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Removal of NH_4^+ Ion from NH_4Cl Solution Using Clinoptilolite: A Dynamic Study Using a Continuous Packed-Bed Column in Up-Flow Mode

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ABSTRACT

An investigation, in the form of dynamic experiments, was designed to investigate equilibrium and kinetic information for the ammonium ion-exchange of clinoptilolite. The process consisted of a packed-bed column operated in up-flow mode. A number of experiments were carried out at laboratory scale. The total ionic strength was kept constant in all runs, and made to resemble the ionic environment of the effluent from the landfill assisted froth flotation (LLAFF) process, in order to validate the feasibility of using clinoptilolite to remove NH_4^+ ion from that wastewater. Breakthrough

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curves and reduced data of the Thomas equation were constructed from a range of experimental tests in order to determine maximum exchange capacity (*q*) and design reaction constant (*k*). Feed rate and packing techniques have a major effect on the dynamic condition inside the column. The influence of multi-component ions on the NH_4^+ ion-exchange performance of clinoptilolite was also studied in order to determine the negative effect of competing cations, i.e., K^+, Ca^{2+}, and Na^+. The results of the study show that the column system gives an acceptable response to variable influent NH_4^+ loads. Desorption phenomena were also investigated when the influent was shifted to very low concentrations of NH_4^+ loads. Overall, a fixed-bed system of clinoptilolite shows high potential to remove NH_4^+ ion from the effluent of the LLAFF process.

Key Words: Ion-exchange; Clinoptilolite; Dynamic study; Up-flow; Ammonium removal; Constant ionic strength.

1. INTRODUCTION

This research is part of an investigation of the landfill leachate assisted froth flotation (LLAFF) process, which concerns the exploitation of organic compounds in landfill leachate having similar structures to the conventional surface-active chemicals used in froth flotation.[1] Although this process can achieve relatively high coal recovery, and remove most of the bio- and non-biodegradable organic substances and total suspended solids simultaneously, the liquid waste derived from the LLAFF process contains relatively high ammoniacal nitrogen concentrations which require further treatment before being discharged to a water treatment plant. A review of recent research revealed that clinoptilolite has high selectivity for ammonium ion and some heavy metals.[2–8] Most researches have been performed to assess clinoptilolite for ammonium removal and to determine the optimum operating conditions, as well as the potential of clinoptilolite for continuous wastewater treatment. However, the potential of clinoptilolite for continuous treatment of industrial wastewater, similar to the effluent from the LLAFF process which contains high NH_4^+ concentrations (up to 200 mg/L) and constant total ionic strength (up to 0.16 N), has not been conducted, and the experimental techniques for dynamic measurements used in many researches were conducted with little concern for constant ionic strength (salinity) in the solution phase.

This research involves an investigation of dynamic experiments, which were designed to investigate equilibrium and kinetic data for the ammonium ion-exchange of clinoptilolite in packed-bed columns in the up-flow mode of operation. A number of experiments were carried out in the columns at laboratory scale. The ionic strength of the feed solution was kept constant, and made to resemble the cationic condition of the effluent from LLAFF in order to validate the feasibility of using clinoptilolite to remove NH_4^+ ion from the effluent of the LLAFF process. The following discussion includes determination of maximum adsorption capacity and equilibrium and kinetic data for NH_4^+ ion exchange in a clinoptilolite column, which are necessary for column design or a scaling up procedure, as well as the influence of multivalent ions on the ion exchange performance of clinoptilolite, the desorption of NH_4^+ ions from the column, the response of the column system to variable influent NH_4^+ loads and the regeneration operation with NaCl solution.

2. EXPERIMENTAL METHODS AND PROCEDURES

2.1 Materials

Ammonium chloride (analytical reagent grade) was obtained from Fisher Scientific (Loughborough, UK) with a stated purity of 99.8%, and used as supplied. Sodium chloride (analytical reagent grade) was obtained from BDH Chemicals Ltd. (Poole, UK) with a stated purity of 99.5%, and used as supplied. Potassium chloride (analytical reagent grade) was obtained from Fisher Scientific with a stated purity of 99.72%, and used as supplied. Calcium chloride (general purpose grade) was obtained from Fisher Scientific in the form of anhydrous lumps, and used as supplied.

2.2 Feed Solutions

The feed solutions used for the dynamic runs under dry and wet conditions are shown in Table 1. The feed composition used for the dynamic

Table 1. Experimental tests when the column was packed in dry condition (poor-packing) and wet condition (re-packing).

Concentration of NH_4^+ in feed solution [mg/L (meq/L)]	
Dry condition	Wet condition
Run 1: 40 (2.22)	Run 7: 21 (1.17)
Run 2: 90 (5.00)	Run 8: 59 (3.28)
Run 3: 230 (12.78)	Run 9: 102 (5.67)
Run 4: 363 (20.17)	Run 10: 152 (8.44)
Run 5: 459 (25.50)	Run 11: 201 (11.17)
Run 6: 590 (32.78)	

Table 2. Operating conditions of Run 11 and 13.

