

Ammonia Removal from Wastewaters Using Natural Australian Zeolite. II. Pilot-Scale Study Using Continuous Packed Column Process

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ABSTRACT

A pilot-scale process was designed and operated to investigate the continuous removal of ammonia from sewage using natural zeolite from Australia. The process consisted of a fixed-bed ion-exchange system operated in the downflow mode. Evaluation of the pilot process was initially undertaken for ammonia removal from tap water spiked with ammonium chloride to provide performance data in the absence of competing cations. The performance of the pilot process was then assessed using sewage as feed. Breakthrough curves were constructed for a range of treatment flow rates. Existing models for packed bed performance were shown to be able to predict the breakthrough behavior of the process. The results of a study are presented that show that Australian natural zeolite, clinoptilolite, may be successfully employed in a fixed-bed ion-exchange process to achieve high ammonia removal efficiencies from aqueous solutions at rates commensurate with sand filtration. The rate of uptake of ammonium by the zeolite is sufficient to support a continuous high rate process.

INTRODUCTION

The discharge of ammonia to inland rivers and streams compromises the health of fish and leads to the proliferation of toxic blue-green algae. The de-

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mand for effective processes for ammonia removal from domestic and industrial wastewaters is increasing as discharge limits and disposal options decrease. Past research has shown that the natural zeolite, clinoptilolite, is highly selective for ammonium over most other cations (1–5) in an aqueous solution. The utilization of this unique property for the continuous removal of ammonia from wastewater streams has been studied using zeolite from various origins, and full-scale operation of this technique has been demonstrated (6). The capacity and diffusion characteristics are specific for each origin, and therefore consistency of performance between different zeolite deposits cannot be assumed. Little work has been performed to assess Australian natural zeolite for ammonia removal performance. Two fundamental studies have been reported (7, 8) which provide some evidence of the ammonium removal capability of Australian natural zeolite. Optimization of operating conditions was not carried out, and so the potential of this zeolite for continuous wastewater treatment is unknown.

This pilot-scale investigation was preceded by an extensive laboratory study, using pure solutions, to investigate the equilibria and kinetic characteristics of ammonium exchange in the zeolite (9). Binary equilibrium experiments provided information on the adsorption characteristics of the Australian zeolite in terms of ammonia capacity at varying solution concentrations. These experiments revealed that the highest ammonium removal efficiency was achieved when the zeolite's exchange sites were converted to the sodium form. Multicomponent equilibrium experiments were carried out to determine the effects of competing cations on the ammonium exchange capacity of the zeolite. The laboratory study quantified the zeolite's selectivity for ammonium ions over other cations typically present in sewage (calcium, magnesium, and potassium), and provided information relevant to the design and operation of a continuous pilot-scale process.

In this paper we investigate the rate of uptake of ammonium ions by the zeolite and develop and test a scaleup technique that can be used to predict large-scale column performance.

The zeolite used in this study was mined at Mount Gipps, some 200 km north of Sydney, Australia. It was essentially clinoptilolite having a bulk density of 1600 kg/m³.

EXPERIMENTAL TECHNIQUES

Kinetics Measurements

Kinetic tests were performed in a 2-L reaction flask with a multisocket "Quickfit" flat flange lid. For each batch rate test, the zeolite sample, of known size range, was accurately weighed. A solution of known ammonium concentration was prepared using analytical-grade NH₄Cl powder dissolved in deion-

ized water. A known volume (1.5 L) of solution was placed in the batch mixer. A pH probe was permanently positioned to measure any change in pH over the course of the test. A sintered glass straw was placed in the solution and stoppered to the lid of the vessel to allow for withdrawal of samples of the liquid during the rate test. A thermometer was also secured to the lid of the vessel to monitor temperature. The vessel was stirred at 400 rpm, using an inclined stirrer shaft, to ensure adequate suspension of the zeolite.

At time zero the zeolite was introduced to the test vessel via a funnel through one of the openings of the lid, and the timer was started. A syringe was used to extract 10 mL volumes of filtered samples at known time intervals over the course of the test. These samples were placed in stoppered vials for future analysis. When samples were extracted, the corresponding pH and temperature were recorded. Triplicate analyses of solution ammonium concentration were performed using the Hach Nessler method described more fully elsewhere (10). Various conditions of solution ammonium concentration and zeolite size fraction were tested to measure the effect of particle size on ammonium uptake rate. Constant pH of the solution indicated that adsorptive action within the system had slowed down, and tests were usually terminated.

The relationship between particle size and diffusion rate was further assessed by employing the "interruption test," where the zeolite was removed from the solution for a brief period of time and was then reimmersed. This pause allowed time for the concentration gradients within the particles of zeolite to level out. With particle diffusion control, the rate immediately following reimmersion is greater than before the interruption. With film diffusion control, no concentration gradients exist, and the rate depends on the concentration difference across the stagnant liquid layer surrounding the particle. So if film diffusion was the mechanism that controlled the rate, there would be no effect of the interruption (11). It was more practical, in light of the reactor employed, to decant out the liquid for the period of time rather than remove the zeolite from the reactor.

Pilot Column

A pilot-scale column 247 mm in diameter was designed and fabricated for continuous adsorption of ammonia from sewage. An outline drawing of the column is given in Fig. 1. The column was fabricated from PVC. A flow sheet of the continuous operation is shown in Fig. 2.

The design of the pilot column was based on the standard packed-bed layout frequently employed for ion exchange or filtration applications. The base of the column was fitted with a perforated steel support plate. The lower 1.2 m of the column was transparent; the upper 2.4 m was nontransparent. Outlets were positioned along the total column height for such duties as backwashing, sampling, draining, etc. An inlet point was positioned at the top of the column, and discharge at the bottom. The discharge line was raised to the equivalent

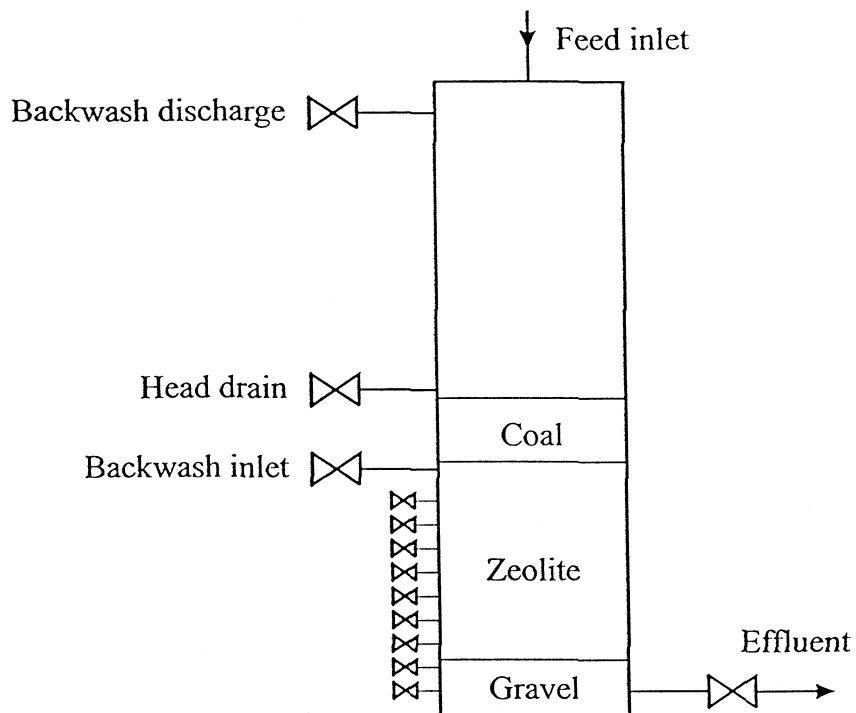


FIG. 1 The pilot column.

