

AMMONIUM ION REMOVAL FROM WASTEWATER USING AUSTRALIAN NATURAL ZEOLITE: BATCH EQUILIBRIUM AND KINETIC STUDIES

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(Received 16 January 1997; Accepted 7 July 1997)

ABSTRACT

The removal of nutrients from wastewater is becoming increasingly important throughout the world. This paper reports work on batch equilibrium and kinetic laboratory studies conducted to establish the efficiency of ammonium ion removal from wastewater effluent using a natural zeolite from the Werris Creek region in New South Wales. Experiments were conducted using samples of secondary treated domestic wastewater effluent and synthetic wastewater (ammonium chloride solution). The amount of powdered zeolite added ranged from 5 to 50 g l⁻¹. Experiments were undertaken to characterise the zeolite in terms of its ion exchange capacity and rate of ammonium ion adsorption under various conditions. The effects of the amount of zeolite added, initial ammonium ion concentration and pH of the sample on ammonium ion removal were studied. Results were analysed using existing ion exchange models. The results indicate that a significant reduction of N as NH₄⁺ (up to 80%) can be achieved using batchwise addition of powdered natural zeolite to NH₄Cl solution. The ammonium ion removal capacity from wastewater effluent using 5 g l⁻¹ zeolite is about 2 mg g⁻¹ (compared to 3.7 mg g⁻¹ from NH₄Cl solution) for an initial ammonium ion concentration of 25 mg l⁻¹. The ammonium ion removal efficiency increases with higher initial ammonium ion concentration and is highest for pH 5.5. Two adsorption models were fitted to the equilibrium data. The Freundlich adsorption model gives a better fit than the Langmuir model in the range of pH studied (pH 4-7) suggesting lateral interactions between adsorbed ions. From kinetic experiments 90% of ammonium ion removal occurs within 10-15 minutes and equilibrium is reached within 1.5 - 2 hours.

Keywords: Nutrient removal, ammonium ion removal, natural zeolite, clinoptilolite, ion exchange.

INTRODUCTION

Environmental problems such as algal blooms have highlighted the effect of excessive amounts of nutrients on natural waterways. The nutrients of concern are primarily nitrogen (ammonium ion and nitrate) and phosphorus (orthophosphate). These nutrients can reach waterways from a variety of sources, including non-point sources such as agricultural runoff, and point sources such as wastewater treatment plant discharges. This project addresses problems presented by the latter source.

Rapid population increase and greater public awareness of environmental issues over the last ten years has meant that the wastewater industry has been faced with the difficult task of keeping up with population growth while meeting increasingly stringent nutrient discharge standards. The trend in regulatory attitudes of Australian States suggests that maximum allowable concentrations for point source effluent discharges to receiving waters may be 10 to 15 mg l⁻¹ for total nitrogen and 0.5 to 2 mg l⁻¹ for total phosphorus [1]. Conventional activated sludge systems and biological filter plants achieve little nutrient removal. Therefore, the vast majority of treatment plants will generally not meet these

future environmental regulations without process adaptation or new plants. Hence there is a need for advanced treatment processes to reduce nutrient levels in wastewater treatment plant discharges from currently operating and new treatment plants.

In this paper, the use of powdered natural zeolite for removing ammonium ion from secondary treated wastewater effluent and from ammonium salt solution is investigated under various conditions. Batch equilibrium experiments to determine isotherms have been conducted to establish the ammonium ion removal capacity and the percent ammonium ion removal by the zeolite. The adsorption of ammonium ion onto zeolite is a time-dependent process. To understand the dynamics of the adsorption of ammonium ion on zeolite, kinetic data are important. Kinetic data were applied to diffusion models and the mechanism of intraparticle diffusion.

Zeolite characteristics

Zeolites are naturally occurring aluminosilicate minerals. There are more than 50 different natural zeolite types, including clinoptilolite which has a high selectivity for

ammonium ions [2]. The zeolite used in this study is from Werris Creek, NSW, Australia, which has proven reserves of 300000 tonnes, with a further indicated resource of another 300000 tonnes [3]. The clinoptilolite content of the zeolite source is approximately 50% [3]. Other impurities include quartz and volcanic glass.

Zeolites possess open frameworks characterised by networks of channels or pores, yielding a very high specific surface area. The structure of zeolite has a negative charge and a high cation exchange capacity. This high cation exchange capacity enables zeolite to adsorb and freely exchange positively charged ions such as ammonium ion.

The potential use of natural clinoptilolite (from Hungary, USA, Italy and Japan) as an ion exchanger for ammonium ion removal from wastewater has been reviewed, and has been to be proven effective [2, 4-7]. Researchers using Hungarian zeolite found the properties of natural zeolites to be similar to those of the much more expensive synthetic zeolites and conventional ion exchangers and that they are reasonably priced for wastewater treatment purposes. Ammonium ion exchange using zeolite was found to be slightly more expensive than nitrification and denitrification, with the disadvantage that a spent regenerant solution, which must be discharged, is produced if the zeolite is to be regenerated and reused [4]. Studies with US zeolite indicated that ammonium ion removal is cost competitive with other total nitrogen removal processes for wastewater treatment [5]. Ammonium ion removal from wastewaters by clinoptilolite, based on the Rim-Nut process (developed in Italy) has been implemented in large scale installations in locations in the US [6] and in Italy [7].

Zeolite can be incorporated into wastewater treatment processes either by using it as a filter media/ion exchanger in a packed bed, or by adding it during a contact stage. It has been reported that the process can be made economic if recovery of ammonium salts, for example as fertiliser, is achievable and if the ion exchanger can be regenerated and reused, if practical [8]. Experiments on the reutilisation of the zeolite and the ammonium ion removed from wastewaters by ion exchange are being conducted [8]. Laboratory scale work

has been conducted in Australia on aspects of the ion exchange processes and regeneration of the NSW zeolite [9-11]. The results of ion exchange capacity characterisation from these authors are discussed under Results and Discussion.

Wastewater characteristics

Wastewater effluent samples from the Fairfield Wastewater Treatment Plant (WWTP), of Brisbane City Council, were used for this study. The problem of treatment plants being overloaded and not achieving nutrient removal is a common dilemma in Brisbane, especially in the older, smaller plants such as Fairfield WWTP. This plant uses a conventional activated sludge process and is designed for organic carbon and solids removal followed by disinfection. The plant treats predominantly domestic wastewater and was designed for a population of 9600. Water quality data for Fairfield wastewater effluent are listed in Table 1 (obtained from Brisbane City Council Laboratories). The average ammonium ion concentration in the wastewater effluent is 29 mg l⁻¹.

EXPERIMENTAL PROCEDURE

Materials

Samples of zeolite used for this study were mined from the Werris Creek region of NSW, Australia and were provided by Zeolite Australia Ltd. The zeolite was used in its natural state as a powder (average particle size 70 microns).