Run	Feed concentration [mg/L (meq/L)]				Feed flow rate (L/day)
	NH_4^+	Ca^{2+}	K^+	Na^+	
11	201 (11.17)	Nil	Nil	Nil	5.5
13	202 (11.22)	170 (8.5)	160 (4.1)	3232 (140.54)	5.5

Note: Runs 11 and 13 have the following molar equivalent fraction compositions (%): 12—$NH^{4+} : Ca^{2+} : K^+ : Na^+ = 100 : 0 : 0 : 0$; 13—$NH^{4+} : Ca^{2+} : K^+ : Na^+ = 6.8 : 5.2 : 2.5 : 85.5$.

runs with multi-component feed solutions is shown in Table 2, 1 bed volume = 0.2 litres.

2.3 Peak Loading Disturbance Tests

In these experiments, the system was operated continuously for 55 hrs and was loaded with four consecutive peaks; a 3-fold or 5-fold disturbance of feed concentration was initiated by shifting feed NH_4^+ concentration from 200 mg/L (11.11 meq/L) to 600 mg/L (33.33 meq/L) or 1000 mg/L (55.55 meq/L). The disturbance was initiated every 5 hrs, each of which lasted for 2 hrs before turning back to the baseline NH_4^+ concentration of 200 mg/L.

2.4 Desorption Runs

After column exhaustion occurred, the inflow was shifted to tap water, which contains very low concentrations of NH_4^+ in order to observe desorption characteristics.

2.5 Regeneration of Column with Brine

Regeneration of the zeolite used in the continuous process was initiated upon ammonium breakthrough using caustic brine solution (10 g/L NaCl), and was achieved by contacting the zeolite without adjusting pH, since the initial pH in the solutions are normally in the range of 7–8.

2.6 Analysis of Data

Ammonia concentration in solution was measured using an ammonia electrode, in conjunction with a digital pH/mV meter. The electrode was supplied by Russell PH Ltd. (Ely, UK) (model 95-5129), and was standardized using 0.1 M ammonium chloride solution. Measurements in the range 4×10^{-6} M–1.0 M ammonia are the most reliable. The electrode measurements are not affected by sample color or turbidity. Anions, cations, and dissolved species other than volatile amines do not interfere with the electrode.

The maximum adsorption level was determined from the results of experimental tests, i.e., the one column-study with a feed flow-rate equal to 5.48 L/day. In order to determine the maximum adsorption capacity of clinoptilolite, the breakthrough runs were conducted at laboratory scale, and the total ionic strength in all runs was kept low at 3.74×10^{-3} M.

The breakthrough curve for an ion exchange column shows the solute or ion concentration in the effluent on the *y*-axis vs. the effluent throughput volume on the *x*-axis. Then, the area above the breakthrough curve represents the amount of solute or ion taken up by the column, which can be described by the following equation:

$$q = (C_0 - C)\,dV$$

from $V = 0$ to $V =$ the allowable throughput volume under consideration.

From the above equation, $C_0 - C$ is plotted against the effluent throughput volume. At the allowable breakthrough volume, V_B, an integration of the area under the breakthrough curve is equal to the amount of ions removed by the column. At complete exhaustion, $C = C_0$ and the area under the breakthrough curve is equal to the maximum amount of ions removed by the column. At complete exhaustion, the entire exchange column is in equilibrium with the influent and effluent flows. Also, the ion concentration in the influent is equal to the ion concentration in the effluent.

Generalized ion exchange isotherms were computed from two methods. One is from direct calculation by an integration of the area under breakthrough curves, i.e., adsorption level (meq/g), and the other a prediction based on the Thomas equation. The design of an ion-exchange column can then be accomplished by either a scale-up or a kinetic approach.[9]

The kinetic equation, based on a derivation by Thomas, is more often used because it is not so complicated and also because of concerns about the ratio between solute concentrations in either influent or effluent, maximum solid phase concentration of the adsorbed solute (meq/g), and feed flow rate. The expression by Thomas for an ion exchange column is as follows:

$$C/C_0 = \frac{1}{1 + e^{[(k_1/Q)(q_0 M - C_0 V)]}} \qquad (1)$$

where $C =$ effluent solute concentration, $C_0 =$ influent solute concentration, $k_1 =$ rate constant, $q_0 =$ maximum solid-phase concentration of the adsorbed solute—for example, grams per gram, $M =$ mass of the adsorbent—for example, grams, $V =$ throughput volume—for example, litres, and $Q =$ flow rate—for example, litres per hour. Assuming the left side equals the right side, cross-multiplying gives:

$$1 + e^{[(k_1/Q)(q_0 M - C_0 V)]} = C_0/C \tag{2}$$

Rearranging and taking the natural logarithms of both sides yields the design equation:

$$\ln\left[\left(\frac{C_0}{C}\right) - 1\right] = \left(\frac{k_1 q_0 M}{Q}\right) - \left(\frac{k_1 C_0 V}{Q}\right) \tag{3}$$

