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Ammonia Removal from Aqueous Solutions by Iranian Natural Zeolite

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Abstract: The capability of Iranian natural clinoptilolite for ammonia removal from aqueous solutions has been thoroughly studied. Both batch and continuous (column) experiments were carried out. The viability of this natural zeolite in reducing the leakage of ammonia to the environment through waste water streams was a main focus of this research. Through the batch experiments, the effect of process variables such as the size of zeolite particles, pH, and ammonia concentration of the feed solution on the kinetics of ammonia uptake were investigated. Ammonia removal occurred rapidly and within the first 15 minutes of contact time, a major part of ammonia was removed from the solution. An adsorption capacity about 17.8 mg NH_4^+/g zeolite at feed ammonia concentration of 50 mg/L was obtained and the optimum range for pH was achieved about 5.5–7.6. The adsorption capacity of clinoptilolite in the continuous mode was about 15.16 and 15.36 mg NH_4^+/g zeolite for the original and regenerated types of clinoptilolite, respectively, where feed ammonium concentration was 50 mg/L. Increasing the feed ammonium concentration to 100 mg/L did not reduce the capability of the column for its ammonium removal and up to a bed volume (BV) of 85, there was only less than 1 mg/L ammonium in the column outlet. Presence of cations such as Ca^{2+}, Mg^{2+} and Na^+ in the feed solution reduced the clinoptilolite adsorption capacity to about 11.68 mg NH_4^+/g zeolite. Regeneration experiments were carried out using concentrated sodium

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chloride solutions, as well as tap water. Where tap water was used as the regenerant, gradual release of ammonium from exhausted clinoptilolite was observed.

Keywords: Ammonia, clinoptilolite, ion exchange, natural zeolite, wastewater, fertilizer

INTRODUCTION

Nitrogen and phosphorus compounds are very essential elements for living organisms. However, when they are more than needed, they can cause a significant pollution burden. Decreased dissolved oxygen required for the aquatic life, toxic effects on fish, reduced disinfection efficiency, and accelerated corrosion of metals and construction materials are among the potential drawbacks of the nitrogen release in water streams. The removal of nitrogen compounds is thus highly needed to protect both the environment and human health (1, 2). The main sources of water contamination with nitrogen compounds are industrial, agricultural, and municipal wastewaters. Among all nitrogen compounds, ammonia is the most important one due to its abundance in the municipal and most of the industrial wastewaters. In addition, urea and complex organic compounds also release ammonia once they get hydrolyzed or de-aminized (3).

The treatment methods for ammonia removal include nitrification-denitrification, break point chlorination, chlorination-dechlorination, air/steam stripping, ion exchange, and some membrane processes (1–5). All the above-mentioned methods experience limitations and shortcomings, however. The conventional methods for ammonium and organic removal from municipal and industrial wastewaters are mostly based on biological treatments (4). However, biological methods are somehow time consuming, spacious, and demand various equipments (5, 6). On the other hand, aquaculture occasionally requires cool water ($\sim 10^\circ$C), which is an unsatisfactory temperature for many biological methods. As the discharge limit of various pollutants becomes more stringent, ion exchange and adsorption become more interesting as feasible treatment methods (7). The ion exchange method is preferred over the other methods since it is stable, suits automation and quality control, and is easy to maintain (8, 9).

Zeolite is a natural porous mineral described as crystalline hydrated aluminosilicates. Inside the framework structure of zeolite, alkali or alkaline-earth cations are reversibly fixed in the cavities and can easily be exchanged by surrounding positive ions (10). Clinoptilolite, one of the natural zeolites, has been found very effective in removing ammonia from water by means of its excellent ion exchange capacity since the seventies of the last century. Many researchers have investigated ammonia removal from water streams by means of ion exchange (7–24).

Iran is a great producer of clinoptilolite zeolite of high purity (85–95 wt%). Iranian natural clinoptilolite have already found widespread domestic use in the catfish-rearing industry and as animal feed supplement. Scientific reports on various characteristics of Iranian clinoptilolite have been published earlier (25–28). An unexplored area for the industrial use of Iranian natural clinoptilolite is its application for ammonia removal. It is the aim of this work to explore the ammonia removal characteristics of an Iranian clinoptilolite form the Semnan region, and to define various operational parameters necessary to remove ammonia efficiently.

MATERIALS AND METHODS

Reagents

All chemicals used were analytical grade reagents from Merck. All aqueous solutions and dilutions were made using distilled water. In particular cases, where the effect of the presence of cations was interested, tap water was used to prepare the ammonia feed solutions. Ammonia concentration in the solution was analyzed by Nesslerization (29). Concentration of ammonia in the samples was measured using UV-Visible Scanning Spectrophotometer, Camspec M350 model.

