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AMMONIUM ION (NH$_4^+$) REMOVAL FROM SECONDARY EFFLUENT THROUGH ION-EXCHANGE: THE EFFECT OF BIOLOGICAL ACTIVITY AND THE PRESENCE OF OTHER CATIONS

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ABSTRACT

This paper is concerned with ion-exchange removal packed bed studies carried out with secondary effluent on a sewage treatment works. The work was carried out over a five month secondment period with Severn Trent Water, situated in the midlands of England. The objective of the work was to compare previous studies with clinoptilolite using synthetic wastewaters, de-ionised water and appropriate salts, with typical process water found on a sewage treatment plant. Experimental results have shown ammonium removal of 90% and greater of the influent NH$_4^+$ concentrations. In this report it has been shown that the biological activity of nitrification takes place during the upflow processing of wastewater through the packed beds. It is also shown how other cations cause an inhibitory effect on the ion-exchange process whereas biological activity leads to improved efficiency. © 1999 Published by Elsevier Science Ltd on behalf of the IAWQ. All rights reserved

KEYWORDS

Ammonium (NH$_4^+$); clinoptilolite; ion-exchange; nitrification; wastewater.

INTRODUCTION

In contrast to biological filtration, ion-exchange offers a more flexible process and does not depend on a steady state environment. The system can respond more rapidly to concentration and overall loading changes. Ion-exchange is used in the water industry primarily for the removal of hardness ions (Mg^{++} and Ca^{++}) from drinking water and is used by other industries to recover valuable waste materials or by-products, particularly ionic forms of gold and silver, (Mercer et al., 1970). This project is concerned with the removal of ammonia in its ionic state from wastewaters by cationic exchange. The process involves metering the wastewater through a trickle filter or upflow bed which has been packed with selected ion-exchanger solid.

Ion-exchange is a process where ions held by electrostatic forces to charged functional groups on the surface of a resin are exchanged for ions of similar charge in a solution that is in contact with the solid. Ames (1967) showed how clinoptilolite had particular preference for ammonium cations compared to others such as calcium and magnesium. If a solution is passed continuously through a column of exchange resin equilibrium is reached and influent concentrations equal effluent and no net ion exchange occurs.

Ion-exchange is a form of chemical adsorption and is represented by the simple stoichiometric reaction equation 1.1. (Helferich, 1966).
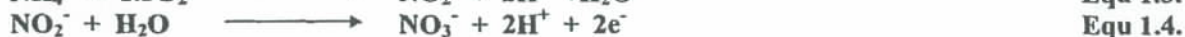
$$A^{n+} + n(R^-)B^+ \longrightarrow nB^+ + (R^-)_nA^{n+} \qquad \text{Equ. 1.1.}$$
(Soln.)   (Clinoptilolite)   (Soln.)   (Clinoptilolite)

Equation 1.1. is written in algebraic form. If we take the process for which this paper is concerned, NH_4^+ removal by cationic exchange using clinoptilolite, equation 1.1. becomes 1.2. Clinoptilolite uses sodium cations to maintain electroneutrality and it is these cations that exchange with NH_4^+ and other cations within the influent.

$$NH_4^+ + (Al_6Si_{30}O_{72})Na^+ \longrightarrow Na^+ + (Al_6Si_{30}O_{72})NH_4^+ \qquad \text{Equ. 1.2.}$$
(Influent)   (Clinoptilolite)   (Effluent)   (Clinoptilolite)

There is also qualitative evidence that nitrifying bacteria will colonise the zeolite, behaving similarly to a biological filter bed (Koon, 1971; Beler-Baykal et al., 1996). Theory would suggest that the ion-exchange process effectively concentrates the NH_4^+ ions in the wastewater and if available to nitrifiers would result in improved biological oxidation kinetics. The work described in this paper tries to establish the workings of both processes, ion-exchange and nitrification, and the possibilities of each phenomenon operating together. Effectively clinoptilolite would adsorb the ammonium onto its surface and then the nitrifying bacteria (*Nitrosomonas* and *Nitrobacter*) would oxidise to nitrite and finally nitrate resulting in an extended cycle life of the resin.