3. RESULTS AND DISCUSSION

3.1. Determination of Maximum Adsorption Level

The NH_4^+ adsorption levels of clinoptilolite are computed from an integration of area under the breakthrough curves of each run, and summarized in Table 3. The adsorption of NH_4^+ ions onto clinoptilolite is 0.29 meq/g of zeolite when the feed concentration of NH_4^+ equals 1.17 meq/L (or 20 mg/L), and increases to 1.95 meq/g zeolite when the feed concentration of NH_4^+ equals 11.17 meq/L (200 mg/L). A plot of ammonium adsorption onto clinoptilolite against feed concentration of NH_4^+ is shown in Fig. 1. From Table 3, the maximum ammonium adsorption level would be the one obtained from Run 11, where the column was operated with 100% NH_4^+ in the feed solution, which equals 1.95 meq/g zeolite. Considering Fig. 1, it seems that the adsorption capacity reaches the maximum level at 2.0 meq/g zeolite, approximately.

Table 3. Ammonium adsorption level of clinoptilolite (total ionic strength $= 3.74 \times 10^{-3}$ M).

Run	NH_4^+ proportion	NH_4^+ adsorption level (as meq/g of zeolite)
7	10% NH_4^+ + 90% Na^+	0.29
8	30% NH_4^+ + 70% Na^+	0.96
9	50% NH_4^+ + 50% Na^+	1.05
10	75% NH_4^+ + 25% Na^+	1.93
11	100% NH_4^+ + 0% Na^+	1.95

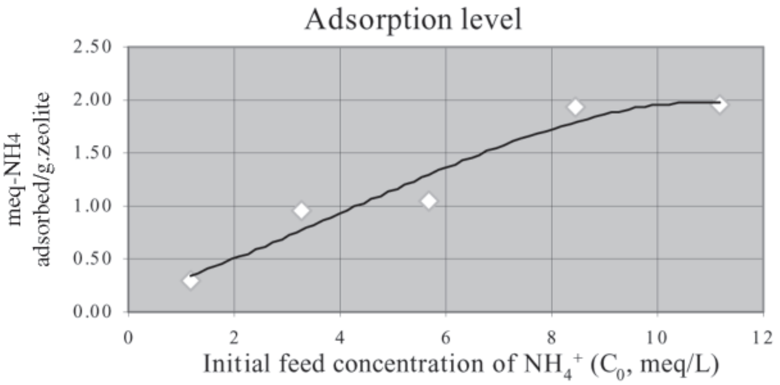

Figure 1. A plot of adsorption level against initial feed concentration of NH_4^+.

3.2. Effect of Dynamic Conditions Inside the Column on the System Performance

In the first experimental condition, the column was operated with a feed flow rate equal to 27.3 L/day, and clinoptilolite was loaded into the column in a dry condition. Concentrations of NH_4 in feed solutions are shown in Table 1. The breakthrough curves of each run are presented in Fig. 2. It was noticed that concentrations of NH_4^+ in the effluent were reasonably high even at

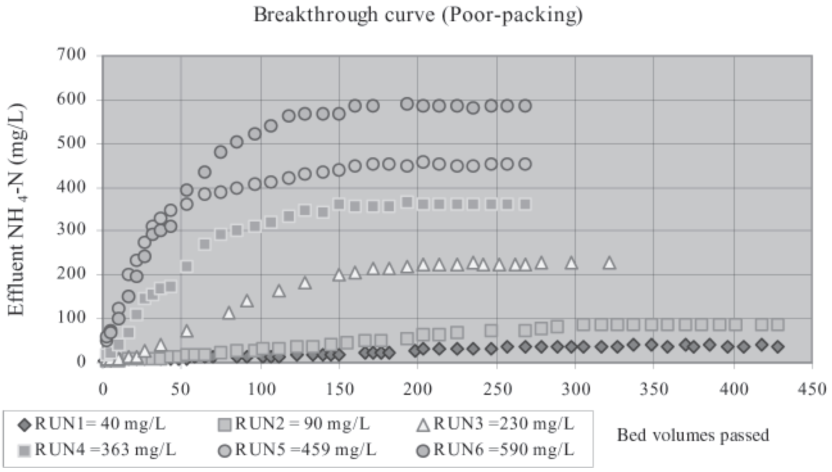

Figure 2. Breakthrough curves when the column was packed in dry condition.

early stages of the operation. This would imply that an amount of NH_4^+ ions have escaped through the column before being adsorbed by the ion-exchange media. From this result, it may be assumed that premature breakthrough has occurred as a result of two possible reasons:

- High feed flow-rate has driven NH_4^+ ions through the column before ion-exchange has properly occurred.
- Poor-packing procedure causes a non-uniform settlement inside the ion exchange bed, leading to channeling.

The packing procedure was then improved by re-packing the column under wet conditions along with a decrease in the feed flow rate to about 5.5 L/day. The breakthrough curves of each run then show a dissimilar pattern to that obtained from dry-packing the column, as presented in Fig. 3. In particular, it was now found that an idealized breakthrough curve (S-shape) could be observed in all runs. From this result, it can be said that packing technique has a major effect on the dynamic conditions inside the column. Additionally, this would imply that adjusting the packing technique will improve adsorption conditions inside the column and prevent an escape of NH_4^+ ions from the column before being adsorbed by the ion exchange media.