Characteristics of Clinoptilolite

The clinoptilolite-rich tuff used as ion exchanger was obtained from the Semnan province of Iran. After being crushed, the clinoptilolite was sieved into 4 ranges of grain sizes namely 2.3–3.5, 1–2, 0.5–1, and 0–0.5 mm. The grains were then washed with distilled water to remove very fine particles and were dried in an electric oven at a temperature of 100°C. The chemical composition of clinoptilolite was determined through XRF analysis. Chemical composition of one used throughout this study is given in Table 1.

To obtain loss of ignition (LOI) for each particular sample, the sample was first weighted. It was weighed again after being heated for two hours at 1050°C. LOI was finally calculated from the following equation:

$$\mathrm{LOI} = 100 \times \frac{\text{Difference between the weights of sample before and after heating}}{\text{Weight of sample before heating}} \tag{1}$$

By dividing the weight percent of components listed in Table 1 into their molecular weights, the approximate chemical formula of the clinoptilolite is obtained:

$$(Na_2O)_{0.45}(CaO)_{0.04}(K_2O)_{0.51} \cdot Al_2O_3.11.35\,SiO_2$$

Table 1. Chemical composition of clinoptilolite

Component	(XRF. Results)	(Normalize to 100%)
Chemical analysis (wt%)		
SiO_2	70.00	78.3
Al_2O_3	10.46	11.7
Na_2O	2.86	3.2
K_2O	4.92	5.5
CaO	0.2	0.23
Fe_2O_3	0.46	0.51
CuO	0.21	0.24
SrO	0.09	0.097
TiO_2	0.02	0.018
ZrO_2	0.03	0.038
SO_3	0.11	0.12
LOI	10.6	—
Total	100	100

The apparent density of the zeolite was measured to be 0.96 gr/cm^3. Specific surface area of the zeolite was also determined by means of BET method for nitrogen adsorption equal to 22 m^2/gr.

Batch Experiments

Batch experiments were conducted in glass beakers. Through this set of experiments the kinetics of ammonia uptake was studied and the effects of the process parameters such as the size of the zeolite particles, the pH, and ammonia concentration of the feed on this kinetics were investigated.

Effect of Zeolite Particle Size

To investigate the effect of the size of the zeolite particles on the rate and amount of ammonia removal, clinoptilolite samples in 4 ranges of grain sizes, i.e., 2–3, 1–2, 0.5–1, and 0–0.5 mm were prepared. 2 grams of each sample was placed in a 250 mL beaker and 200 mL of ammonia solution with a concentration of 50 mg NH_4/L was added to it. The beaker was then sealed by means of a parafilm and was stirred on a shaker at a fixed temperature of 28°C and a stirring rate of 200 rpm. In order to determine the rate of adsorption, samples were taken from the ammonia solution in particular time intervals and kept aside in sealed test tubes. To avoid the effect of turbidity on the measurement of ammonium ion concentration, the tubes were centrifuged for 3 minutes before samples were taken and analyzed.

Ammonium Uptake Kinetics and Effects of Ammonium Concentration and pH of the Feed Solution

To study the kinetics of ammonium uptake, the grain size of 1–2 mm of the clinoptilolite was chosen. 2-gram zeolite samples were added to 200 mL of 50 mg/L ammonium solutions in 250 mL beakers and the mixture was stirred at a fixed temperature of 28°C and a stirring rate of 200 rpm. Analyses were then conducted as explained above.

The effect of initial ammonium concentration, i.e., 50, 75, and 100 mgNH$_4$/L, on the removal efficiency was investigated at the same working conditions ($T = 28°C$, $pH = 5.5$, 200 rpm).

To investigate the effect of pH on the kinetics of ammonium uptake, a 1 M solution of NaOH was used to adjust the pH of the solutions. The same experiments were conducted using 50 mg/L ammonium feed solutions with pH values of 5.5, 7.6, and 10. It is notable that experiments over a wider range of pH were not conducted since the mentioned range covers the pH of most abundant waste water streams.

Adsorption Isotherms

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

$$NaZ + NH_4^+ \longleftrightarrow Na^+ + NH_4Z \qquad (2)$$

The ion exchange isotherms characterize the equilibrium concentration of an ion in the solid phase with that in the liquid phase. Graphical representation usually shows all possible experimental conditions at a given temperature. Ammonium removal capacities for zeolite were examined with ion exchange isotherms. It is notable that for an effective utilization of a natural zeolite as an ion exchanger, it is essential to employ thermodynamic models to accurately describe the NH_4^+ equilibrium.