Experiments were conducted using secondary treated wastewater effluent from Fairfield Wastewater Treatment Plant, Brisbane, Australia. One litre samples were collected prior to chlorination at the plant. Solutions of ammonium chloride NH₄Cl (Ajax Chemicals) were made up as synthetic wastewater samples of known ammonium ion concentration. All chemicals used were of analytical grade, in non-buffered deionised water solutions.

Table 1. Water quality data for Fairfield wastewater effluent.

Parameter	Value (average)	Sample period
pH	7.5	4/3/93 to 24/2/94
Temperature	24°C	4/3/93 to 24/2/94
Dissolved Oxygen	4 mg l ⁻¹	4/3/93 to 24/2/94
BOD	11 mg l ⁻¹	4/3/93 to 24/2/94
Non-filtrable residue	9 mg l ⁻¹	4/3/93 to 24/2/94
Total Organic Carbon	20 mg l ⁻¹	4/3/93 to 24/2/94
Ammonium-N	29 mg l ⁻¹	4/3/93 to 24/2/94
Nitrate-N	1.3 mg l ⁻¹	4/3/93 to 24/2/94
Nitrite-N	0.6 mg l ⁻¹	4/3/93 to 24/2/94
Orthophosphate (P)*	7 mg l ⁻¹	21/12/93 to 1/2/94
Total phosphorus (P)*	8 mg l ⁻¹	21/12/93 to 1/2/94

* From analyses conducted by author

Batch experiments

Experiments to investigate the adsorption isotherms were carried out using a cylindrical vial into which 100 ml of ammonium solution (ammonium chloride or wastewater effluent) of known initial concentration (between 5 and 50 mg $\text{NH}_4^+ \text{l}^{-1}$) was placed together with a fixed mass of adsorbent (5 to 50 g l^{-1} zeolite). The mixture was placed on a rotary shaker for 24 hours to ensure equilibrium was reached. The experiments were carried out at ambient temperature ($T = 21 \pm 1^\circ\text{C}$). The changes in pH when zeolite is added to NH_4Cl solution and during the batch experiments were recorded.

The ammonium ion concentration of the samples was analysed before and after equilibrium. Isotherms were drawn by plotting the amount of NH_4^+ adsorbed onto the zeolite, Q (mg $\text{NH}_4^+ \cdot \text{l}^{-1}$) against the equilibrium concentration of NH_4^+ in solution, C_e .

The experiments were repeated for samples of different ammonium ion concentrations, different amounts of zeolite added and different pH values. The pH of the samples was adjusted with dilute sodium hydroxide or dilute sulphuric acid. The effect of pH on uptake capacity and adsorption isotherms was studied for NH_4Cl solution and two models (Langmuir and Freundlich models) were used to describe the adsorption data. The next stage of experimentation involved investigating ammonium ion removal using zeolite from wastewater effluent samples.

Kinetic experiments

Kinetic experiments were carried out by placing a known amount of zeolite (5 to 50 g l^{-1}) into 500 ml of solution, agitation being provided by propeller stirrers (60 rpm). The initial and equilibrium pH values were recorded. For specific experiments the pH was initially adjusted to a fixed value with solutions of NaOH or H_2SO_4 . The ammonium ion concentration of the solutions was measured periodically to determine the time required to reach equilibrium, the rate of adsorption and the ammonium ion removal capacity of the zeolite. Kinetic experiments using NH_4Cl were conducted for different amounts of zeolite added, initial ammonium ion concentrations and solution pH. An intraparticle diffusion model was used to plot the data and determine the rate limiting step in the adsorption process and to determine the initial rate constants for different conditions. Kinetic experiments were conducted using wastewater effluent samples and these results were compared with the results using NH_4Cl solutions.

Method of ammonium ion analysis

Measurements of the ammonium ion concentration in solution were conducted using an Ammonium Selective Electrode (Orion). The results of analyses using this method were found to be accurate with results from analyses using

procedures in Standard Methods for Examination of Water and Wastewater [12].

For the wastewater effluent samples, analyses of filtered and non-filtered samples were compared. Since the amount of non-filterable material was found to be negligible, the analyses were conducted on non-filtered samples. Duplicate analyses were conducted every 5-10 samples in accordance with procedures in APHA [12].

RESULTS AND DISCUSSION

Batch experiments: ammonium ion removal from NH_4Cl solution

The suspension of zeolite in wastewater and ammonium chloride solutions induces variations in the final pH of the solution. This effect for batch experiments is shown in Figure 1. It was observed during the equilibrium studies that in non-buffered ammonium chloride solutions, the pH of the solution increases with the addition of zeolite and during adsorption. An increase in pH after the addition of zeolite could result from adsorption of H^+ ions from solution when the zeolite is added. Figure 1 shows the initial and equilibrium pH values for a range of initial ammonium ion concentrations (C_0) varying from 5 - 50 mg l^{-1} . Generally, the pH of the zeolite and ammonium ion solution increases from pH 7.5 to between 8 and 8.7 during adsorption. The pH increase is slightly less significant with higher initial concentration.

The effect of pH on ammonium ion uptake capacity of zeolite was studied using two ammonium ion concentrations (10 and 25 mg l^{-1}). Figure 2 demonstrates this effect for NH_4Cl and shows that the ammonium ion removal is favoured at initial pH values in the range of 4 to 5.5 for both concentrations.

For both the ammonium ion concentrations, the sharpest increase in ammonium ion removal was observed between pH 2 and 3. The optimum pH for ammonium ion adsorption depends on the initial ammonium ion concentration. Greater removal capacity was achieved for the more concentrated solution. The capacity increases up to pH 5.5 for initial concentration of 25 mg l^{-1} (2.5 mg g^{-1}) and the capacity increases up to pH 4 for an initial ammonium ion concentration of 10 mg l^{-1} (1.5 mg g^{-1}). Increasing the pH past 5.5 reduces the removal capacity for both the ammonium ion concentrations. Comparisons with other authors of the pH effect on ammonium ion removal using natural zeolite are made later.

Isotherms are used to describe the adsorption of ammonium ion on zeolite and they are shown in Figure 3 for different initial pH conditions. The adsorption isotherms present the amount of ammonium ion adsorbed onto the zeolite per gram of zeolite, Q (mg $\text{NH}_4^+ \text{g}^{-1}$ zeolite) as a function of the equilibrium concentration of ammonium ion in bulk solution, C_e , at constant temperature for different initial pH values.