The generalized ion-exchange isotherms provide quantitative information about the distribution of NH_4^+ ions from solution to clinoptilolite surfaces. In both dry-packing and wet-packing conditions, the NH_4^+ ion has more preference for the solid phase than the solution phase.

In other words, it can be assumed that under dynamic conditions NH_4^+ ions tend to be adsorbed preferentially on the clinoptilolite relative to the

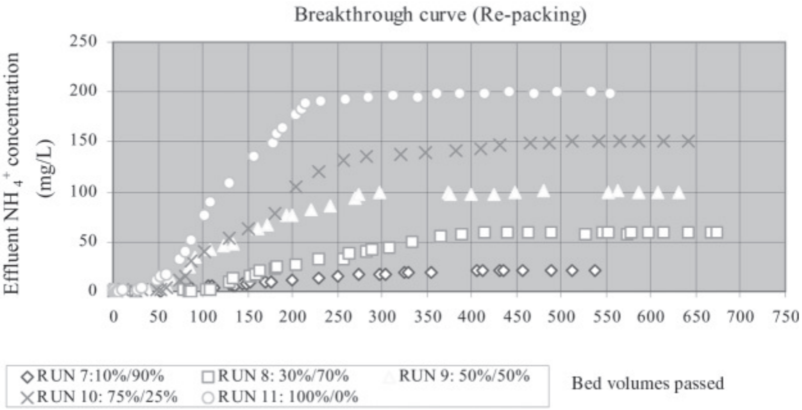

Figure 3. Breakthrough curves when the column was packed in wet condition.

Na^+ ions. A quantitative expression of the exchange of NH_4^+ ion onto clinoptilolite was also studied to determine the selectivity of clinoptilolite for NH_4^+ ion, as presented in Fig. 4. Based on the law of mass action, it is shown that the separation factor (α NH_4^+, Na^+) obtained from dry and poor packing conditions equals 1.2573 while α NH_4^+, Na^+ for wet packing equals 4.4179. This seems to indicate that, after having been re-packed, the conditions for adsorption inside the column have improved. Undoubtedly, the quality of column packing will have a large influence on the available surface area for ion-exchange and on reducing the tendency for channeling to occur. This promotes the adsorption of NH_4^+ ions from the solution phase to the solid phase and provides a better environment for the ion-exchange to occur.

3.3. The Influence of Multi-component Ions on the NH_4^+ Ion-Exchange Performance of Clinoptilolite

The extent of the inhibitory effects of competing cations, i.e., K^+, Ca^{2+}, and Na^+, in the solution was investigated, as well as the relationships between the concentrations of particular cations and the NH_4^+ ion-exchange capacity of clinoptilolite.

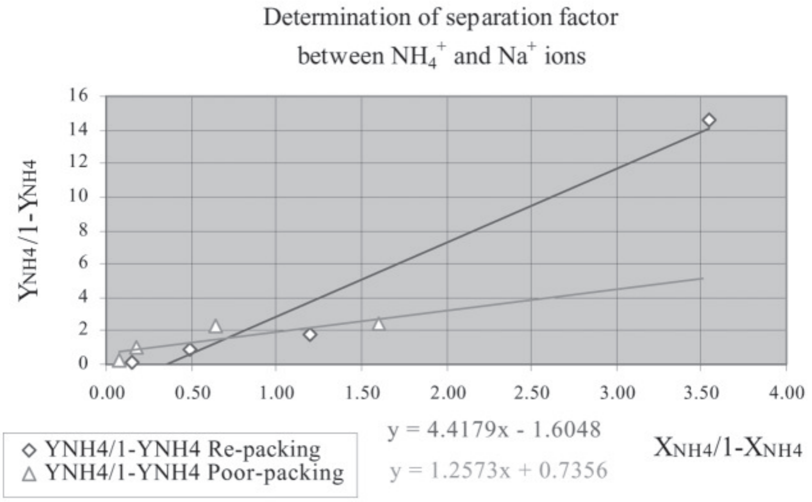

Figure 4. The effect of dynamic conditions inside the column on the system: determination of separation factor.

This investigation was conducted with a one column system. A number of dynamic runs using solutions of differing composition were undertaken to evaluate the effect of competing cations on the equilibrium capacity of clinoptilolite. The column was carefully packed under wet conditions. The actual flow-rate was kept constant at 5.5 L/day in all runs. Clinoptilolite was pre-treated in order to transform most of the exchangeable sites from a mixture of Na- and K- to Na-form. The total ionic strength in the solution was set at 0.16 N, based on the characteristics of the effluent from multistage froth flotation. The results of adsorption level and separation factor are summarized in Table 4 for binary mixtures of NH_4^+ and Na^+. Hence, determination of the effects caused by the presence of cations in the feed solution on exchange performance of clinoptilolite can be executed by comparing *k*-values and adsorption levels (meq/g), derived from the Thomas equation. As can be expected, increasing feed concentration of NH_4^+ causes a decrease in design reaction constant (k). Further analysis was carried out by plotting *k*-value against initial feed concentration of NH_4^+, as shown in Fig. 5. From Fig. 5, it can be seen that when the column was operated with 100% of NH_4^+, having a concentration of 200 mg/L (11.11 meq/L), the *k*-value is reaching a lower plateau of about 50 L/eq/day.