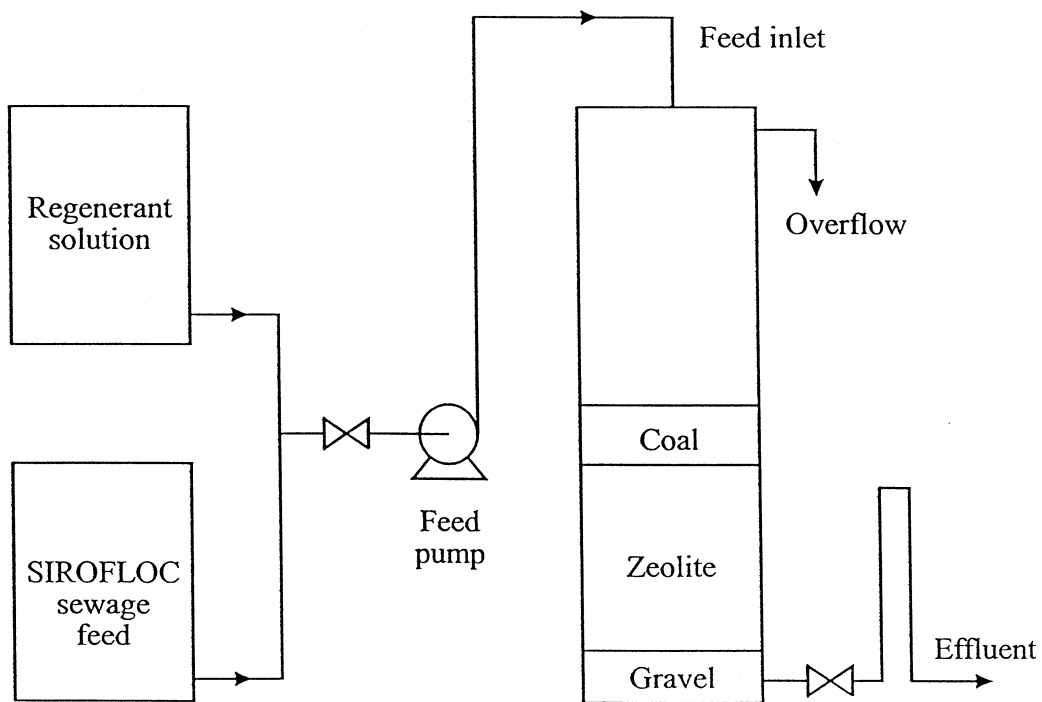


FIG. 2 Pilot-scale zeolite process flow sheet.

height of the top of the bed to ensure the bed was always fully immersed. In the column, 100 mm depth of coarse-grade gravel (8–10 mm diameter), followed by 100 mm of finer-grade gravel (3–5 mm diameter), was used to support the zeolite bed and prevent the zeolite being lost through the holes in the base plate. Approximately 50 kg of “turf grade” zeolite (supplied by Zeolite Australia Ltd.) was loaded into the column. A backwashing procedure was performed to eliminate the finer-sized zeolite particles from the bed, leaving an average particle size of 0.82 mm.

Above the zeolite bed a 150-mm thick layer of filter coal (2 mm diameter) was placed to act as a filter for incoming fines and magnetite associated with the treated sewage feed. The ammonium ion-exchange capacity of the coal was assumed to be negligible, based on saturation capacity tests using pure NH_4Cl solution. The inlet for backwashing was situated at the interface between the zeolite and the coal, connected to a horizontal, perforated pipe positioned directly below the coal bed to minimize the amount of zeolite being disturbed during backwash proceedings. The density differential between the coal and zeolite [bulk density of Australian natural zeolite = 1600 kg/m^3 (12); anthracite coal = $801\text{--}929 \text{ kg/m}^3$ (13)] ensured that settling rates of the zeolite would always exceed those of the coal. Thus the coal would always settle on top of the zeolite bed. This backwashing procedure eliminated the possibility of altering the adsorption profile within the zeolite bed due to intermittent backwashing during loading operations.

The physical characteristics of the column, in terms of flow distribution profile across the zeolite bed, were measured by performing a residence time distribution (RTD) analysis. KMnO_4 was used as the tracer, as it was shown to be inert and not to oxidize or adsorb onto the zeolite or coal. Several injection techniques were tested to assess the most accurate technique for this work. The best results were achieved by operating the column with tap water only and then replacing the feed with a known concentration of KMnO_4 solution until discharge concentration equaled inlet concentration. At this time the KMnO_4 solution was replaced with tap water. Samples were taken of the discharge stream and analyzed for their KMnO_4 concentration while the axial dispersion coefficients for the packed column were determined from a moment analysis (14).

Continuous operation of the zeolite pilot column commenced using tap water spiked with ammonium chloride to assess the ammonium adsorption performance in the relative absence of competing cations. The process was operated with spiked tap water as feed until the outlet ammonium concentration approached the feed concentration, thus providing a conclusive breakthrough curve for each of the flow rates tested.

The zeolite process was operated as a polishing process for the secondary treated water from the wastewater treatment facility at Lower Plenty in Melbourne. Secondary treatment of the sewage was achieved using the pilot-scale SIROFLOC process, a high-rate coagulation/flocculation process based on the

use of magnetite particles (15). Due to the diurnal concentration variation of all components in the sewage, a range of ammonium feed concentrations was experienced at the inlet to the zeolite process. Periodic backwashing of the pilot column was necessary to reduce the pressure drop across the bed. Pressure measurements were taken at various points down the bed, and they revealed that almost all of the pressure drop was related to the top 50 mm of the bed. By backwashing the coal filter only, the pressure drop across the bed was reduced without disturbing the zeolite's NH_4^+ adsorption profile. The loading cycles with secondary treated sewage as feed were continued until the outlet concentration from the zeolite column reached 5 mg $\text{NH}_4^+\text{-N/L}$, the Victorian EPA discharge limit for ammonium. Upon exhaustion of the zeolite bed, the regeneration cycle was initiated.

In order to convert the exhausted zeolite bed back to the sodium form for maximum ammonium adsorption capacity, a solution of caustic brine was passed down through the column. A solution of 0.6 M NaCl was prepared by dissolving coarse-grade NaCl into tap water. NaOH (4 M) was added to the brine solution to raise the pH to 10. Operation of the regeneration cycle was in the downflow mode, as for the loading cycles.

RESULTS AND DISCUSSION

Kinetics

Batch kinetic tests were performed to determine the rate-controlling mechanism for the uptake of ammonia.

The kinetics of ammonium ion exchange using zeolite may be divided into five steps (11):

1. Diffusion of the counterions through the film solution to the surface of the zeolite (film diffusion)
2. Diffusion of the counterions within the zeolite (particle phase diffusion)
3. Chemical reaction between the counterions and the ion-exchange sites
4. Diffusion of the displaced ions out of the zeolite
5. Diffusion of the displaced ions from the zeolite surface into the bulk solution

Steps 4 and 5 are the reverse of Steps 2 and 1.

The slowest step of the ion-exchange process for a given system controls the speed of ion exchange and is said to be the rate-limiting step.

Two mechanisms generally control the rate of adsorption within porous solids: these are either film diffusion (Step 1) or particle diffusion (Step 2). Both mechanisms are present in practice, although normally one mechanism (the slower) dominates.

It can be shown that for particle diffusion control (11):

$$\text{Rate} \propto 1/r_p^2 \quad (1)$$

and for film diffusion control:

$$\text{Rate} \propto 1/r_p \quad (2)$$

where r_p is the radius of the particle. By using these relationships it is possible to identify the rate-controlling mechanism.

Results similar to those in Figs. 3 and 4 reveal that particle diffusion is the rate-controlling mechanism for the exchange of ammonium from dilute NH_4Cl solutions (1.8 to 7.1 mmol) onto sodium-pretreated zeolite. Conventional ion-exchange models for particle diffusion control have been used for the analysis of the ion exchanger, clinoptilolite. Vermeulen's model (11) for the fractional attainment of equilibrium, X , given particle diffusion control