Batch adsorption isotherms for ammonia distribution were investigated. Empirical equations of Freundlich and Langmuir were fitted to the experimental data. Batch adsorption isotherm was determined through experiments conducted in 250 mL beakers. First ammonia solutions with concentrations of 10, 25, 40, 50, 60, 75, 90, 100, 120, 150, 175, 190, 200, and 220 mg NH$_4$/L were prepared. Weighed amounts (2 grams) of clinoptilolite were then introduced into the beakers, to which 200 mL of the ammonia solution with mentioned concentrations at a pH of about 5.5 had been previously added. The beakers were shaken for 180 minutes at 200 rpm. Preliminary tests had confirmed that 180 min contact time was sufficient to reach equilibrium concentration of ammonia in the solution. After this period of time, the remaining ammonia concentration in the solution was analyzed after being centrifuged. Application of standard solution (ammonium chloride without zeolite) showed that shaking and centrifuging would not result in ammonium chloride loss in the beakers which were sealed by parafilm. The total amount of adsorbed ammonium was divided by the dry weight of zeolite to calculate the average amount adsorbed. The latter was plotted against effluent ammonium concentration to report an isotherm experiment.

Column (Continuous) Experiments

To investigate the ammonia adsorption behavior of clinoptilolite in a continuous system, an adsorption column was employed. A column of 60 mm diameter and 600 mm height was filled with 500 g zeolite of either 1–2 mm or 0.25–0.6 mm grain size and was operated in a continuous-flow mode. The bed height and volume of the clinoptilolite were 195 mm and 521.87 cm^3, respectively. In order to support the zeolite bed and avoid discarding the particles, a soft sponge was located in the bottom of the column and some glass balls were mounted on top of it. After loading the zeolite particles into the column, a bulk of gravels with a height of 3 cm was put on them to insure that zeolite particles would not move within the column.

The experimental set up consisted of 4 tanks for water, ammonia, regenerant, and effluent solutions, 2 pumps to pump the feed and regenerant solutions, and several valves. A schematic representation of the experimental setup is illustrated in Fig. 1.

Column Breakthrough Curves for Ammonia

In order to obtain the column adsorption breakthrough curve, solutions with average concentrations of 50 mg NH_4/L were passed through the zeolite bed. In certain volumetric intervals, i.e., each 3 liters, a sample was taken from the outlet stream and its ammonia concentration was measured. This procedure was continued until the outlet concentration reached the same value as that of the inlet stream to the column. To determine the breakthrough curve of the column, its outlet concentration was plotted versus the dimensionless number of the bed volume passed (BV).

$$BV = V_t/V_B \tag{3}$$

where V_B is the bed volume, and V_t is the total volume of the solution passed the adsorption column during the time t (30).

After saturation of zeolite with ammonium ion, the column was regenerated using a concentrated solution of sodium chloride and the same procedure was repeated. The regenerated zeolite, is called Na-form zeolite throughout this study.

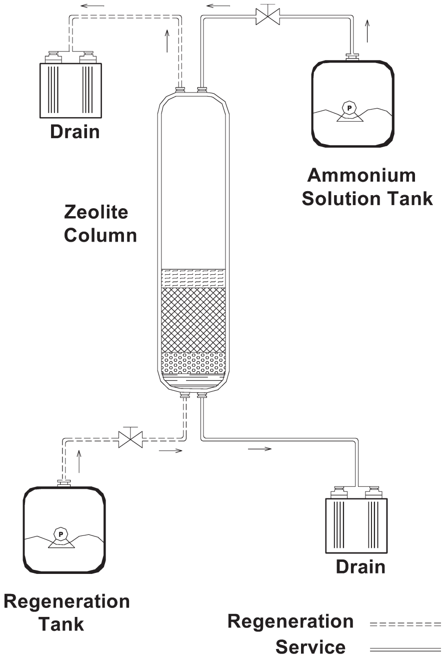

Figure 1. The schematic representation of the experimental set up.

Effect of Ammonia Concentration and Presence of Rival Ions in the Solution

To investigate the effect of feed ammonia concentration on the column adsorption behavior, a solution of 100 mg NH_4/L was passed through the column and its breakthrough curve was investigated.

In order to study the effect of the present rival ions in the solution on the adsorption capacity of Na form zeolite, solutions of 50 mg NH_4/L ammonia were made using tap water, instead of distilled water. The latter solutions were passed through the column to determine their breakthrough curves. The chemical analysis of tap water used in this set of experiments is given in Table 2.

Regeneration Experiments

Regarding the fact that the counter-current mode of flow has a higher efficiency comparing to that of the co-current mode, the column regeneration experiments were conducted in the former mode. A solution of 1 M NaCl was used as the regenerant. Prior to any regeneration process, the column was first washed with distilled water and then the sodium chloride solution was passed through the column counter-current wise. Detecting the ammonia in

Table 2. Chemical analysis of tap water used in the experiments

Total acidity (mg $CaCO_3$/L)	44.8
Total alkalinity (mg $CaCO_3$/L)	184
Total hardness (mg $CaCO_3$/L)	210
Calcium hardness (mg Ca^{2+}/L)	56.64
Magnesium hardness (mg Mg^{2+}/L)	16.77
Chloride ion (mg Cl^-/L)	34
Free chloride (mg Cl_2/L)	—
Conductivity (μS)	345

the effluent, its absence indicated the completion of the regeneration process. The column was then washed with distilled water to ensure that no sodium chloride is left among the zeolite particles. To investigate the rate of the column regeneration, samples were taken from the column outlet and analyzed for their ammonia contents at certain volumetric intervals.