Further study was conducted to investigate the inhibitory effects of other cations, such as K^+ and Ca^{2+}. Another experimental run was conducted with a weight fraction of 10% NH_4^+ and 90% K^+ (Run 12) in order to compare the ion-exchange performance of the clinoptilolite with the result from Run 7 (10% NH_4^+ and 90% Na^+); the total salinity of the feed solution remains the same at 0.16 N.

The adsorption level (q) and design reaction constant (k) were calculated, either from an integration of the area under the breakthrough curve or by applying the Thomas equation to the reduced data, as shown in Fig. 6. The adsorption levels derived from the breakthrough curves are nearly equal while the value obtained from the Thomas plot of Run 12 (0.483 meq/g) is

Table 4. Adsorption capacities and *k*-values (total normality = 0.16 N).

Experimental runs	Initial feed concentration of NH_4^+, C_0 [mg/L (meq/L)]	Adsorption capacity from Thomas equation, q (meq/g)	*k*-value (L/eq/day)
7	21 (1.17)	0.54	352.22
8	59 (3.28)	1.79	131.49
9	102 (5.67)	2.50	81.67
10	152 (8.44)	3.54	53.83
11	201 (11.17)	3.92	60.01

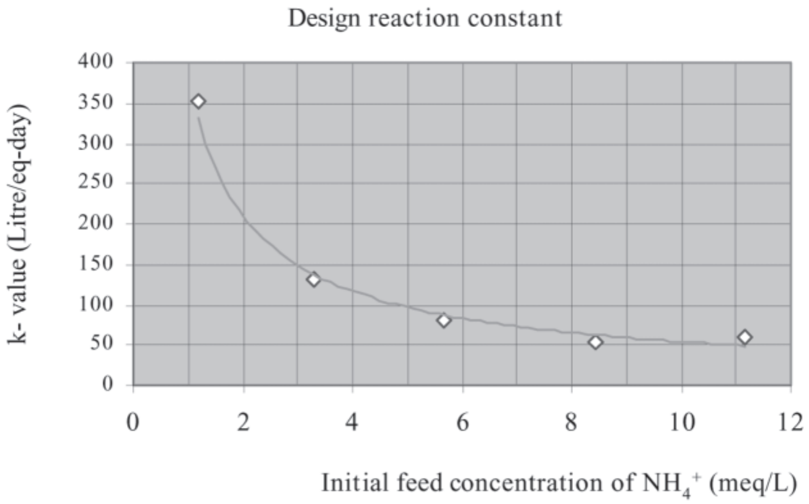

Figure 5. Relationship between design reaction constant and initial feed concentration of NH_4^+.

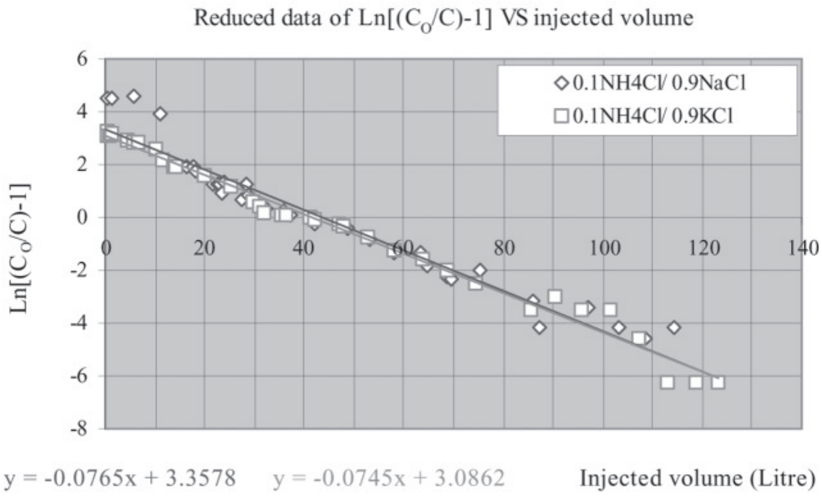

Figure 6. Reduced data of $\ln[(C_0/C)-1]$ against injected volume.

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slightly lower than that of Run 7 (0.540 meq/g). There is no significant difference in *k*-value between Run 7 (352.2 L/eq/day) and Run 12 (323.7 litre/eq/day). Overall, the presence of the K^+ ion in the initial feed solution does not cause a significant effect on NH_4^+ ion exchange performance of clinoptilolite, as far as the adsorption level (*q*) and reaction constant (*k*) are concerned.

Another set of experiments was established with multi-component cations (Run 13). Feed solution was made up to resemble the ionic speciation of the effluent from the LLAFF process. The result from this run (Run 13) is compared with the control experimental run (Run 11). The zeolite used in this experiment was saturated with 0.16 N of NaCl. The operating conditions of Run 11 and Run 13 are shown in Table 2. Based on the reduced data shown in Fig. 7, the adsorption level for NH_4^+ on clinoptilolite from Thomas plots of Run 11 and 13 are 3.92 meq/g and 3.98 meq/g, respectively. It can be said that the cationic condition in Run 13 does not significantly affect the adsorption level for NH_4^+ on clinoptilolite.