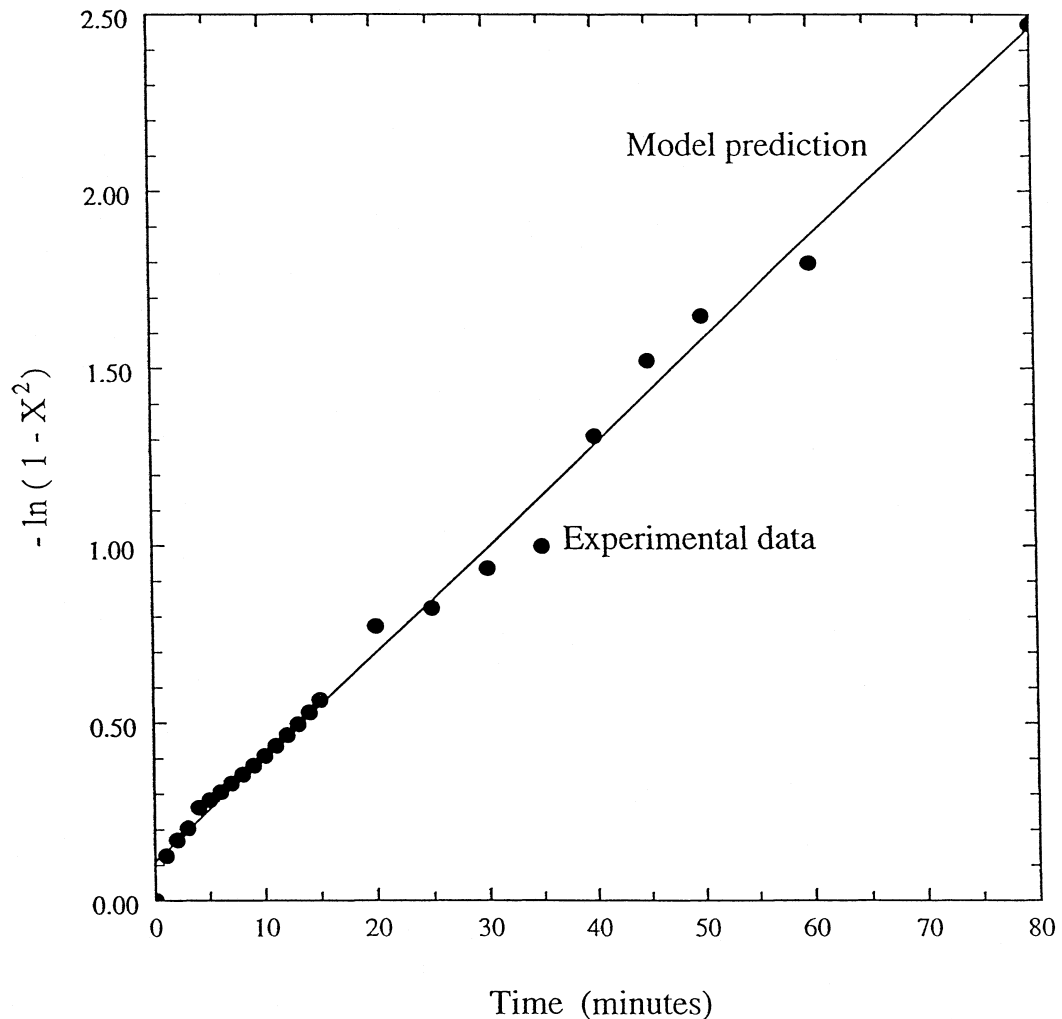


FIG. 3 Rate test results applied to Vermeulen's approximation. Ammonium adsorption onto Na-form zeolite. Initial solution concentration 50 mg $\text{NH}_4\text{-N/L}$. Zeolite size range 425 to 600 μm .

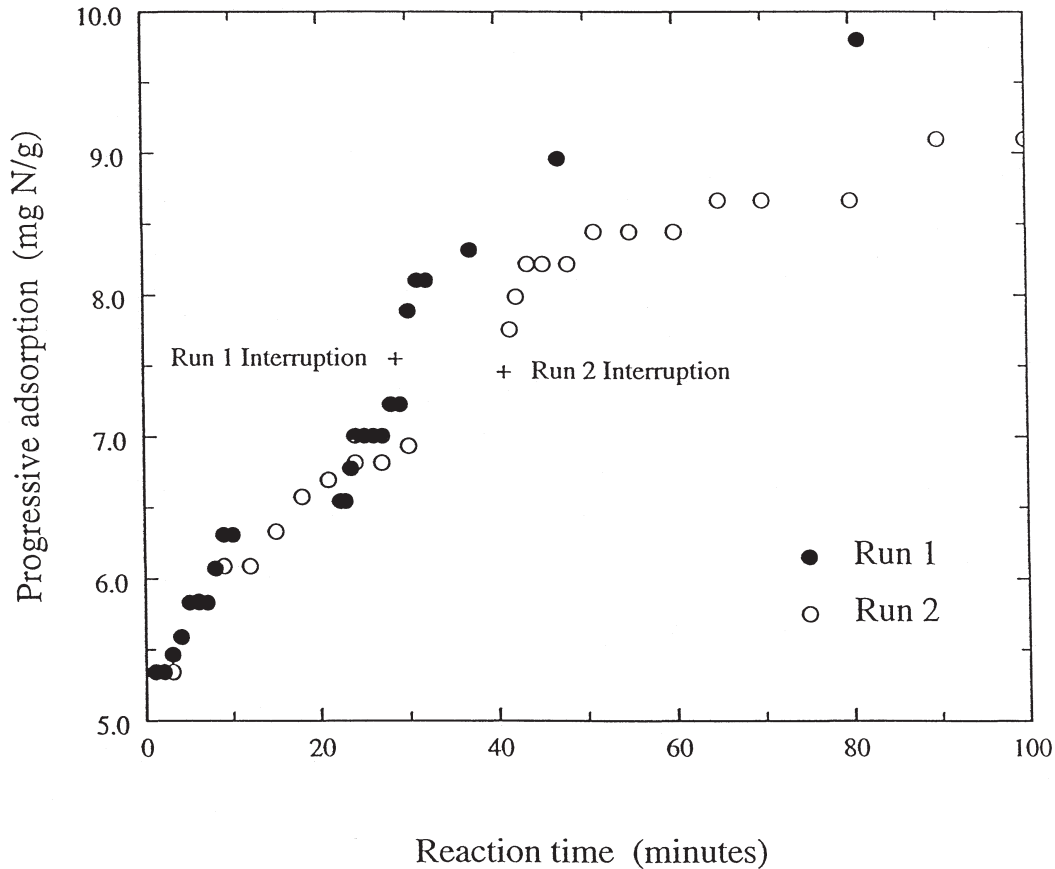


FIG. 4 Interruption tests for ammonium adsorption onto Australian natural zeolite.

with infinite solution volume boundary conditions, is given by

$$X = \left[-1 \exp \left(\frac{-D_p \pi t}{r_p^2} \right) \right]^{1/2} \quad (3)$$

where D_p is the diffusion coefficient, t is time, and r_p is the radius of the particle. Rearranging Eq. (3) yields

$$-\ln(1 - X^2) = t \left(\frac{D_p \pi^2}{r_p^2} \right) \quad (4)$$

The most convenient way to verify this model for the system is to plot time against calculated values for $-\ln(1 - X^2)$ for given X values (see Fig. 3). The diffusion coefficient, D_p , is obtained from the slope of the line in Fig. 3. This is presented for various size fractions in Table 1 and is shown to be relatively independent of particle size. The interruption tests (Fig. 4) also show a change in the rate of absorption after the interruption, further confirming particle diffusion is controlling.

TABLE 1
Diffusion Coefficients for Adsorption of Ammonium Ions onto Na-Pre-treated Zeolite as
Obtained by Vermeulen's Approximation

Particle diameter (μm)	Initial solution concentration (mg N/L)	Diffusion coefficient D_p (m^2/s)
1000–1200	25	3.21×10^{-12}
850–1000	25	3.48×10^{-12}
425–600	25	3.49×10^{-12}
425–600	50	3.26×10^{-12}

Breakthrough Curves

Typical breakthrough curves for NH_4^+ , Ca^{2+} , Mg^{2+} , and K^+ from the pilot-scale process fed with secondary treated sewage are presented in Fig. 5 for typical feed concentrations given in Table 2. The data clearly show that all four cations were taken up by the zeolite. Breakthrough of the NH_4^+ ions occurred first, probably as a result of being displaced by the Ca^{2+} ions.