To study the behavior of ammonium release from the saturated zeolite against the passage of a water solution containing cations, tap water was passed through the column containing exhausted zeolite. Each 20 liters of effluent was collected in a tank while the solution was stirred vigorously. The tank solutions were then analyzed for their contents of the released ammonium ion.

RESULTS AND DISCUSSIONS

Batch Experiments

Effect of Zeolite Particle Size

The effect of zeolite particle size on the extraction was investigated using grain sizes of 0–0.5, 0.5–1, 1–2, and 2–3 mm. The results are shown in Fig. 2. As it can be seen, the size of the zeolite particles in the first 3 ranges has an almost negligible influence on the amount of ammonium adsorbed and the total capacity of zeolite is almost the same. The rate of adsorption is very fast and almost the same in those three ranges. This behavior is logical regarding the Mumpton, Flaningen theory (1981). According to their theory, the external surface of particles incorporates only 1% of the total surface of the zeolite (20).

However, as it can be seen, the rate of adsorption is slightly lower in the range of 2–3 mm. The latter can be attributed to the change of diffusion mechanism from “micropore diffusion” to the “macropore diffusion.” Therefore, larger sizes of particles can be used in the column, to avoid the operating problems such as large pressure drops, problems in regenerating

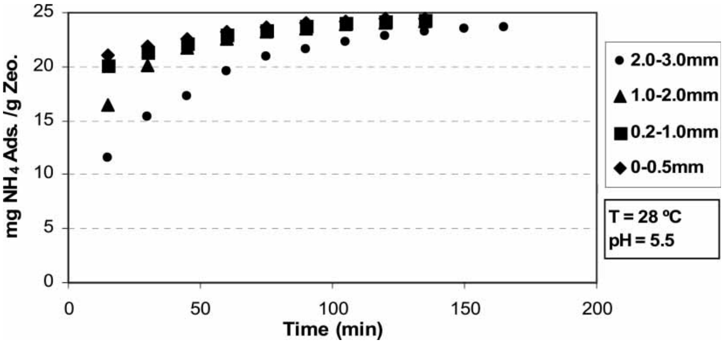

Figure 2. Effect of zeolite particle size on ammonia uptake.

the column, and flow rate control. Based on these facts, particle size of 1–2 mm was chosen for the conduction of further experiments.

Ammonium Uptake Kinetics and Effects of Ammonium Concentration and pH

In order to investigate the ammonium uptake kinetics, the amount of ammonium adsorbed by 1 gram of zeolite was measured against stirring time (Fig. 3). As it is illustrated in the figure, after 15 minutes, 91% of the total capacity of zeolite was filled. This result also shows how rapid the ammonium uptake is. Although it takes about 3 hours to reach the equilibrium, ammonia removal occurs very rapidly and within the first 15 minutes of contact time a major part of ammonia is removed from the solution. The total amount of ammonium uptake by clinoptilolite zeolite in the batch mode, for an initial ammonia concentration of 50 mg/L was about 17.8 mg NH_4^+/g zeolite.

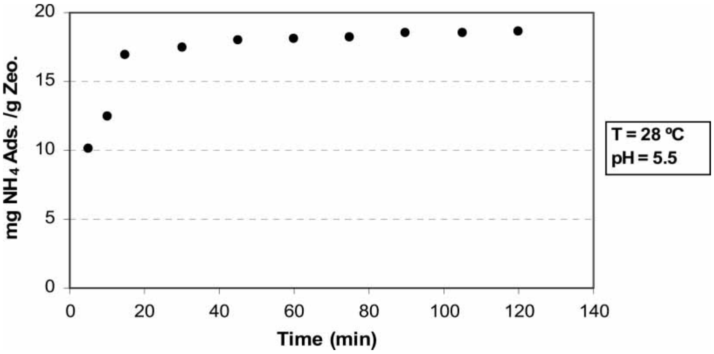

Figure 3. Ammonium adsorption kinetics.

Generally two mechanisms control the rate of adsorption into an adsorbent: Film diffusion, in which the adsorbed material diffuses through the stationary boundary layer to reach the adsorbent surface, and intraparticle diffusion in which the adsorbed material diffuses through the adsorbent to reach the adsorption sites. In fact, both mechanisms exist but usually it is one of them (the slower one) which control the diffusion kinetics. Usually ion exchange models, in which intraparticle pore diffusion governs the system, are used to analyze the behavior of the adsorption rate onto clinoptilolite zeolite (12).