Considering the ionic environment in Run 11 and 13, the total ionic strength is 0.16 N and Na^+ ion is the dominant species in both runs. Run 13, which contains assorted cations of NH_4^+, Ca^{2+}, K^+, and Na^+ having similar concentrations to that of the effluent from the LLAFF process, does not show a major negative impact on the system performance in terms of the adsorption capacity (*q*); however, the design reaction constant (*k*) of Run 13 (46.20 L/eq/day) is considerably

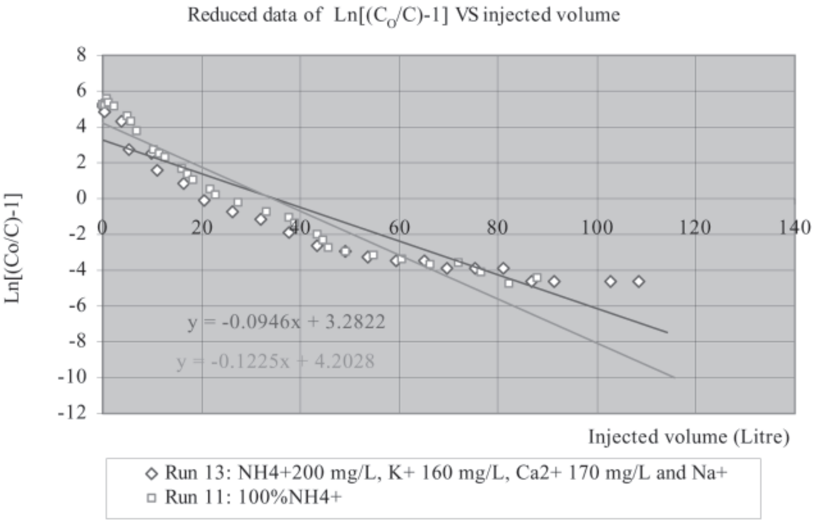

Figure 7. Reduced data of $\ln[(C_0/C)-1]$ against injected volume of Run 11 [100% NH_4^+] and Run 13 [NH_4^+ 200 mg/L, K^+ 160 mg/L, Ca^{2+} 170 mg/L, and Na^+].

lower than that of Run 11 (60.01 L/eq/day) by a factor of 1.3. The lower the reaction constant (k), the larger the exchange bed expected.

3.4. Desorption of NH_4^+ Ions from the Column

Desorption from the exhausted column under very low concentrations of NH_4^+ was also investigated to acquire an understanding of system behavior during periods of low concentration following peak ammonium concentrations. This experiment was conducted on the exhausted columns, Fig. 8. It was found that a maximum desorption level of about 16% can be observed in the first hour of NH_4^+ desorption study, after which desorption of NH_4^+ from the system decreases evenly for 3 hr. Up to 29% of NH_4^+ desorption can be reached after 5 hr. The significant result obtained from this run is that, at times when the influent NH_4^+ concentration is very low, desorption would be responsible for increasing the effluent concentration from an exhausted column. In this regard, effluent NH_4^+ concentrations that exceed the influent level may occur due to the desorption effect.

3.5. Response of the Column System to Variable Influent NH_4^+ Loads

Further experiments were carried out to observe the behavior of clinoptilolite columns under unsteady feed conditions. Figure 9 shows the system

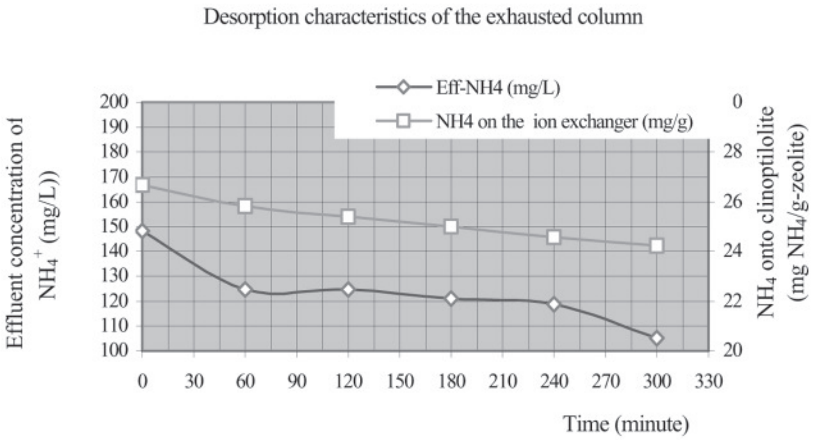

Figure 8. Desorption characteristics of the exhausted column.