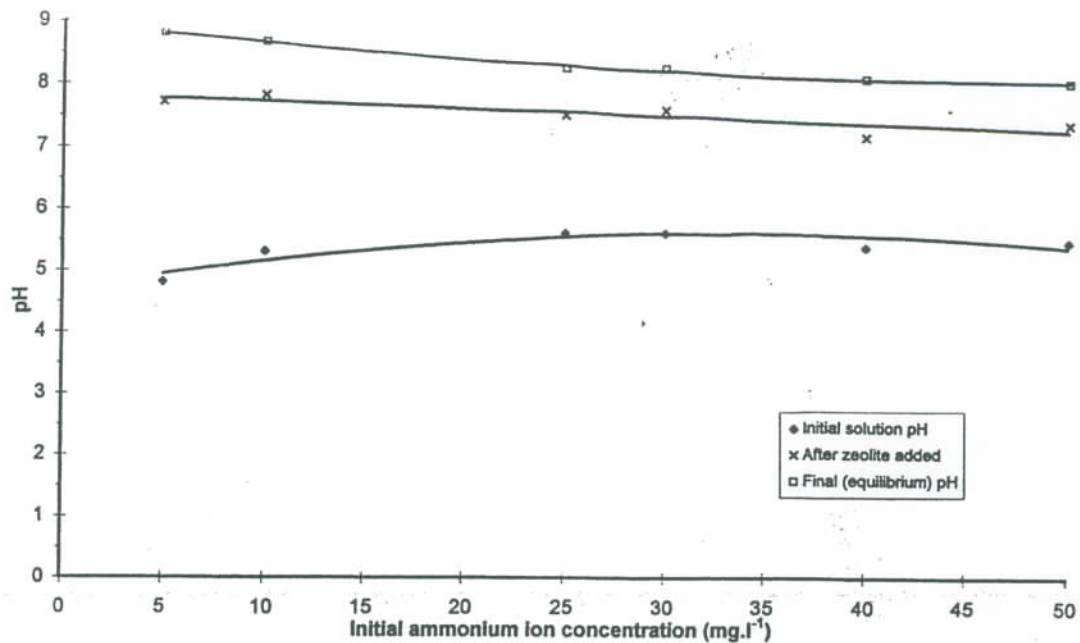


Figure 1. Changes in pH during batch experiments using NH_4Cl at different initial ammonium ion concentrations (5g l^{-1} zeolite added, equilibrium time 24 hours).

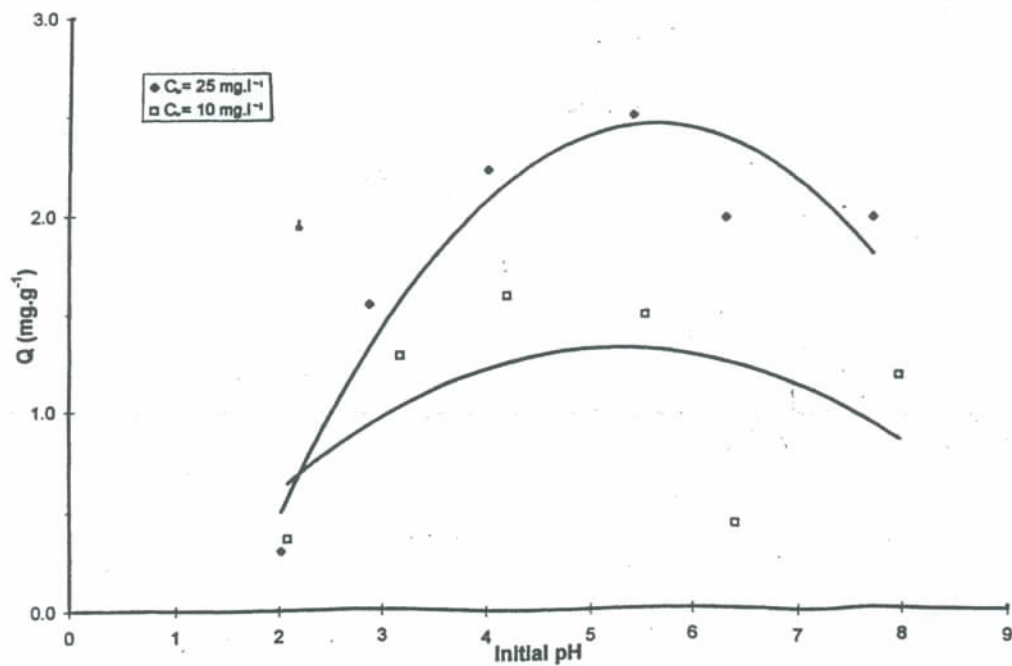


Figure 2. The effect of pH on ammonium ion uptake capacity for NH_4Cl for two initial ammonium ion concentrations (5g l^{-1} zeolite added).

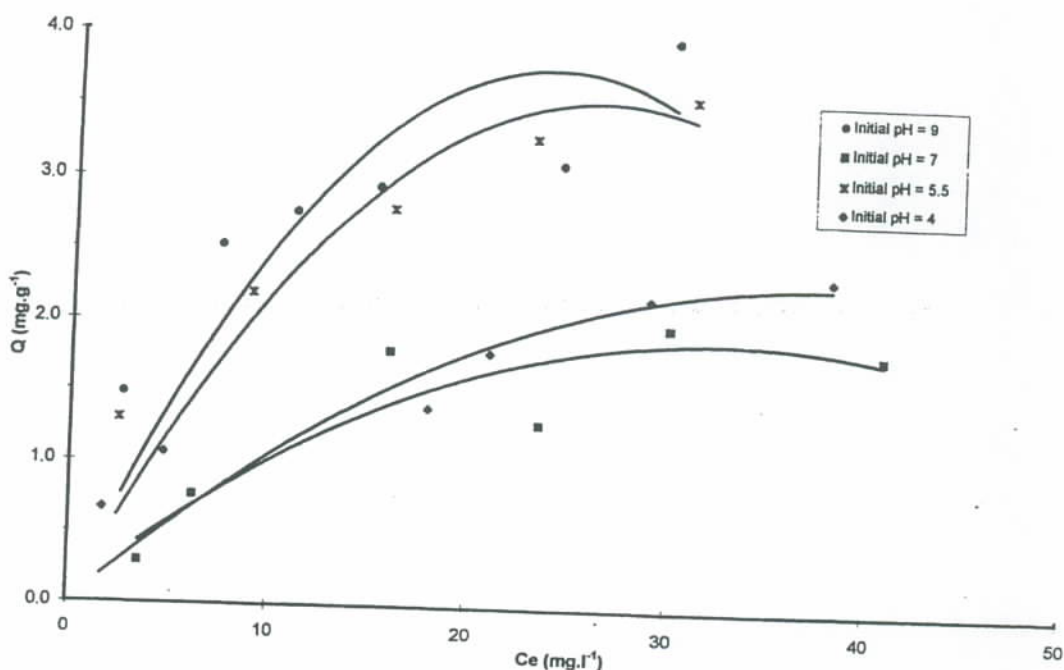


Figure 3. Adsorption isotherms for NH_4Cl at different initial pH (5g l^{-1} zeolite added).