To investigate the effect of ammonia concentration on the ammonium uptake kinetics, experiments were conducted using solutions with ammonia concentrations of 50, 75, and/or 100 mg/L. The results which are shown in Fig. 4 exhibit an increase in the amount of ammonium adsorbed on zeolite sites with increasing the ammonium feed concentration. Such a behavior is expected considering the desired isotherm of ammonium adsorption onto natural zeolite. It can also be interpreted by the fact that higher ammonia concentration in the solution provides a higher solute concentration gradient, and the latter provides the necessary driving force for the ion exchange process.

Figure 5 shows the change in ammonium uptake at pH values of 5.5, 7.6, and 10 for ammonia initial concentration of 50 mg/L. As it is illustrated, changing the pH from 5.5 to 7.6 does not change the capacity and rate of the adsorption significantly. However, increasing the pH up to 10 will cause a dramatic decrease in adsorption capacity of adsorbent.

The value of pH has an obvious impact on ammonia removal by clinoptilolite since it can influence both the character of the exchanging ions as well as the character of the clinoptilolite itself. At lower pH values, the ammonium ions have to compete with hydrogen ions among the exchange sites. However, at higher pH values, the ammonium ions will shift into aqueous ammonia. On the other hand, a variety of impurities that occupy micropores and macropores of clinoptilolite, such as calcium

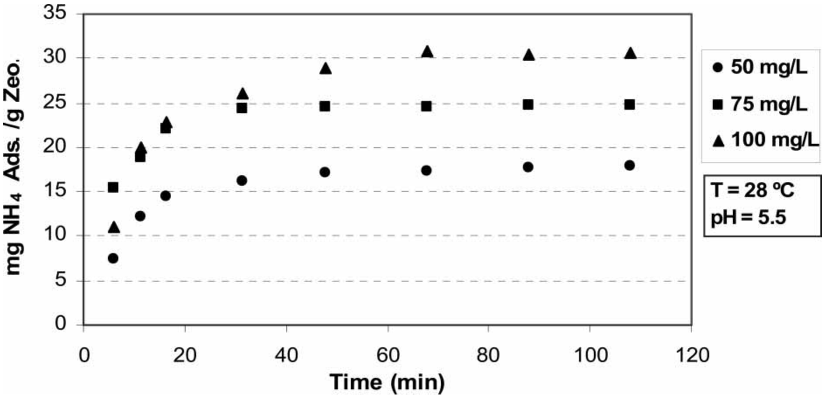

Figure 4. Effect of ammonia initial concentration on ammonium adsorption kinetics.

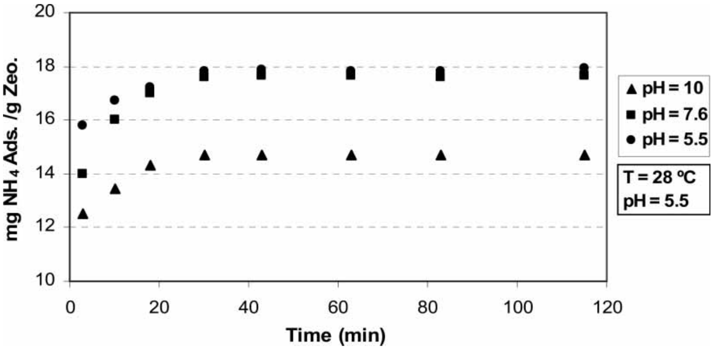

Figure 5. Effect of pH on ammonium adsorption kinetics.

carbonate, unaltered glass, etc., are perhaps removed by hydrogen ions at lower pH values (13). This process contributes to improve the exchange capacity of clinoptilolite.

Adsorption Isotherm

Adsorption isotherm of ammonium on clinoptilolite adsorbent is illustrated in Figure 6. As it can be seen, by increasing the ammonia concentration the amount of equilibrium adsorption increases up to a saturation point beyond that ammonia concentration does not influence the amount of adsorption significantly.

The Freundlich and Langmuir isotherm models are used to simulate the experimental results. Such empirical equations are useful in the interpretation and the prediction of the adsorption system. The constants of these isotherms obtained through fitting the isotherm equations with the experimental data are given in Table 3.

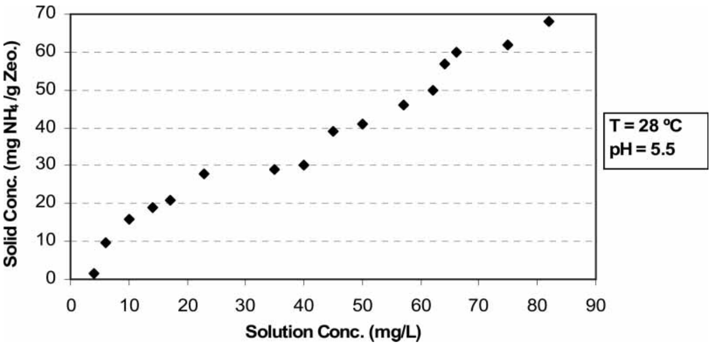

Figure 6. Ammonium adsorption isotherm on clinoptilolite.