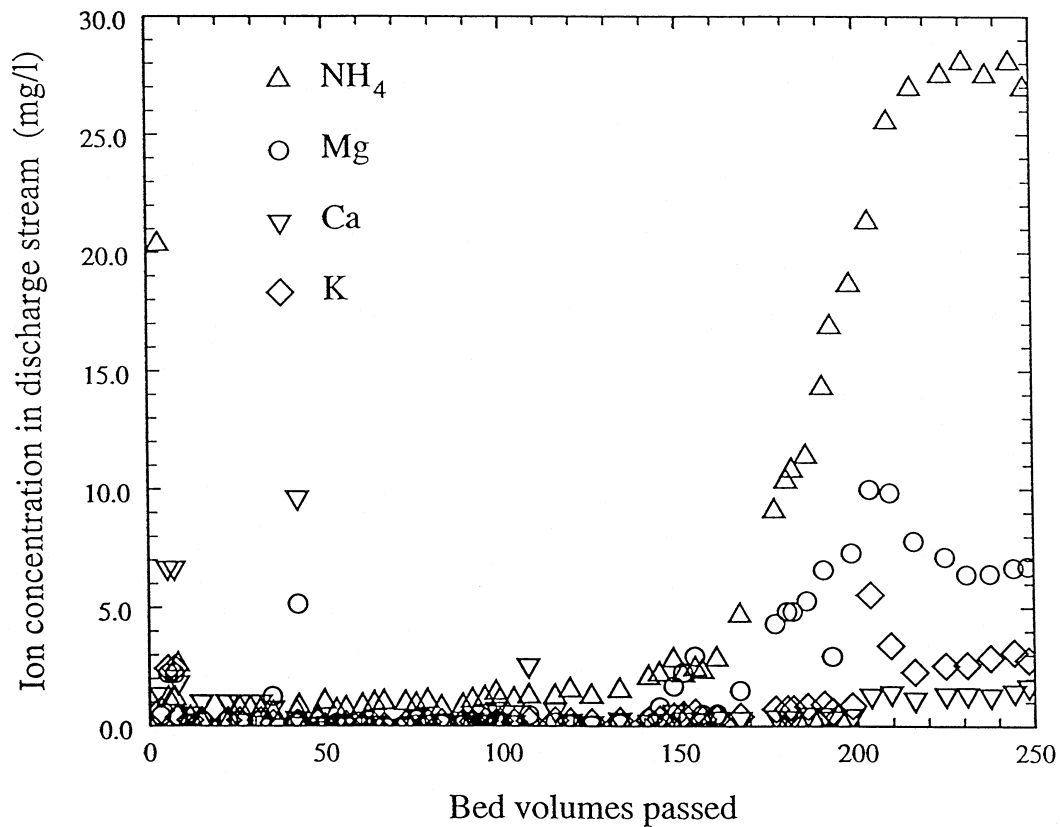


FIG. 5 Typical breakthrough curves for ammonium and competing cations for zeolite column fed with SIROFLOC secondary treated sewage of the composition specified in Table 2. Flow rate is 8 BV/h.

TABLE 2
 Typical Composition of SIROFLOC
 Secondary Treated Sewage from
 CSIRO Lower Plenty, Victoria,
 Australia

Component	Concentration
Ammonium	30 mg N/L
Calcium	12 mg Ca ²⁺ /L
Magnesium	10 mg Mg ²⁺ /L
Potassium	15 mg K ⁺ /L

Regeneration of the Zeolite Bed

Regeneration of the zeolite in the pilot process, between ammonia removal cycles, was effectively achieved by contacting the zeolite with a 0.6 M NaCl solution adjusted to pH 10 with NaOH. The regeneration protocol adopted was shown to displace the ammonia and other cations adsorbed on the zeolite

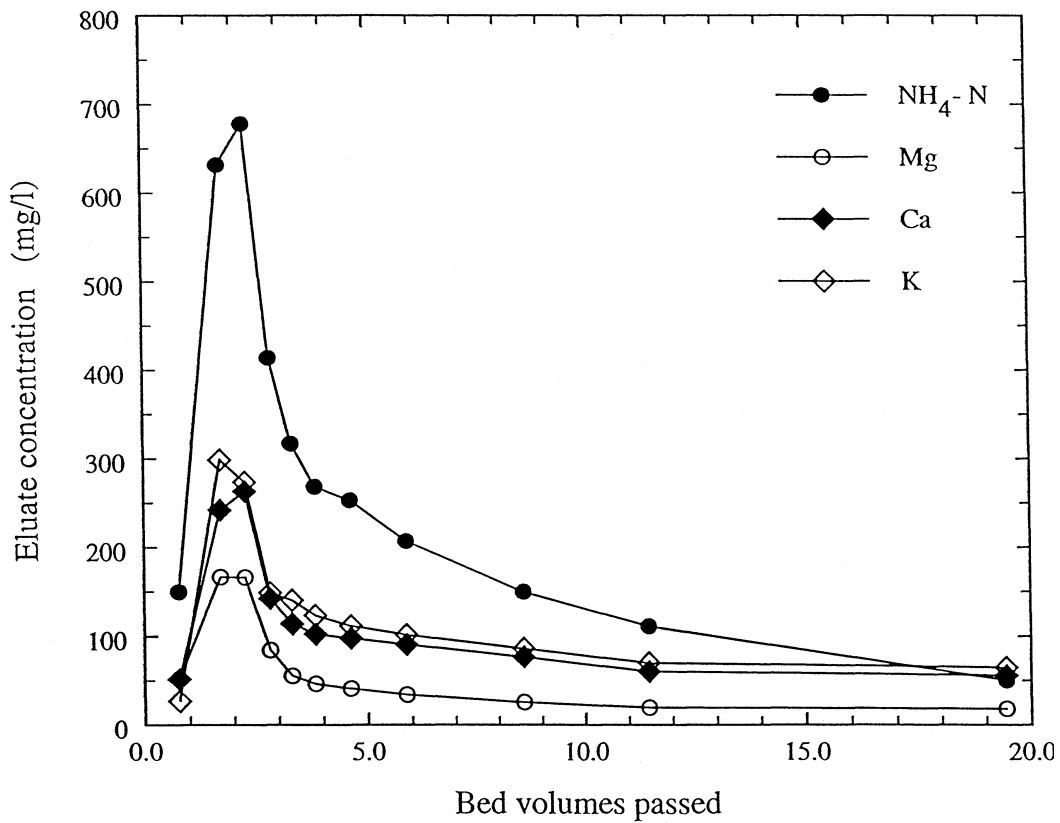


FIG. 6 Typical elution profiles for NH₄⁺ and competing cations. Regenerant is 0.6 M NaCl at pH 10.

during the sewage treatment cycle (see Fig. 6). The desorption of appreciable amounts of all four cations suggests that the regeneration technique is successful.

Zeolite Life Determination

Twelve repetitive sewage treatment cycles, under identical conditions, indicated the reproducibility of performance, and no deterioration of the zeolite's ammonium exchange capacity was observed. Figures 7 and 8 show that the total mass adsorption and subsequent desorption of ammonium were closely matched for a series of exhaustion and desorption cycles. The differences in the curves shown in Fig. 7 for successive runs may be attributed to