For NH_4Cl solutions with no pH adjustment (pH 5.5), the ammonium ion removal capacity is in the range $3.2 - 3.7\text{ mg g}^{-1}$. A Hungarian natural zeolite was found to have a capacity of 11 mg g^{-1} for NH_4Cl [4]. Australian studies have noted an apparently lower ammonium ion exchange capacity of the zeolite from Werris Creek, NSW; Ritchie [10] reported a capacity of 1.2 mg g^{-1} for ammonium ion removal from wastewater effluent at pH 2.6, and Schulz [11] reported a capacity of 1.5 mg g^{-1} for removal from an ammonium chloride solution using a larger particle size zeolite than that used in this study. The lower ammonium ion exchange capacities reported may be attributed to some characteristic of the zeolite such as its low porosity compared with other zeolites.

Table 2 and Figure 3 show that the ammonium ion reduction is highest for pH 9. However, the ammonium ion removal would not be due to ion exchange on the zeolite alone. Since ammonium ion has a $\text{p}K_a$ of approximately 9.2, 50% of ammonium ion is converted to ammonia at pH 9.2. The results at pH 9 therefore are not representative of the amount that is removed using zeolite as an ion exchanger and are not discussed further.

The maximal ammonium ion uptake by ion exchange mechanism is highest for pH 5.5 ($3.2 - 3.7\text{ mg g}^{-1}$), at higher and lower pH (pH 7 and 4), the uptake is reduced. These results agree with the results presented in Figure 2. The reason for the pH effect is not clear, although in simplistic terms, as pH increases ammonium ion exists as free ammonia which is not available for zeolite ion exchange. Little work can be found that investigates the ammonium ion exchange

Table 2. Maximum ammonium ion adsorption capacity (Q) for NH_4Cl at different initial pH.

pH	Q ($\text{mg NH}_4^+ \text{g}^{-1}$ zeolite)
4	2.2 - 2.4
5.5	3.2 - 3.7
7	1.8 - 2.0
9	3.5 - 4.0

capacity of zeolite at various pH values. Marking and Bills [13] found ammonium ion removal was best for neutral or near neutral pH and diminished as pH reduced or increased. However, Ritchie [10] found the optimum exchange capacity to be at pH 2.6, but this is unlikely to be practical for wastewater applications.

Two models are used to describe the adsorption data: the Langmuir and Freundlich adsorption models. The Langmuir model hypothesises adsorption with homogenous distribution of adsorption sites and adsorption energy without interaction between the adsorbed molecules. The Freundlich model suggests the energetic distribution of the sites is heterogenous, due to the diversity of the adsorption sites or the diverse nature of the ions adsorbed [14].

The Langmuir model is described by the following equation:

$$Q = Q_m \cdot \frac{b \cdot C_e}{1 + b \cdot C_e}$$

where Q_m (mg g^{-1} zeolite) is the adsorption capacity, C_e is the ammonium ion concentration (mg l^{-1}) in solution at equilibrium and b is a constant (1 mg^{-1}).

The Freundlich model equation is of the form:

$$Q = K.C_e^{1/n}$$

where K and n are the Freundlich constants. Data at different pH values were used to obtain the isotherm parameters by substituting the equilibrium concentrations in the above equations. Table 3 summarises the Langmuir and Freundlich constants of ammonium ion adsorption at different initial pH values.

The maximum capacity, Q_m , determined from the Langmuir isotherm defines the total capacity of the zeolite for ammonium ion. Table 3 shows that zeolite is an effective adsorbent for ammonium ion within the pH range of 4 to 7. The Langmuir constants Q_m (maximum adsorption capacity) and b (a measure of adsorption affinity) do not vary greatly for pH 4, 5.5 and 7 and are highest for pH 5.5. The Freundlich parameters K and n show a similar trend. The regression coefficients for both models are the same at pH 5.5. Results obtained at pH 7 are difficult to correlate to the Langmuir model suggesting that this model of monolayer adsorption does not match the adsorption mechanism at pH 7 very well and more complex phenomena may be at work, possibly including adsorption by a surface precipitation model [15]. The application of the Freundlich model to experimental results at pH 4 ($R^2=0.96$) leads to the conclusion that for ammonium ion adsorption there exists lateral interactions between adsorbed molecules.

Figure 4 shows the Freundlich representation of the adsorption isotherms for pH 4, 5.5 and 7. A steep slope ($1/n$ close to 1) on the Freundlich plot, as for pH 7, indicates a high adsorptive capacity at high equilibrium concentrations that rapidly diminishes at lower concentrations covered by the isotherm [16]. A relatively flat slope indicates that the adsorptive capacity is only slightly reduced at lower equilibrium.

Batch experiments: ammonium ion removal from wastewater effluent

Wastewater effluent samples were collected on three different dates and two sets of batch experiments conducted on each - with an undiluted sample and 1:1 dilution. For wastewater effluent samples ammonium ion removal

capacity generally increases with increasing C_o , as was the case for the NH_4Cl solutions. The percent ammonium ion removal increases for a lower C_o , except for the 29/4/96 sample which has a lower removal than expected.

Figure 5 shows the adsorption isotherms for ammonium chloride solution and a wastewater effluent sample both with 5 g l^{-1} zeolite added. The different concentrations of the wastewater sample for the isotherm were made by diluting the sample to a range of concentrations. Due to the variability of wastewater quality the isotherm produced would be particular to that sample. The ammonium ion removal capacity is 3.7 mg g^{-1} (40% ammonium ion removal) for the wastewater sample. The ammonium ion removal capacity for the ammonium chloride solution is approximately 40% greater than that for wastewater, for the initial ammonium ion concentration range of 5 to 50 mg l^{-1} . The decreased ammonium ion removal for wastewater may be attributed to by the existence of competing cations in the wastewater effluent samples, which reduce the ammonium ion exchange capacity. Similar results were found comparing distilled water solutions (with ammonium ion) and wastewater [4]: a lower NH_4^+ removal capacity was found for wastewater than for distilled water, which was thought to be mainly due to Ca^{2+} ions present in the wastewater. Although clinoptilolite exhibits preference for ammonium ions, it also removes calcium. The wastewater sample used contains concentrations of calcium of the order of 30 mg l^{-1} . It has been shown that as the concentration of Ca^{2+} (and Na^+) increases, less capacity is available for NH_4^+ ions, and zeolite is less effective in ammonium ion removal [4, 17]. Other authors similarly have noted that the presence of calcium and magnesium ions substantially reduces the ammonium ion adsorption by zeolite [18, 19].