The nitrification process is a two step reaction described by the equations below. Ammonium is broken down to nitrite (equation 1.3.) (Barnes et al., 1983), and this nitrite is further oxidised to nitrate (equation 1.4.) (Barnes et al., 1983), a less harmful compound than ammonia to plant and animal life.

$$NH_4^+ + 1.5O_2 \longrightarrow NO_2^- + 2H^+ + H_2O \qquad \text{Equ 1.3.}$$
$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^- \qquad \text{Equ 1.4.}$$

The nitrifying bacteria responsible for these reactions are mainly *Nitrosomonas* and *Nitrobacter*, respectively. These bacteria fall into the category of chemo-autotrophs and the energy generated from these reactions is used to synthesise new cells from carbon dioxide. From equations 1.3. & 1.4. it can be seen that nitrification is dependent on oxygen and in wastewater treatment the concentration of dissolved oxygen is extremely important. The growth of these organisms is slow in comparison to heterotrophic organisms and if bacteria concentrations are low within the wastewater it can take up to 5 weeks for a culture to establish on a biological filter bed (Metcalf and Eddy, 1991).
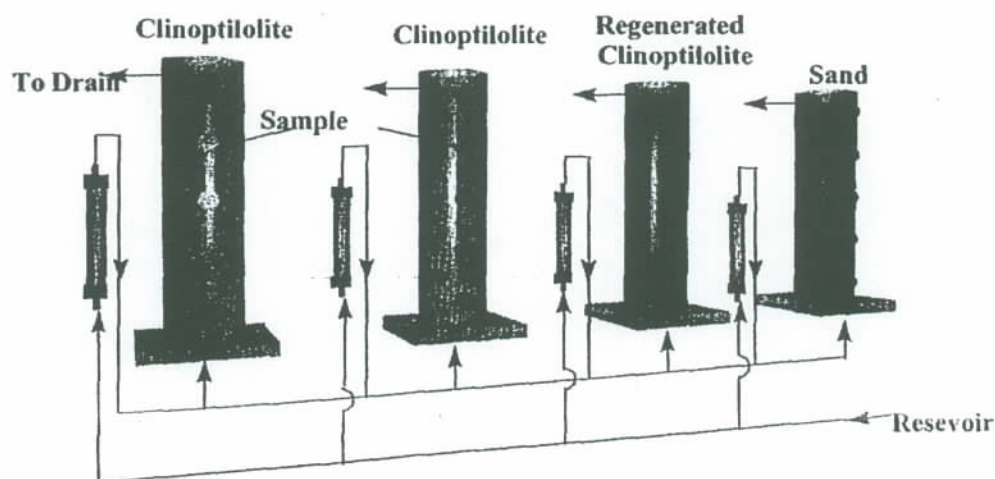

Figure 1. Experimental rig used for processing wastewater.

METHODS AND MATERIALS

The small-scale experimental rig used for the packed bed investigations is presented in Figure 1. The rig consists of 4 columns, 5 cm x 50 cm, each packed with media, of bed height 25 cm and bed volume 0.49 litres. Using rotameters to monitor flow rate, influent flow rates were kept constant through each column. A tracer experiment was used to calculate the residence time of the wastewater through column 1 packed with clinoptilolite. At a flow rate of 20 cm^3/min the water spends 12-15 minutes in the packed bed and this can be assumed true for each type of media having similar characteristics. The media takes up half the volume of the column and with a voidage of 0.5 the total residence time from inlet to outlet is 40-42 minutes. The process fluid is passed through each packed bed and then leaves through a drain at the top of the column.

The holding tank (reservoir) was filled and this wastewater processed for 48 hours, after this time the remaining water was emptied and the tank was rinsed and refilled with another batch of wastewater. Aeration of the wastewater was continual to keep dissolved oxygen levels at a maximum, optimising conditions for biological activity. NH_4^+ concentrations tended to be low in the secondary treated water (0.5 mg/l) and increases to viable levels were made by the addition of NH_4Cl.

The process water used in this project for experimental work was secondary effluent from a Severn Trent Water sewage treatment works illustrated in Figure 2. Table 1 shows the average concentrations of various determinands in the wastewater during the period that this work was carried out.
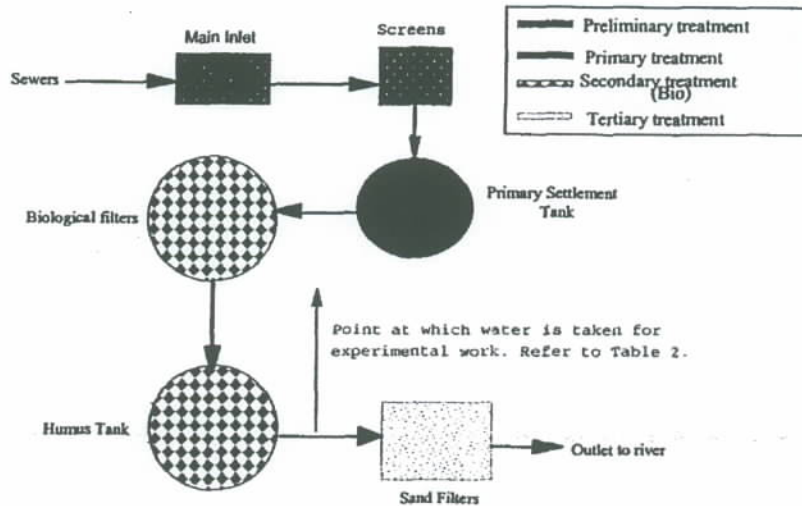

Figure 2. Simplified flow diagram of sewage treatment plant and point where process water was taken from.