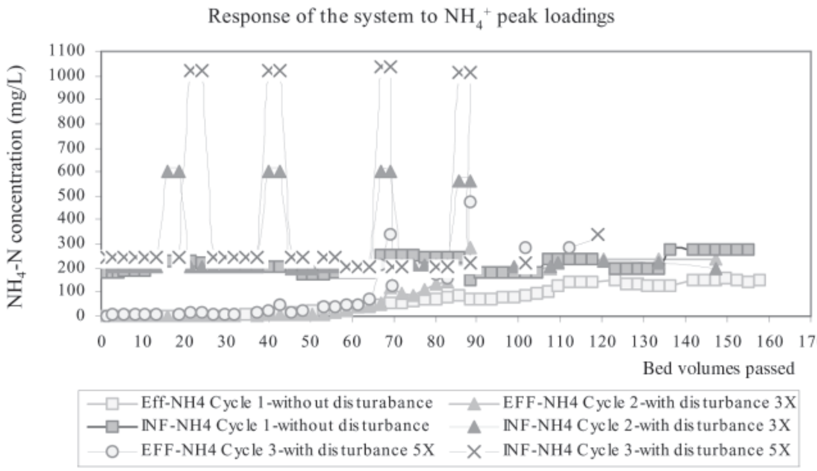

Figure 9. Response of the clinoptilolite system with NH_4^+ peak loadings.

response to a three-times increase in the influent NH_4^+ concentration in continuous peak-loading disturbances, as compared with the non-disturbance response. By comparing the system performances of cycle 2 (3-fold) with the non-disturbing one (cycle 1), it was found that the system with 3-fold disturbance provided satisfactory results; the effluent concentration of NH_4^+ of both operating conditions remained below the target effluent of 50 mg NH_4/L for 24 hr of operation. In other words, it can be said that the system can tolerate 3-fold peak disturbances for at least 24 hrs. As the operation proceeded, the effect caused by peak disturbance becomes more obvious. As a result, the first fluctuation of effluent NH_4 concentration was observed after the third disturbance. Initially, it was expected that the system would have been able to balance itself for the new conditions after the disturbance. However, this could not be observed during the 5 hr before the next disturbance strikes the system again. The system was likely to reach exhaustion faster than that of a non-disturbance system.

The response of the system to the 5-fold NH_4^+ peak loadings is also shown in Fig. 9, cycle 3. A similar pattern of NH_4^+ concentration in the effluent to that obtained from a 3-fold disturbance was observed. However, the breakthrough seems to occur sooner than in cycle 2 (3-fold), as the effluent NH_4^+ concentration in cycle 3 (5-fold) rises above 5 mg NH_4/L after it has been operated for just 2 hr. Overall, the system still provides acceptable results as the effluent concentration of NH_4^+ is kept below the target concentration of 50 mg/L for 24 hr of the operation.

Following the step-down disturbance in cycles 2 and 3, the effect of desorption giving higher values of effluent NH_4 than the influent can be observed as it approached exhaustion. Especially in cycle 3, a mark increase in NH_4^+ concentration in the effluent over that in the influent becomes noticeable after the third disturbance. This confirms the effect of desorption, and should be born in mind when clinoptilolite is used to remove ammoniacal nitrogen under highly variable influent NH_4^+ concentrations, since the adsorbed NH_4^+ ion may be released from the exchange site back to the waste stream.

3.6. Regeneration with NaCl

An elution curve obtained from the column is shown in Fig. 10. Considering the regeneration with 10 g NaCl/L and flow rate 1 L/hr, it is clear that the displacement of NH_4^+ with Na^+ ions has occurred rapidly within the first 1.5 hr of the contact. Overall, maximum regeneration rate can be observed within the first 5–6 hr of the operation. Up to 80% of ammonium desorption can be achieved by 6 hr of regeneration. Further, investigations involving Na-regeneration with different operating conditions were also conducted. Regeneration of the exhausted column with 10 g NaCl/L and a flow-rate of 4 L/hr was executed to observe the effect of flow rate on the displacement of NH_4^+ ions from clinoptilolite back into the solution. From Fig. 10, it is seen that the displacement of NH_4^+ with Na^+ ions has occurred rapidly within 15 min of the contact. Overall, maximum regeneration rate can be observed within the first 45 min of the operation. Up to 80% of ammonium desorption

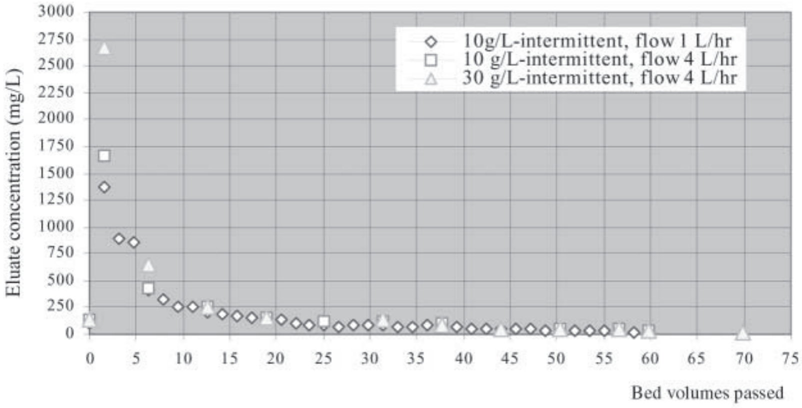

Figure 10. Regeneration curve for elution of NH_4^+ ions from clinoptilolite.