It would be expected that there would be some relationship between C_o and the amount of ammonium ion removed from solution since adsorption of any cation by a cation exchanger is a function of the concentration of the cation in the system. Table 4 shows the variation in ammonium ion removal with different initial ammonium ion concentrations for wastewater effluent. Adsorbed quantities at equilibrium usually increase with an increase in the solute concentration [16]. McLaren and Farquhar [21] studied certain factors suspected to affect the ammonium ion removal efficiency of zeolite and suggested that initial ammonium ion concentration had the greatest effect on removal. Murphy [22] found that a higher initial ammonium ion concentration increased the exchange capacity through system dynamics.

Table 3. Langmuir and Freundlich isotherm constants for NH_4^+ adsorption by zeolite at different pH values.

pH	Langmuir constants			Freundlich constants		
	b (mg l^{-1}) ⁻¹	Q_m (mg g^{-1})	R^2	K ($\text{mg g}^{-1} \cdot (\text{mg g}^{-1})^{-1/n}$)	$1/n$	R^2
4	0.12	2.7	0.91	0.77	0.4	0.96
5.5	0.12	4.5	0.99	0.93	0.43	0.99
7	0.04	3.0	0.73	0.46	0.71	0.85

as was the ammonium ion the 29/4/96 d. or ammonium ple both with tions of the e by diluting the variability d would be ion removal oval) for the l capacity for y 40% greater monium ion e decreased attributed to wastewater on exchange ing distilled ewater [4]: a ewater than ainly due to clinoptilolite lso removes l contains ; l⁻¹. It has (and Na⁺) nd zeolite is [7]. Other calcium and nonium ion

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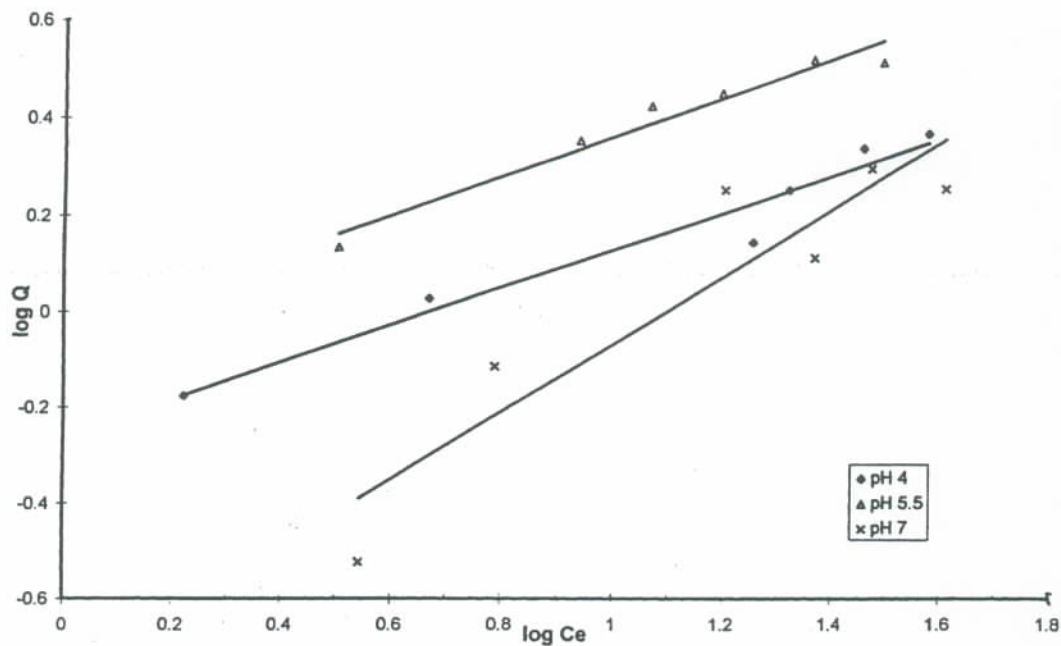


Figure 4. Freundlich representation of ammonium ion adsorption isotherm (Q : $\text{mgNH}_4^+ \text{g}^{-1}$ zeolite; C_e : $\text{mgNH}_4^+ \text{l}^{-1}$) (5g l^{-1} zeolite added, $C_o = 25 \text{mg l}^{-1}$).

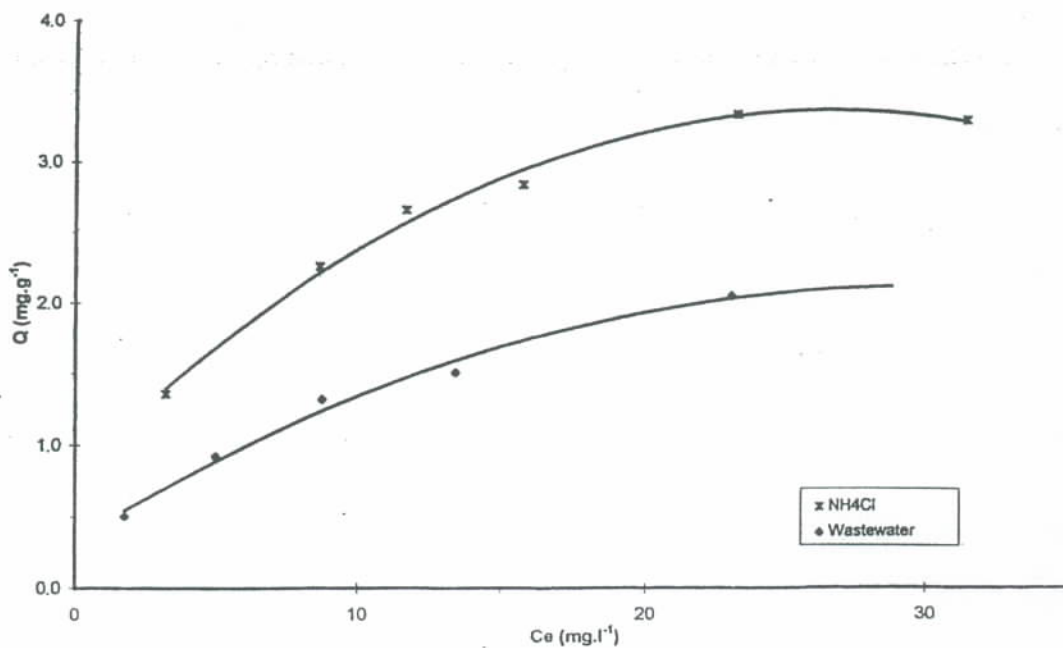


Figure 5. Comparison of ammonium ion removal capacity for wastewater and ammonium ion chloride solution (5g l^{-1} zeolite added).

Table 4. Percent ammonium ion removal and capacity for wastewater effluent samples with different initial ammonium ion concentrations (C_0).