Table 3. Langmuir and Freundlich model parameters and corresponding correlation coefficients

Freundlich model $X = KC_e^{1/n}$				Langmuir model $X = X_m bC_e/1 + bC_e$			
$\sum E^2$	R^2	n	K	$\sum E^2$	R^2	b	X_m
323.337	0.9843	1.2566	2.0711	423.8002	0.9727	0.0136	107.527

Column (Continuous) Experiments

Ammonium Breakthrough Curves for Natural and Regenerated (Na form) Zeolite

In Fig. 7 the breakthrough curve of natural zeolite is compared with that of regenerated type of Na form. As it is illustrated, in the case of natural zeolite, leakage of ammonium in the outlet stream begins much faster (123 BV) in comparison with that of Na form zeolite (201 BV). However, the slope of the breakthrough curve in the case of Na form zeolite is higher than that of the natural zeolite.

By calculating the area under breakthrough curves (for concentrations up to 50 mg/L) and multiplying it by bed volume the total amount of adsorbed ammonium is obtained. By dividing the result to the amount of zeolite in the column (500 g), the ammonium adsorption capacity per unit mass of zeolite is obtained for the continuous system. The results are shown in Table 4. As it can be seen, not only the adsorption capacity of zeolite is not reduced after the regeneration process, but also it has improved to some extent. The latter might be due to the fact that clinoptilolite can be converted to single ionic sodium-form during regeneration process which has a higher capacity.

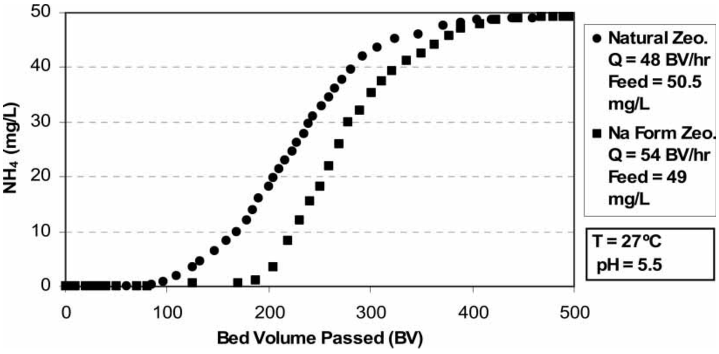

Figure 7. Ammonium breakthrough curves of natural and Na form zeolite.

Table 4. Ammonium adsorption capacity of natural and Na form clinoptilolite in continuous mode

Zeolite	Total ammonium adsorbed (mg)	Adsorption capacity (mg NH_4^+/g zeolite)
Natural zeolite	7579.77	15.16
Na form zeolite	7682.34	15.36

Effect of Ammonia Concentration and the Presence of Rival Ions in the Solution

To investigate the effect of ammonium concentration on breakthrough curves, the Na form of zeolite was employed. Figure 8 compares the breakthrough curves when 50 mg/L and 100 mg/L ammonia solutions were passed through the column. As it can be seen, for solution of 100 mg/L while increasing the ammonia concentration, by passing a less volume of feed solution through the column (almost the half) ammonium leakage was observed in the outlet stream and the curve increases with a higher slope comparing to that of 50 mg/L ammonia solution. However, it is important to notice the fact that although the ammonia concentration has increased to 100 mg/L, the ammonium concentration in the outlet stream remains less than 1 mg/L up to BV = 85.

It is also necessary to remind that clinoptilolite treatment is not an appropriate system for the waste waters containing high ammonia concentrations. In such a case, a preliminary treatment is recommended to reduce the ammonia concentration up to a certain limit and then a clinoptilolite ion exchange column can be used as a secondary treatment system to get the effluent to the standard level of ammonium concentration.

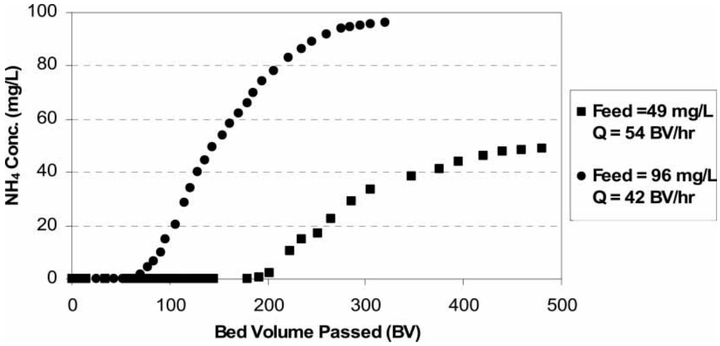

Figure 8. Effect of ammonium concentration on column breakthrough curves.