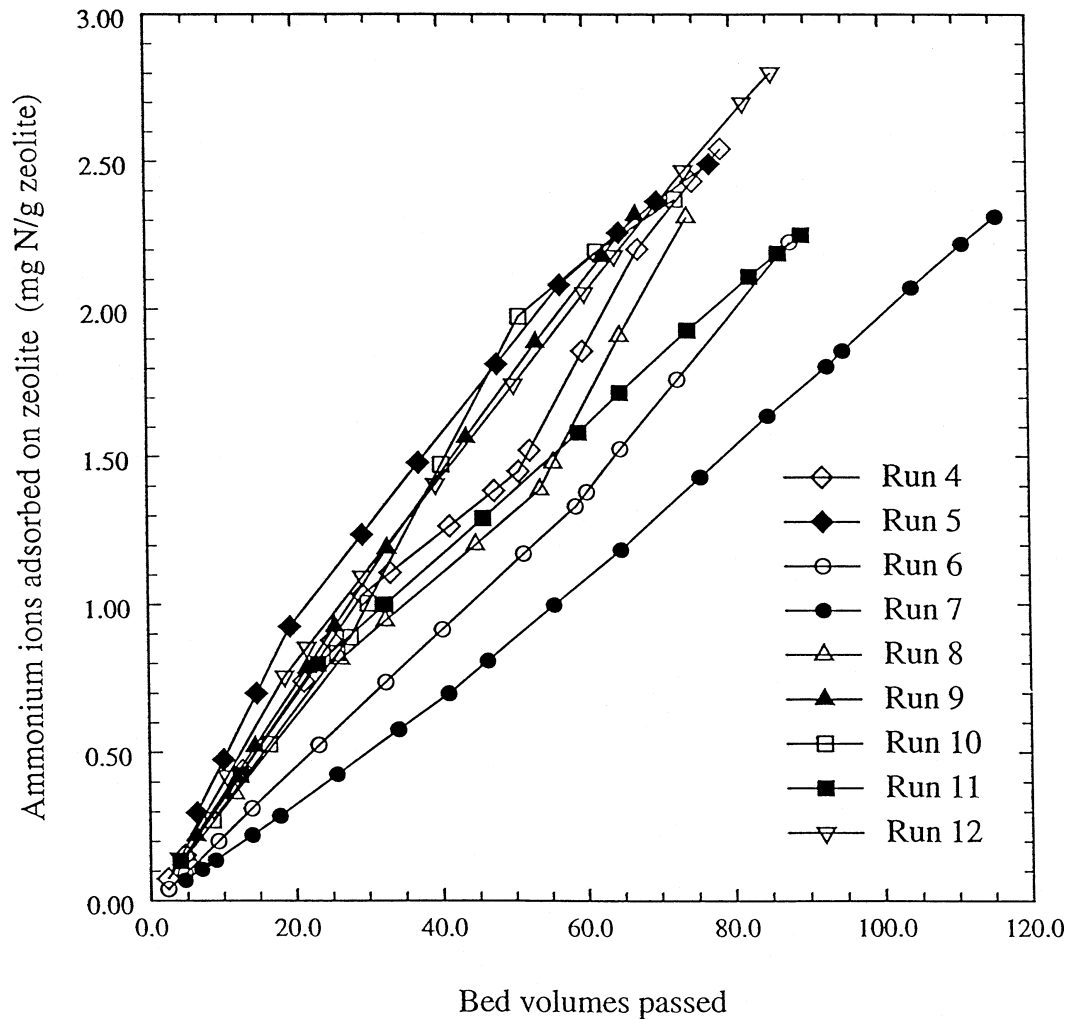


FIG. 7 Zeolite pilot column adsorption of ammonium from SIROFLOC treated sewage. Flow rate is 9.3 BV/h and filtration rate is 6.9 m/h. Average ammonium feed concentration varies between each run (see Table 3).

the variability of the treated sewage ammonium concentrations, primarily due to diurnal changes coupled with infiltration of storm water during wet weather. This is particularly apparent for Run 7, during which the feed ammonium concentration averaged $25.5 \text{ mg NH}_4^+ \text{-N/L}$. See also Table 3.

The regeneration profiles for successive cycles as shown in Fig. 8 are seen to be consistent. It may therefore be concluded that the quality of the zeolite as an adsorption media for ammonia removal from sewage does not show signs of deterioration over the limited period of this study. It is anticipated that, over repeated use, the zeolite will eventually erode to some extent and the bed will require topping up. This would indicate physical deterioration or loss by attrition rather than any accumulation of cations within the zeolite particles.

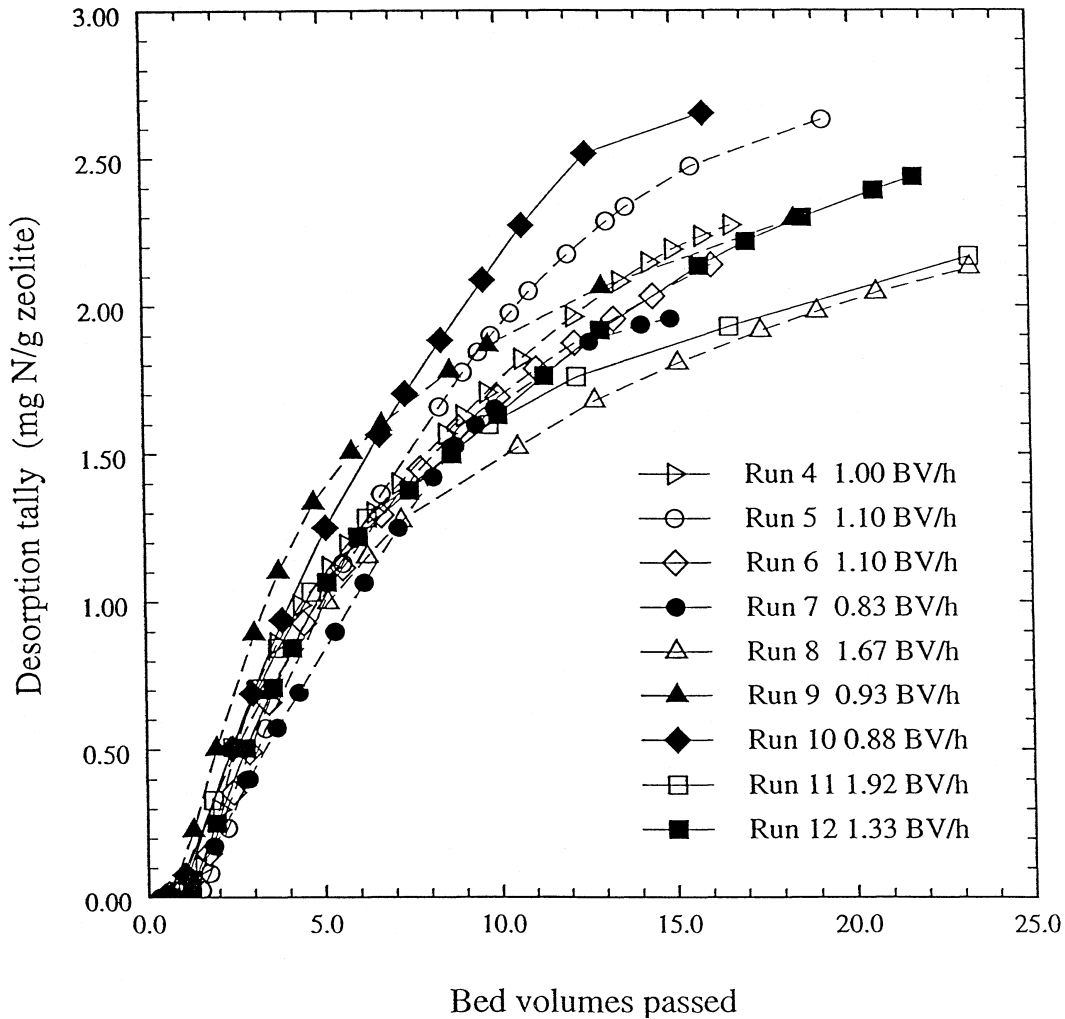


FIG. 8 Regenerant of exhausted zeolite bed after loading SIROFLOC sewage. Comparison of nine different flow rates. Regenerant is 0.6 M NaCl at pH 10.

TABLE 3
Average Free Ammonium Concentrations for Each of
the Zeolite Life Determination Runs

Run	Average feed ammonium concentration (mg NH ₄ ⁺ -N/L)
4	41.4
5	44.9
6	32.4
7	25.5
8	40.2
9	43.3
10	43.2
11	31.4
12	40.4

The cations posing a possible threat of binding to the exchange sites within the zeolite were shown to be completely eluted during the regeneration cycle using caustic brine.

A One-Dimensional Model for Predicting Continuous Ammonia Removal Performance

A number of models for ion-exchange performance of a column have been proposed in the past. Slater (16) presented a comprehensive summary of the many models developed to predict fixed-bed performance. Most of these models are limited in practice to considering the exchange between just three ions.

Dynamic modeling of the adsorption of ammonium from sewage using a fixed zeolite bed required information about the equilibrium between the zeolite and the solution and the rate of approach to equilibrium which entailed a knowledge of the rate-controlling mechanisms.

The performance was predicted from a simple one-dimensional diffusion model with axial dispersion. The model is based upon the simple material balance (10)

$$E_0 \frac{\delta^2 C}{\delta z^2} - \frac{u_L}{e} \frac{\delta C}{\delta z} - a_p N_0 = \frac{\delta C}{\delta t} \quad (5)$$

where E_0 is the axial dispersion coefficient (liquid phase), u_L is the flow rate of liquid/bed area, C is the solution ammonium concentration, z is the distance along the bed, N_0 is the mass flux of ammonium from the solution to the zeolite, t is the time, a_p is the zeolite particle surface area per unit bed volume [= $3(1 - e)/R$], e is the bed voidage, and R is the radius of the zeolite particle. The model is discussed more fully elsewhere (17).

Particle Diffusion Control

When particle diffusion is assumed to be the rate-controlling mechanism, the flux, N_0 , is described by the particle diffusion coefficient, D_p :

$$N_0 = \frac{(dq/dt)}{a_p} = D_p \left. \frac{\delta q}{\delta r} \right|_{r=r_p} \quad (6)$$

where a_p is the external surface area of the zeolite, q is the solid phase ammonium concentration, and r_p is the radius of the zeolite particle.

The ammonium ion concentration at the outer surface of the zeolite particle, q_s , is assumed to be constant and uniform about the surface. If the zeolite particle is assumed to be spherical with radius r_p , and if the ammonium ion concentration is assumed to constant at q_0 (i.e., $q = q_0$ for $r < r_p$ at $t = 0$), then Eq. (5) may be solved for the concentration of the ammonium ions within the bed as a function of the radius and time (16):

$$\frac{q - q_0}{q_s - q_0} = 1 + \frac{2r_p}{\pi r \sum_{n=1}^{\infty} \left[\frac{(-1)^n}{n} \sin\left(\frac{n\pi r}{r_p}\right) \exp\left(\frac{-D_p n^2 \pi^2 t}{r_p^2}\right) \right]} \quad (7)$$

where n is a counter.