Sample collected	Zeolite added (g l^{-1})	C_0 (mg l^{-1})	% ammonium ion removal	Capacity, Q (mg g^{-1})
24/4/96	5	46	22	2.1
24/4/96	5	23	32	1.5
29/4/96	5	27	15	0.8
29/4/96	5	13.5	30	0.7
29/5/96	5	6.2	38	0.5
29/5/96	5	2.6	46	0.25

This is consistent with the work of Koon and Kaufman [19]. Conversely, Vaughan [18] reported that clinoptilolite performs best when the cation to be removed is present in low concentrations.

When increasing the amount of zeolite added from 5 to 20 g l^{-1} , the percent ammonium ion increases since for the same concentration more zeolite is available for exchange and hence more ammonium ion is removed. Increasing the amount of zeolite added decreases the capacity which comes directly from the calculation of capacity ($Q = \text{ammonium ion removed/g zeolite}$) and the initial rate decreases. Similar results were found by Jorgensen [4] who showed that the specific capacity increased with an increase in the amount of zeolite added.

Kinetic experiments: ammonium ion removal from NH_4Cl

Figure 6 shows the adsorption kinetics of ammonium ion removal by plotting the ammonium ion uptake capacity, Q , versus time for three different initial ammonium ion concentrations and two amounts of zeolite added. For all runs, there is an initial rapid rate of adsorption on contact decreasing within 10-15 minutes to give a gradual approach to equilibrium conditions (90% removal occurs within this first 10-15 minutes). For all the solution conditions studied, the equilibrium was reached within 1.5 to 2 hours and only slight additional adsorption was noted beyond 2 hours.

Increasing the amount of zeolite added slightly reduced the time to reach equilibrium. Increasing C_0 did not appear to

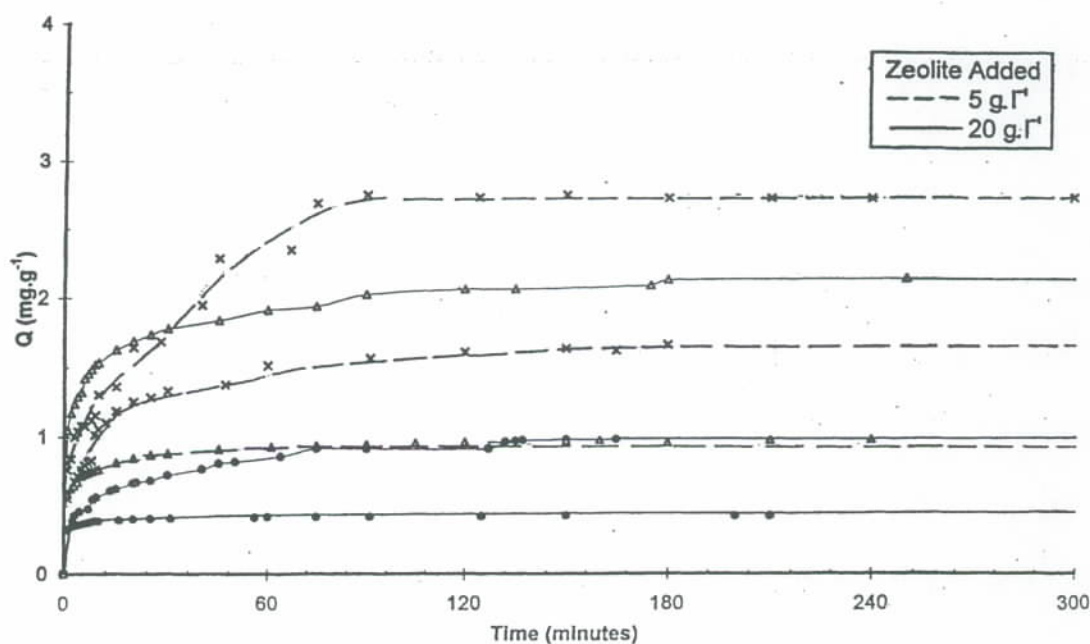


Figure 6. Adsorption kinetics of ammonium ion uptake for NH_4Cl at pH 5.5 at various initial ammonium ion concentrations and amount of zeolite (initial ammonium ion concentration: 50 mg l^{-1} , 25 mg l^{-1} and 8 mg l^{-1}).

alter significantly the time to reach equilibrium.

An increase in the amount of zeolite added from 5 to 20 g l⁻¹ results in half the uptake capacity. A maximum uptake capacity of 2.14 mg g⁻¹ was found for 5 g l⁻¹ zeolite added and initial ammonium ion concentration of 25 mg l⁻¹. The ammonium ion removal capacity values from the kinetic experiments are approximately 20% lower than the capacity found from the batch equilibrium experiments. It would be expected that the two capacities would be equal since both capacity measurements represent equilibrium conditions. The discrepancy between the capacity determined from the equilibrium and kinetic experiments may be attributed to the gradual ammonium ion adsorption that continues beyond 2 hours (the completion of the kinetic experiments). The batch equilibrium measurements were determined after 24 hours whereas the kinetic experiment measurements were determined after 2 hours, when it appeared that equilibrium had been reached. Another factor that could attribute for the lower capacity determined from the kinetic experiments is the effect of pH. Figure 6 shows the adsorption kinetics at pH 5.5. As the kinetic experiment proceeded the pH increases which, as previous experiments to determine the effect of pH show, the adsorption would be decreased.

In a description of adsorption kinetics, three consecutive steps are proposed for the zeolite:

(i) transport of ammonium ion from bulk solution through a liquid film to the zeolite external surface, called film diffusion.

(ii) ammonium ion diffusion into the zeolite pores and surface diffusion termed surface diffusion.

(iii) adsorption of ammonium ion on zeolite internal pores surfaces.

Since the adsorption step (iii) is rapid it does not influence the overall kinetics. The overall rate of the adsorption process will be controlled by the slowest step of film diffusion or intraparticle diffusion. In solutions above 0.1 M ammonium ion generally particle diffusion controls the overall rate [16].

An intraparticle diffusion model is used and a linear plot of Q versus the square root of time suggests intraparticle diffusion to be the rate limiting step in the overall kinetic process [16], as shown in Figure 8. This dependence, according to Fickien's Law, is deduced by considering the adsorption process as being influenced by diffusion in the particle and by convective diffusion in the solution [20]. Relative rate constants, k are taken from the slopes of straight lines between $t = 0$ and t_{im} (where t_{im} is the breakpoint of first resistance intraparticle diffusion range) and are expressed in units of mg ammonium ion per weight zeolite.minute^{-0.5}. The k values are not true reaction rates but are useful for comparison [16]. The intraparticle diffusion model was fitted with respect to different initial ammonium ion concentration, pH and amount of zeolite added (Figures 7 and 8, Table 5).