can be achieved within 55 min of regeneration. By comparing the operational time to reach 80% of NH_4^+ desorption using 10 g NaCl/L and flow-rate 1 L/hr vs. 10 g NaCl/L and flow rate 4 L/hr, it was found that increasing the feed-rate of brine solution would shorten the operation time of the regeneration cycle; increasing flow rate from 1 L/hr to 4 L/hr may shorten the regeneration time from 6 hr to 55 min. Another operating condition of regeneration was studied with 30 g NaCl/L and a flow-rate 4 L/hr, as presented in Fig. 10. The release of NH_4^+ ions from clinoptilolite back to the solution has occurred within 15 min of the operation. It was also revealed that regeneration with a high concentration of Na^+ causes a high concentration of NH_4^+ ion in the eluate. A summary of the NH_4^+ ion concentrations in the eluate from the regeneration with different brine concentrations is presented in Table 5.

It was found that the amount of NH_4^+ ions released in the eluate, when the system was fed with 30 g NaCl/L, is higher than that when fed with 10 g NaCl/L. From this, it can be expected that regeneration with a higher concentration of Na^+ may reach completion sooner than regenerating with a lower concentration of Na^+. In conclusion, it can be said that NH_4^+ ions are appreciably desorbed from the zeolite. This indicates that regeneration with NaCl transfers most of the NH_4^+ ions, returning the clinoptilolite structure back to the Na-form. It is seen that regeneration with a high concentration of Na^+ and flow-rate enhances the transformation of the exchangeable ions from NH_4^+ to Na^+. In addition, it can be suggested that increasing either flow-rate or concentration of NaCl can be used as alternative options to improve the regeneration process, as long as the minimum contact time is provided to allow sufficient time for an exchange of NH_4^+ with Na^+ to occur.

4. CONCLUSIONS

A number of dynamic-experiments conducted at laboratory scale reveal some important characteristics of clinoptilolite in its capability in removing

Table 5. Summary of the NH_4^+ ion concentrations in the eluate from the regeneration (with flow rate 4 L/hr).

Concentration of feed NaCl (g/L)	Peak concentration[a]
10	1665
30	2670

[a] Peak concentration of NH_4^+ ion in the eluate after 15 min of the operation.

NH_4^+ ion from the solution under continuous operation. The process consisted of a fixed-bed ion exchange system operated in up-flow mode. Based on the results of this investigation, the following conclusions are made.

The NH_4^+ adsorption capacity of clinoptilolite at low salinity reaches a maximum level of 2.0 meq/g zeolite, approximately. However, the packing technique has a major effect on the dynamic conditions inside the column, as idealized breakthrough curves can be more fully realized after the columns are re-packed under wet conditions. The latter reduces the tendency for channeling and improves the available surface area.

A number of experimental runs at a high total salinity of 0.16 N reveals that a design reaction constant (k) of 50 L/eq/day and an adsorption level (q) of 3.92 meq/g should be used in the design process. Increasing the feed concentration of NH_4^+ causes a decrease in design reaction constant (k).

A multi-component feed which contains assorted cations of NH_4^+, Ca^{2+}, K^+, and Na^+ and having similar concentrations to that of the effluent from the LLAFF process, does not show a major negative impact on the system performance (in Run 13) in terms of the adsorption capacity (q) as compared to an ammonium and sodium only feed (Run 11). This is probably due to the fact that the cationic environment in both runs is similar, where Na^+ is the dominant other cation in the solution. Further, substituting the weight fraction of 10% Na^+ with 10% K^+ in the feed solution would not significantly affect the NH_4^+ ion exchange performance of clinoptilolite, as far as the adsorption level (q) and reaction constant (k) are concerned.

The system with 3-fold disturbance is likely to reach exhaustion faster than that of a non-disturbance system. The response of the system to the 5-fold NH_4^+ peak loading is similar to that obtained from the 3-fold disturbance; however, the breakthrough seems to occur sooner than in the 3-fold disturbance. The system with a 5-fold disturbance still provides an acceptable result, as the effluent concentration of NH_4^+ is kept below the target concentration of 50 mg/L for 24 hr of the operation.

Increasing the regeneration flow rate from 1 L/hr to 4 L/hr revealed that the displacement of NH_4^+ ions with Na^+ ions has occurred in 55 min rather than 6 hr. It can also be concluded that increasing the feed-rate of the brine solution (to 30 g NaCl/L) would shorten the operation time for regeneration; at 4 L/hr the regeneration time is shortened further to 15 min. Therefore, increasing either flow rate or concentration of NaCl can be used as alternative options to improve the regeneration process, as long as a minimum contact time is provided to allow a completion of the displacement of NH_4^+ by Na^+ to occur. This minimum is determined by the kinetics of the displacement process.

It is interesting to note that when the influent NH_4^+ concentration drops to a low value, desorption of the column may be responsible for a "roll-up" phenomenon, in which the effluent concentration increases above the feed level for a near-exhausted column.

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