The prediction of the ammonium adsorption performance of the pilot zeolite process for treatment of secondary sewage was carried out without correction for the complex interactions of competing cations on the equilibrium constant for the Na-zeolite and the ammonium in the sewage feed.

The ammonium equilibrium between the zeolite and surrounding solution was described by the Freundlich relationship, which was established previously (10), and is given by

$$q = 0.3156C^{0.388} \quad (8)$$

where q is the ammonium ion concentration in the zeolite.

The batch kinetic tests showed that the rate of ammonium transfer from solution to the zeolite may be described by the Vermeulen model for particle diffusion control, where the particle diffusion coefficient was 3.4×10^{-12} m²/s (Table 1). The void fraction of the packed column was determined to be 0.45 ± 0.05 . For the zeolite pilot process the degree of axial mixing of water in the zeolite bed was determined by performing a residence time distribution (RTD) study using a nonadsorbable tracer (10). The axial dispersion coefficient (E_0) used was 1.4×10^{-6} m/s for the coordinates used in the experiments. The partial differentials in Eq. (5) were solved with respect to distance along the zeolite bed and retention time using a finite difference technique.

Pilot Column Performance Prediction

The prediction of the ammonium adsorption of the pilot zeolite process, for SIROFLOC STP effluent treatment, was carried out using both the rigorous model described earlier and the Glueckauf model (18). The Glueckauf model incorporates an internal particle mass transfer coefficient and considers the number of absorbent phase transfer units. Calculation of these variables relies on knowledge of the operating bed capacity and the initial solution ammonium concentration. It has been noted from multicomponent batch equilibrium studies that the exchange capacity of the zeolite is significantly reduced for solutions containing competing cations. Consequently,

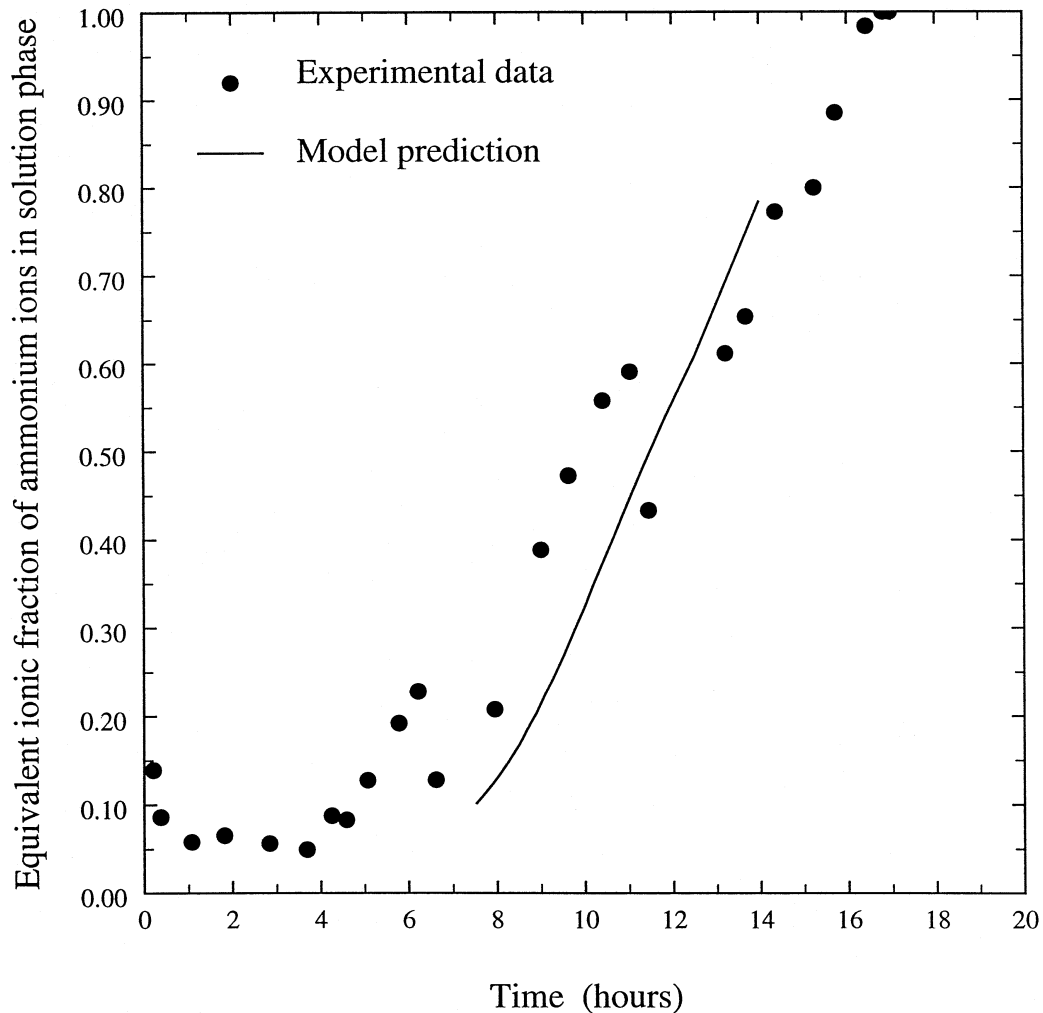


FIG. 9 Comparison between model prediction and experimental data for breakthrough curve for treated sewage feed flow of 11 BV/h.

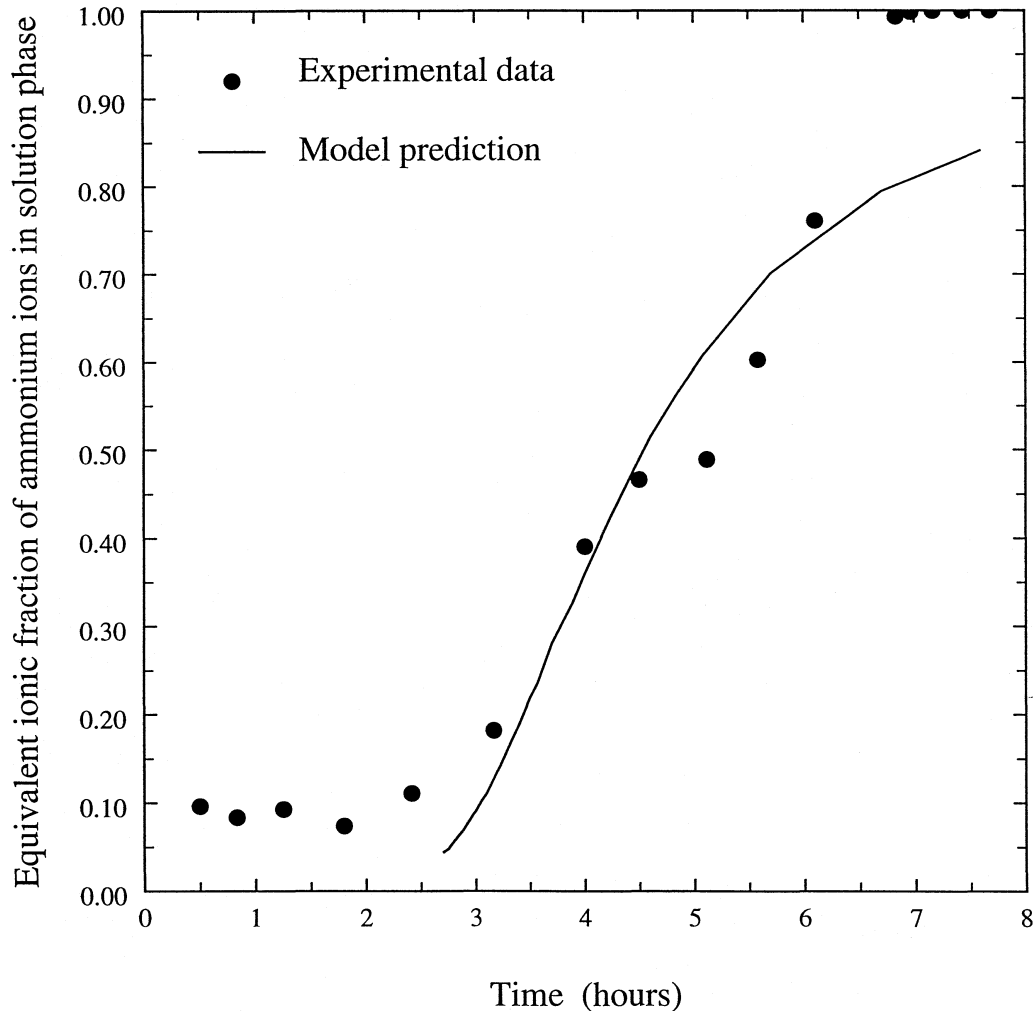


FIG. 10 Comparison between model prediction and experimental data for breakthrough curve for treated sewage feed flow of 13.2 BV/h.

the value adopted for the capacity will affect the accuracy of the breakthrough profile predictions for SIROFLOC STP effluent. Also, the fluctuations in the initial ammonium concentrations of the SIROFLOC STP effluent will adversely affect the shape of the predicted breakthrough curves. Binary selectivity coefficients were used for the Glueckauf model in order to simplify the calculations.