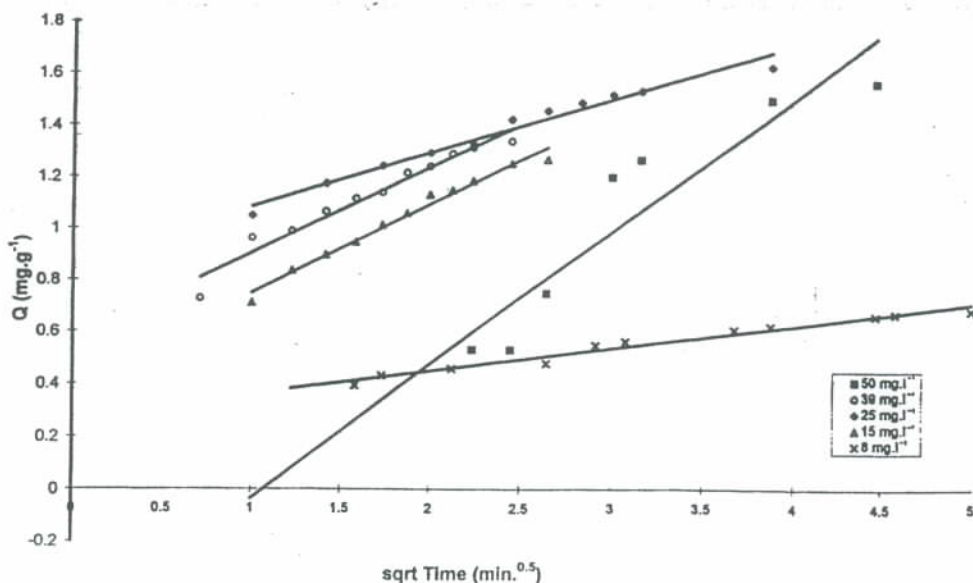


Figure 7. Plot of adsorption capacity versus sqrt time showing the effect of initial ammonium ion concentration on intraparticle diffusion model (pH = 5.5, 5 g l⁻¹ zeolite added).

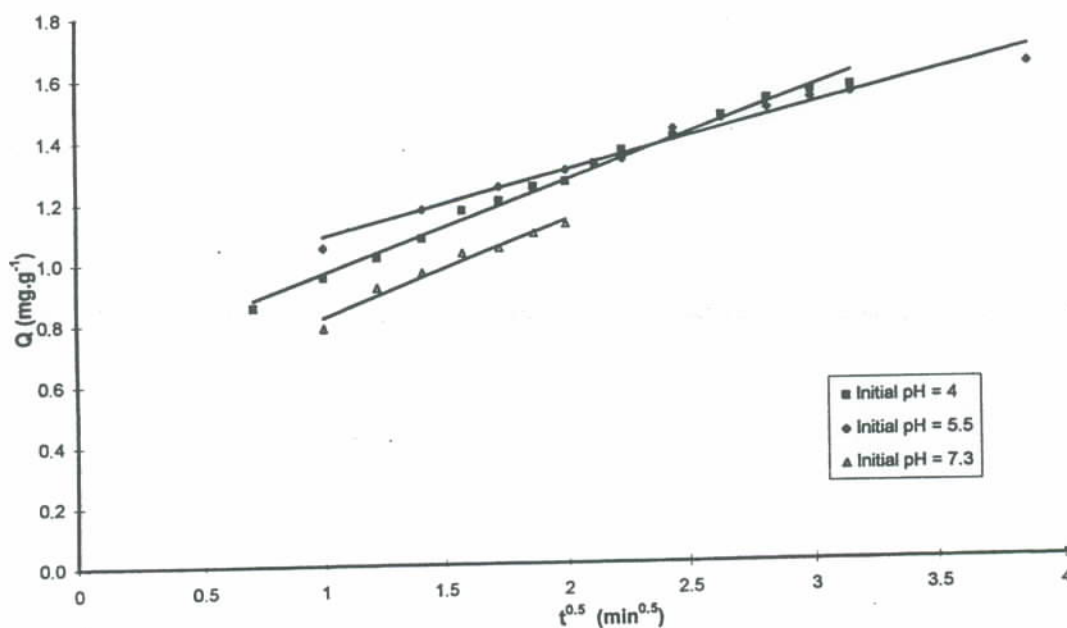


Figure 8. Plot of adsorption capacity versus sqrt time showing the effect of pH on intraparticle diffusion model (initial ammonium ion concentration 25 mg l⁻¹, 5 g l⁻¹ zeolite added).

Figure 7 and Table 5 show the effect of initial concentration on intraparticle rate constant (k). Intraparticle diffusion rates for NH₄Cl and 5 g l⁻¹ zeolite added range between 0.09 - 0.5 mg g⁻¹.min^{-0.5}. The more concentrated the solution the more rapid is the initial uptake rate. This may be due to a greater driving force with increasing C_o . When C_o is increased from 8 to 15 mg l⁻¹ there is a marked effect on the initial rate of intraparticle diffusion. Above C_o 15 mg l⁻¹ the effect is small. It should be noted that the k values account for the adsorption rate only over a limited (initial) range of the Q versus sqrt time curve.

The uptake capacity, Q , increases with increasing C_o . It would appear that increasing the ammonium ion concentration in solution seems to enhance diffusion in the

solid. The percent ammonium ion removed decreases for increasing C_o . The t_{lim} (which represents the initial uptake period) increases with increasing C_o as there is more ammonium ion to remove from solution even though the uptake rate is faster. The concentration in a specific wastewater would thus be of particular significance in determining how much ammonium ion can be removed. For the same amount of zeolite added (5 g l⁻¹) and initial ammonium ion concentration (25 mg l⁻¹) the maximal uptake capacity (2.14 mg g⁻¹) and maximal percent ammonium ion removal (42%) is for pH 5.5 then 4 and 7.3, which agrees with the results of batch experiments. The initial rate is highest (0.32 mg g⁻¹.min^{-0.5}) for pH 7.3 then 4 and 5.5.

Table 5. Initial rate of intraparticle diffusion, k (mg g⁻¹ zeolite.min^{-0.5}): effect of amount of zeolite added, initial ammonium ion concentration and pH for NH₄Cl.