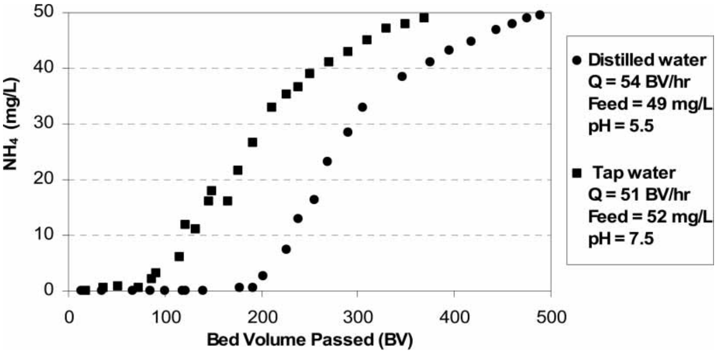

Figure 9. Effect of presence of other rival ions in feed solution on breakthrough curve.

Figure 9 shows the effect of the presence of other rival ions in the feed solution. These rival ions caused a lower adsorption capacity, i.e., the adsorption capacity of 15.34 NH_4/g zeolite, for the solutions made with distilled water, reduced to a capacity of 11.68 NH_4/g zeolite, for the solutions made with tap water. This is due to the fact that the present cations will compete to occupy the sites on the zeolite, hence lowering the capacity for the ammonium ions. For the current study, the presence of high contents of Ca^{2+} and Mg^{2+} ions would definitely decrease the capacity of the zeolite for ammonium uptake.

Regeneration Experiments

The ammonium concentration in the outlet stream is plotted versus BV (Fig. 10). As it can be seen, the concentration of ammonium ion is exponentially decreased. Therefore Na^+ is a good regenerant reagent to remove the ammonium ion from loaded zeolite. It is also noticed that after passing

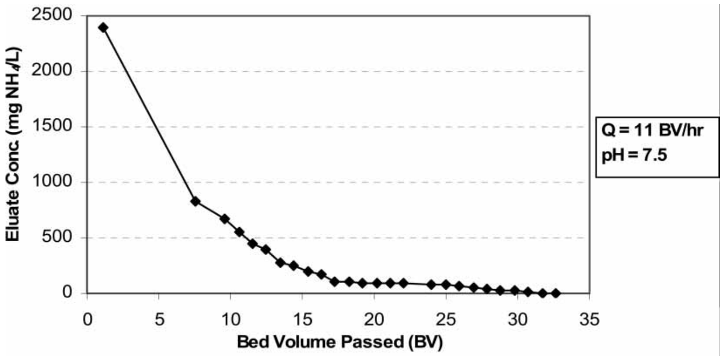

Figure 10. Regeneration rate of column using 1 M NaCl solution.

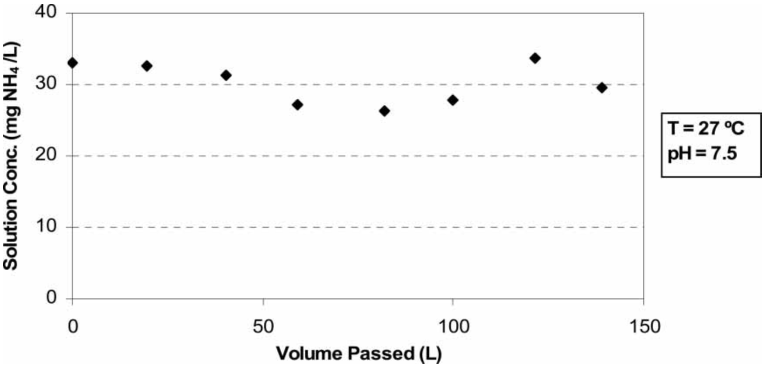

Figure 11. Regeneration rate of column using tap water.

33 BV of regenerant solution through the column no ammonium ion is detected in the outlet stream. Therefore, after passing 20 L of regenerant solution, i.e. 36 BV of regenerant solution, the regeneration process is complete. Therefore, to regenerate the clinoptilolite column 20 L of 1 M NaCl solution should be passed through the column. After the regeneration process was completed, the column was washed with 5 L distilled water to assure that no sodium chloride is left between the zeolite particles.

To investigate the release behavior of ammonium from the saturated zeolite, tap water was passed through the column containing exhausted zeolite. Each 20 L of effluent was collected in a tank and was then analyzed for its ammonium contents. The results which are shown in Fig. 11 represent that ammonium is only gradually released. By calculating the area under the curve it was determined that after passing 140 L water through the column, total amount of 4172.8 mg ammonium ion was released.