In nearly all cases the predictions of our model agreed more closely with the experimental data than did the predictions of the Glueckauf model. The Glueckauf model is limited by considering the zeolite bed as a whole unit, so that the mass balance is performed with respect to the inlet and outlet concentrations of the zeolite bed. Our model involves the simultaneous solution of a number of mass balances over a number of elements along the length of the bed.

Figures 9 and 10 compare the predictions of our model with the experimental data. The presence of the ammonium ions initially in the column effluent ($t < 4.0$ hours in Fig. 9 and $t < 2.5$ hours in Fig. 10) is largely due to the leakage of the feedstream down the walls of the column. As our model is essentially one-dimensional, this leakage cannot be predicted. It is for this reason that in Figs. 9 and 10 we do not present the model predictions during the early stages of the two runs.

The model was applied to the prediction of the elution of NH_4^+ from the zeolite using caustic brine (NaCl at pH 10) solution. The prediction of elution profiles for three separate runs (Figs. 11 to 13) was reasonably accurate using the model except in the early stages of the operation. Since no account was made of the discharge of interstitial solution remaining in the column after the

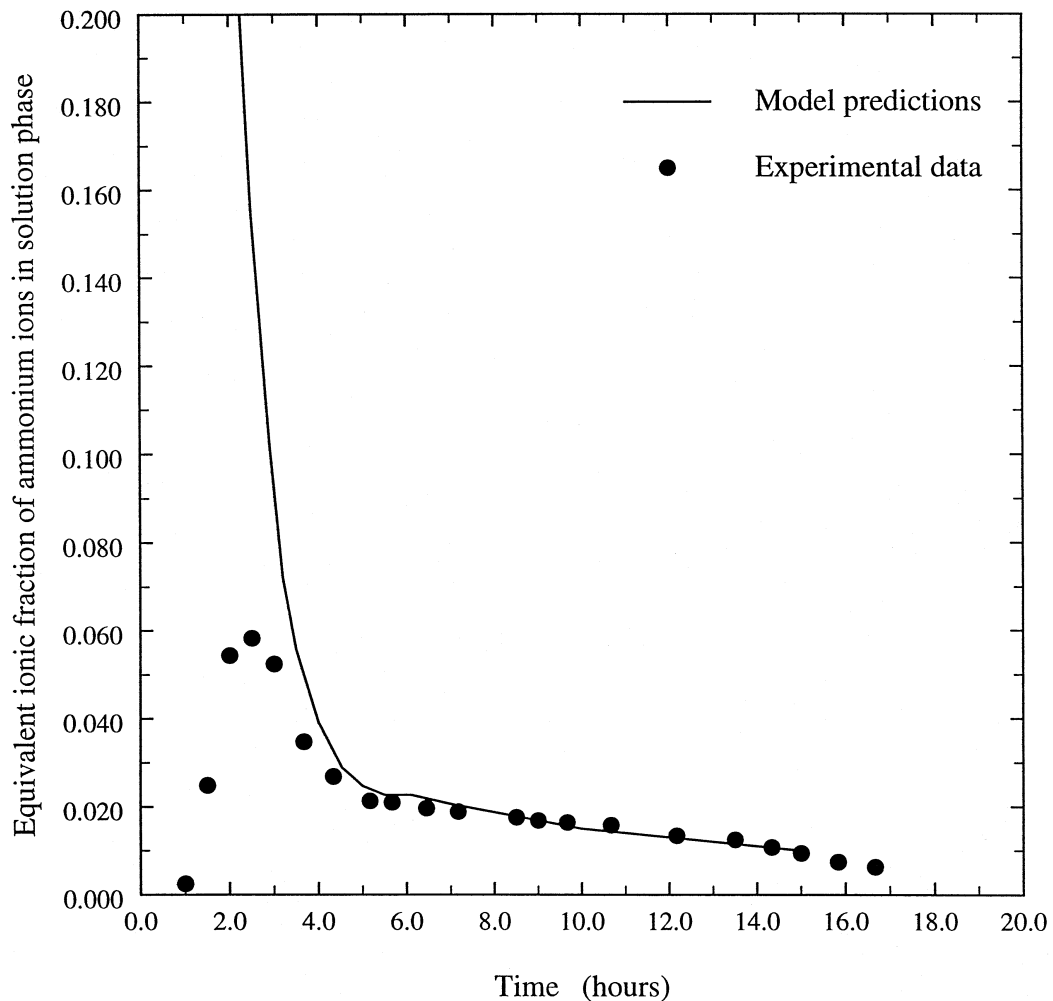


FIG. 11 Comparison between model prediction and experimental data for elution of ammonium at a flow rate of 1 BV/h.

previous loading cycle, the first bed volume discharged from the column was not adequately represented by the model. However, the model provided a good approximation of the subsequent displacement of ammonium from the zeolite bed. Consequently, this model may be used to approximate the total time required for the complete or partial elution of the zeolite bed, given the initial conditions of solution and solid concentrations.

Investigations revealed that the column's ammonium removal performance was dependent upon both initial ammonium concentration and feed flow rate. Ammonium concentrations were reduced from 30 mg $\text{NH}_4^+\text{-N/L}$ to less than 2 mg/L when flow rates up to 10 BV/h were applied. The breakthrough volume, indicated when the discharge concentration reached 5 mg $\text{NH}_4^+\text{-N/L}$, exceeded 120 BV when a flow rate of 9.3 BV/h was used (or 150 BV when flow rate = 8 BV/h). A flow rate around 9 BV/h (around 7 m/h) was consid-

