration and all the breakthrough curves exhibited a rapid rise after 125 BV. The optimum regeneration of clinoptilolite was obtained with 30 g/l NaCl solution at pH 11.5. The regeneration of ammonia from clinoptilolite increases in the first 10 min up to an ammonia concentration of 20 mg/l followed by a decrease at the same rate and then becomes nearly zero after 20 min.

Clinoptilolite was successfully regenerated twice, and after the third regeneration the ion exchange capacity decreased but did not fall below the original clinoptilolite. It is predicted that the specific surface of clinoptilolite increases in the first and second regeneration, but begins to decrease in the third regeneration. Also, the breakthrough curves showed that reservoir and synthetic waters have similar characteristics.

## NOMENCLATURE

$a$  = Langmuir constant (mg/g)

$b$  = Langmuir constant (l/mg)

$BV$  = bed volume

$C$  = effluent ammonia concentration (mg/l)

$C_o$  = influent ammonia concentration (mg/l)

$C_r$  = equilibrium ammonia concentration (mg/l)

$EBCT$  = empty bed contact time (min)

$Q_F$  = flow rate in the bed ( $m^3/s$ )

$V_F$  = total water volume passing column during the adsorption process ( $m^3$ )

$V_R$  = fixed bed volume ( $m^3$ )

$x/m$  = adsorption density as amount of ammonia adsorbed by adsorbent (mg/g)

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