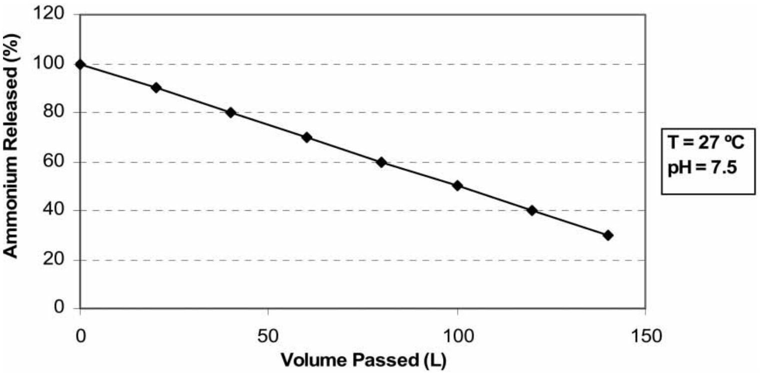

Figure 12. Ammonium released from saturated zeolite.

To get a better understanding of the pattern of ammonium release, the percentage of ammonium released from the saturated zeolite was plotted against the volume of tap water passed through the column (Fig. 12). As it can be seen, the trend of release is linear and ammonium is uniformly released. Accomplishment of such a release behavior, saturated zeolite with ammonia can be used as a slow release carrier fertilizer. In agriculture the natural zeolites are widely used as slow releasing carriers of fertilizers (31).

CONCLUSIONS

Iranian clinoptilolite form the Semnan region proved to have a high affinity toward ammonium ion. That affinity is observed for a wide range of ammonium concentrations in the context of wastewater treatment. The following conclusions could be drawn from the results of the experiments conducted in the course of this study:

The particle size of the zeolite does not have a significant influence on the ammonia removal in the range studied. Ammonium uptake occurs very rapidly and within the first 15 minutes of contact time the main part of ammonium is removed from the solution. In the batch mode experiments, ammonium adsorption capacity of clinoptilolite is obtained about 17.8 mg NH_4^+/g zeolite at an ammonia feed concentration of 50 mg/L. The adsorption capacity of clinoptilolite increases with ammonia concentration in the feed; however, the clinoptilolite ion exchange process does not exhibit efficiency for very high ammonia concentrations (e.g., >100 mg NH_4/L). The pH value of the synthetic ammonia solution also influences ammonia removal, i.e., increasing the pH value of the solution towards alkalinity decreases the ammonia removal. Therefore controlling the pH value in the range of 5.5–7.5 was recommended. The ammonium adsorption isotherm of clinoptilolite is a Langmuir type isotherm which shows that this type of zeolite is selective for ammonium ion. Both Freundlich and Langmuir models fit the experimental data, although the uptake is described with a higher accuracy by the Freundlich model.

Through continuous mode studies, breakthrough curves of ammonia removal using both original and regenerated (Na form) clinoptilolite were obtained. While using the Na form zeolite in the column, breakthrough curves show a more desirable characteristic and improved ammonia removal capacity. The latter observation is attributed to the fact that clinoptilolite can be converted to a single ionic sodium form during the regeneration process. Clinoptilolite adsorption capacity in the continuous system is measured about 15.16 mg NH_4^+/g zeolite for the original clinoptilolite and 15.36 mg NH_4^+/g zeolite for Na form regenerated clinoptilolite; at a feed concentration of 50 mg/L. Increasing the ammonium concentration to 100 mg/L does not reduce the capability of the column for ammonium removal and up to a BV of equal to 85, only less than 1 mg of ammonium in the column outlet is observed.

The presence of the other cations such as Ca^{2+}, Mg^{2+}, and Na^{+} reduces the clinoptilolite adsorption capacity to about 11.68 mg NH_4^+/g zeolite. The proper rate of the regeneration process shows that the sodium chloride solution is an appropriate regenerant for the exhausted zeolite. Regeneration was also performed using tap water while the gradual release of ammonium from the exhausted clinoptilolite is observed. The latter characteristic makes this type of zeolite useful as a slow carrier fertilizer. A bed volume (BV) equal to 35 of a 1 M sodium chloride solution at a pH of 7.5 exhibited sufficient for a complete regeneration of clinoptilolite in the column. Passage of the tap water through the exhausted column results in the gradual release of the adsorbed ammonia. That indicates the possible application of saturated clinoptilolite in agriculture as a slow releasing carrier fertilizer. A clinoptilolite-containing soil can adsorb the ammonia contents of the water streams and release the same ammonia in subsequent irrigations gradually. Such a slow release behavior of the soil would reduce the environmental drawback of the application of both urea fertilizers and ammonia-containing waste water streams for agriculture purposes.

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