Zeolite added (g l ⁻¹)	C_o (mg l ⁻¹)	pH	% ammonium ion removal	t_{lim} (min.)	Initial rate, k (mg l ⁻¹ .min ^{-0.5})	Capacity, Q (mg g ⁻¹)
5	50	5.5	20	60	0.5	1.9
5	39	5.5	31	100	0.33	2.0
5	25	5.5	42	90	0.21	2.14
5	15	5.5	53	90	0.34	1.64
5	8	5.5	60	70	0.09	0.98
5	25	4	39	30	0.30	1.7
5	25	7.3	31	40	0.32	1.54
20	25	5.5	80	120	0.09	0.98

Kinetic experiments: ammonium ion removal from wastewater effluent

Table 6 and Figure 9 show the results of kinetic experiments conducted on four wastewater effluent samples. Intraparticle diffusion rates for wastewater with 5 g l^{-1} zeolite added range between $0.03\text{--}0.25 \text{ mg g}^{-1} \text{ min}^{-0.5}$. The wastewater effluent sample with C_0 46 mg l^{-1} has a higher than expected removal rate and capacity. For the wastewater samples, generally the more concentrated is the effluent (with respect to ammonium ion concentration), the higher are the removal capacity and initial rate, which is also the case for NH_4Cl .

As can be seen from Figure 9 the removal is much

slower for the wastewater effluent (removal takes over 60 minutes) than for the NH_4Cl . When comparing the removal of ammonium ion from wastewater effluent and from NH_4Cl , the percent removal, initial rate and the uptake capacity are lower for wastewater than for NH_4Cl for the same amount of zeolite added and the same C_0 . This would be expected due to the presence of competing cations present in the wastewater and agrees with the results of batch experiments. For the same amount of zeolite added (5 g l^{-1}) and initial ammonium ion concentration (25 mg g^{-1}), the ammonium ion removal capacity is 2.14 mg g^{-1} (42% ammonium ion removal) for NH_4Cl solution and 0.8 mg g^{-1} (15% removal) for wastewater effluent.

Table 6. Initial rate of intraparticle diffusion, k ($\text{mg g}^{-1} \cdot \text{min}^{-0.5}$): effect of amount of zeolite added, initial ammonium ion concentration and pH for wastewater.

Zeolite added (g l^{-1})	C_0 (mg l^{-1})	pH	% ammonium ion removal	t_{lim} (min.)	Initial rate, k ($\text{mg g}^{-1} \cdot \text{min}^{-0.5}$)	Capacity, Q (mg g^{-1})
5	46	7.5	54	30	1.6	5.0
5	33	7.5	27	60	0.25	1.8
5	29	7.5	12	100	0.21	0.7
5	28	7.5	34	120	0.03	1.0

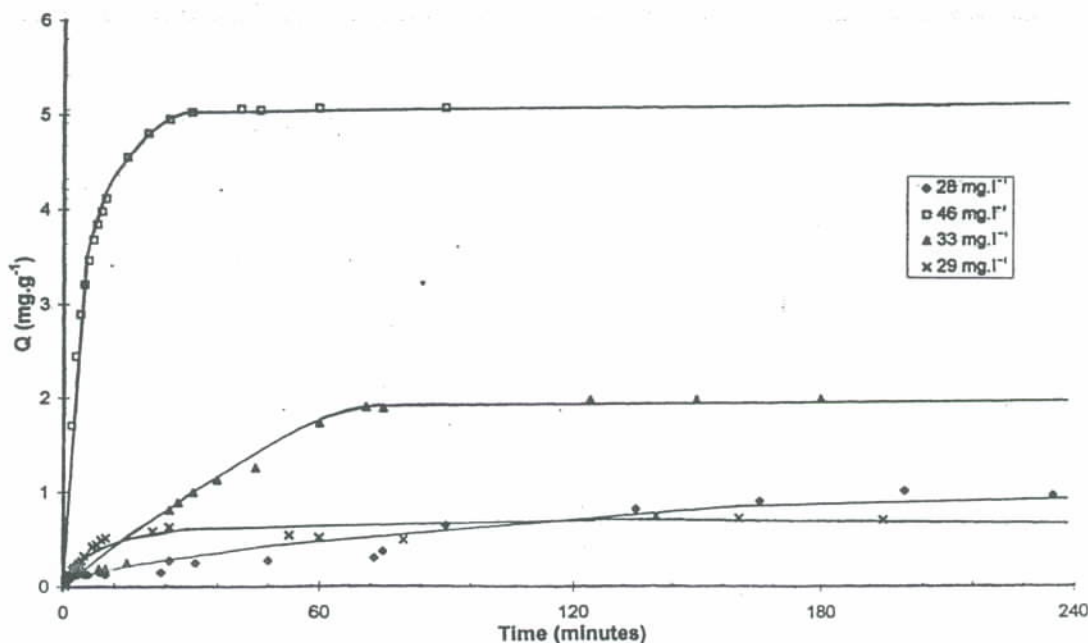


Figure 9. Adsorption kinetics of ammonium ion uptake for wastewater effluent at pH 7.5 for four initial ammonium ion concentrations.

CONCLUSIONS

From the results of batch equilibrium and kinetic experiments conducted on ammonium ion removal using natural zeolite, several conclusions can be made:

Ammonium ion removal capacity is less for wastewater effluent than for solutions of simple ammonium salts (using 5 g l^{-1} zeolite the ammonium ion removal capacity from wastewater effluent is 2 mg g^{-1} , compared to 3.7 mg g^{-1} for NH_4Cl for an initial ammonium ion concentration of 25 mg l^{-1}).

Ammonium ion removal efficiency of natural zeolite depends on the solution characteristics (such as initial ammonium ion concentration, and pH), which in the case of wastewater will vary considerably. For ammonium ion removal using zeolite from NH_4Cl solutions the effect of pH is not significant. Removal is slightly higher for pH = 5.5 (capacity = 3.5 mg g^{-1}) than for above and below this pH. For the same initial ammonium ion concentration of 25 mg l^{-1} , increasing the amount of zeolite added (from 5 to 20 g l^{-1}) decreases the uptake capacity and the uptake rate by a factor of 2. Increasing the initial ammonium ion concentration of the solution results in more rapid uptake.

At pH 4 and 5.5, the adsorption isotherms of ammonium ion on zeolite can be described by Freundlich and

Langmuir models (correlation coefficients >0.91) which suggests monolayer adsorption. The Freundlich model gives a better fit than the Langmuir in the pH range studied (pH 4 - 7).

For wastewater effluent samples and ammonium chloride solutions, 90% of ammonium ion removal occurs in 10-15 minutes (and 100% removal occurs within 1.5-2 hours). Intraparticle diffusion was found to be the main rate limiting step in kinetics.

Comparing ammonium ion removal kinetics for wastewater and NH_4Cl , the percentage removal, initial uptake rate, and uptake capacity are lower for wastewater than for NH_4Cl .

This study progresses the understanding of the performance of zeolite ion exchangers and should find practical application in upgrading existing conventional activated sludge plants to meet nitrogen removal requirements without the need for major plant modifications. For existing wastewater treatment plants, application of the use of zeolites to remove ammonia will attract low capital cost and moderate operating cost.

ACKNOWLEDGMENT

This project is supported, in part, by the Australian Research Council.

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