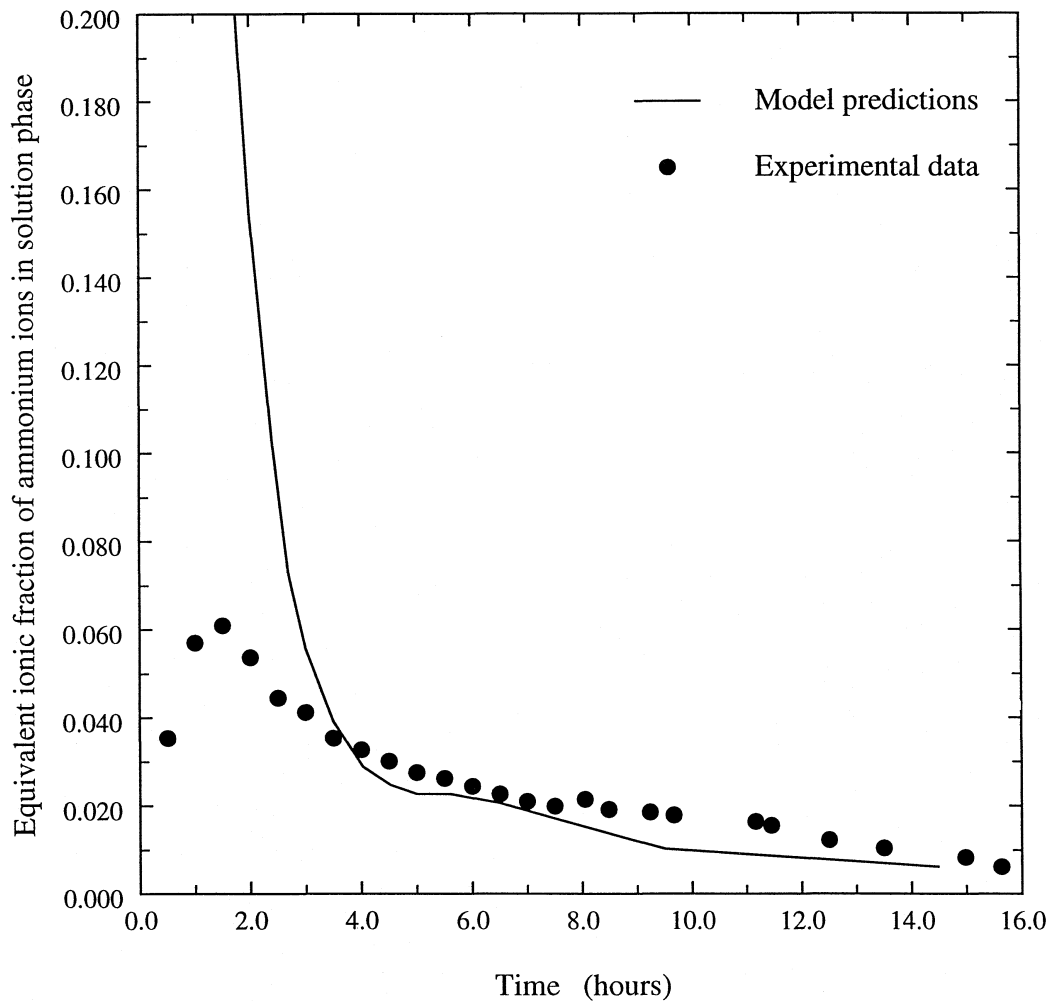


FIG. 12 Comparison between model prediction and experimental data for elution of ammonium at a flow rate of 1.22 BV/h.

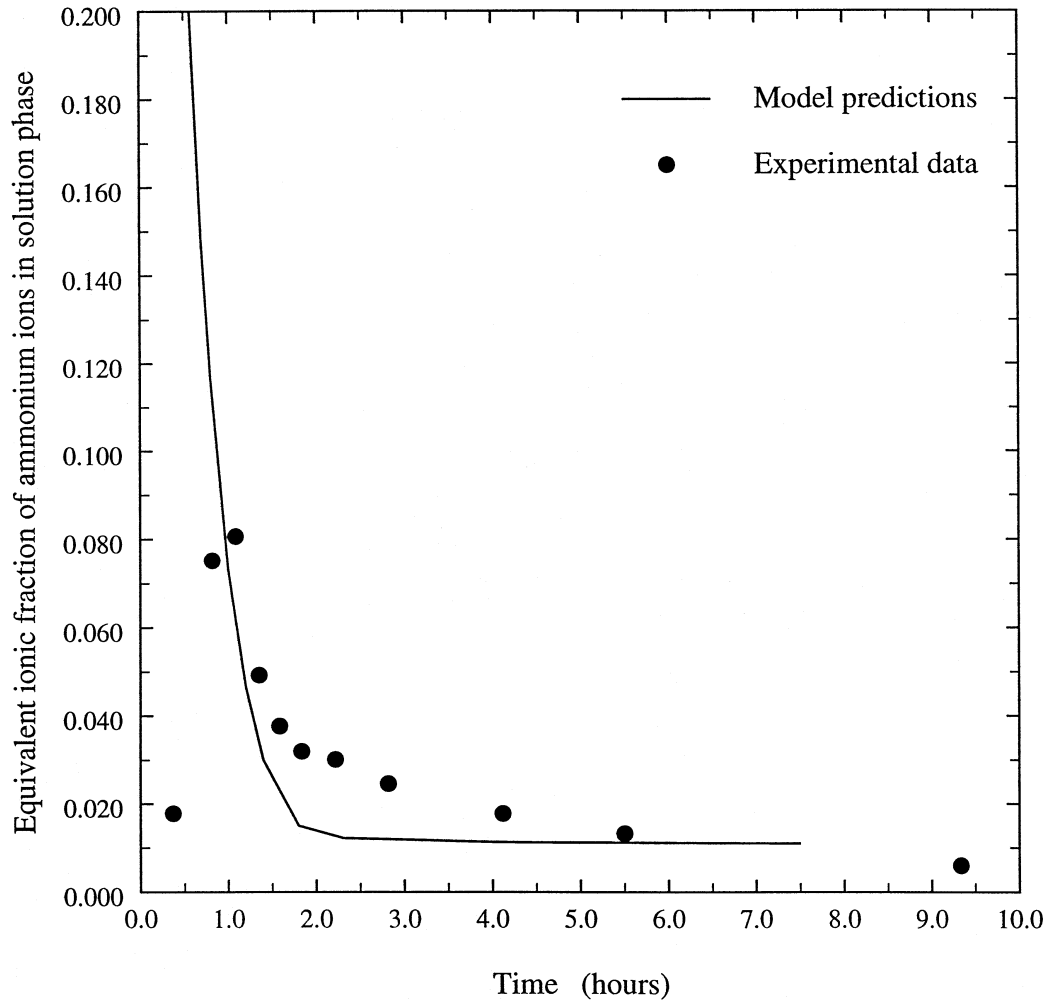


FIG. 13 Comparison between model prediction and experimental data for elution of ammonium at a flow rate of 2 BV/h.

ered to give the optimum performance of the column while being commensurate with flow rates for conventional (gravity) sand filtration.

CONCLUSIONS

The design and operation of the zeolite pilot-scale process enabled the evaluation of continuous, high-rate, ammonium removal from secondary treated sewage effluent. The physical characterization of the column, and subsequent loading and regeneration cycles, revealed a number of important conclusions:

- By applying a rigorous model for solving the overall rate equation (Eq. 1), the ammonium breakthrough and elution profiles for the pilot zeolite column were able to be closely predicted

- Continuous chemical regeneration of the Australian natural zeolite, using 0.6 M NaCl at pH 10, effectively restored the exchange sites back to the sodium form. Regeneration flow rates, ranging between 1 and 2 BV/h, were tested; peak eluate NH_4^+ concentrations were around 500 mg/L
- Subjecting the zeolite bed to repeated loading and regeneration cycles did not reveal any deterioration of ammonium removal performance. Effective desorption of competing cations, during the elution cycle, restored the ammonium exchange capacity of the zeolite. This ensured that consistent column performance was maintained over many cycles

REFERENCES

1. L. L. Ames, *Am. Mineral.*, 45 (1960).
2. L. L. Ames, *Can. Mineral.*, 8, 325 (1965).
3. R. M. Barrer and M. B. Makki, *Can. J. Chem.*, 42, 1481 (1964).
4. R. M. Barrer, *The Properties and Applications of Zeolites* (R. P. Townsend, Ed.), The City University, London, 1979.
5. B. W. Mercer, L. L. Ames, C. J. Touhill, W. J. Van Slyke, and R. B. Dean, *J. Water Pollut. Control Fed.*, 42 (1970).
6. L. Liberti, N. Limoni, A. Lopez, R. Passino, and G. Boari, *Water Res.*, 20, 735 (1986).
7. S. Komarowski, Q. Yu, P. Jones, and A. MacDougall, *Proceedings of the 2nd Australian Biological Nutrient Removal (BNR2) Conference*, Albury, NSW, Australia, 1994.
8. T. Schulz and M. Sriharan, *Testing of Zeolite Samples for Nutrient Removal*, Report 88/5/3, Centre for Wastewater Treatment, NSW, Australia, 1988.
9. E. L. Cooney, N. A. Booker, D. C. Shallcross, and G. W. Stevens, submitted to *Sol. Extr. Ion Exch.* (1998).
10. E. L. Cooney, "Ammonia Removal from SIROFLOC[®] Treated Sewage Using Natural Zeolite from Australia," Ph.D. Thesis, University of Melbourne, Australia, 1996.
11. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, NY, 1962.
12. P. G. Flood, The Application of Zeolites for Environmental Solutions Conference, University of NSW, 1993.
13. R. H. Perry and D. Green, *Perry's Chemical Engineer's Handbook*, 6th ed., McGraw-Hill, New York, NY, 1984.
14. O. Levenspiel, *Chemical Reaction Engineering*, Wiley, New York, NY, 1972.
15. N. A. Booker, E. L. Cooney, G. Ocal, and A. Priestley, "The SIROFLOC[®] Sewage Treatment Process," in *Proceedings of the 16th Federal Convention, Australian Water and Wastewater Association*, Sydney, Australia, 1995.
16. M. J. Slater, *The Principles of Ion Exchange Technology*, Butterworth and Heinemann, Oxford, 1991, pp. 54–90.
17. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, Oxford, 1975.
18. E. Glueckauf, *Ion Exchange and Its Application*, Society of Chemical Industry, London, 1955.

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