Table 1. Average concentrations of various determinands in the secondary wastewater

Total oxidised nitrogen	24 mg/l
pH	7.20
total NH_3 as N	0.5 mg/l
Ca^{++}	60 mg/l
Na^+	186 mg/l
Mg^{++}	8 mg/l
K^+	23 mg/l
Alkalinity	108 mg/l
Nitrite NO_2^-	0.5 mg/l

RESULTS AND DISCUSSION

Figure 3 shows the removal fraction of ammonia through each column for the first experimental run (see also Table 2). It can be seen that there is 80%+ removal for up to 750 bed volumes, the process then begins to approach breakthrough which is reached at 1100 bed volumes in columns 1 and 2. Column 4, which contains biological filter sand, shows a much lower ammonium removal. The initial removal in this column may be due to adsorption capabilities of the sand with nitrification establishing as the process runs on.
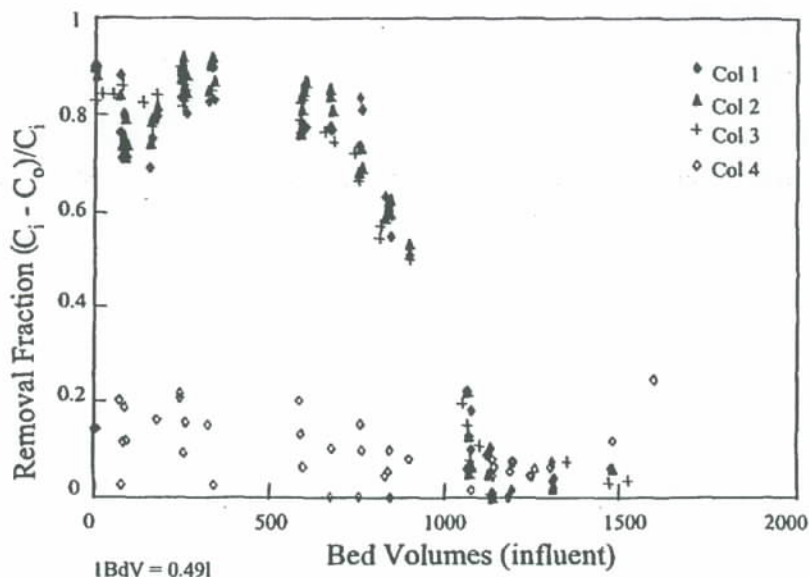
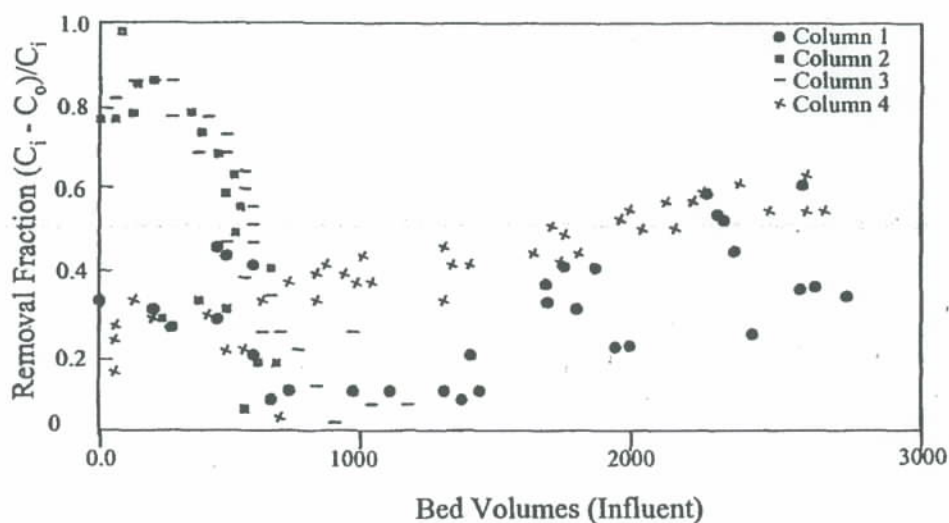Figure 3. Ammonium removal fraction against bed volumes.

Figure 4. Concentration changes during the second experimental run.

Figure 4 shows how the packed beds of column 2 and column 3 behave similarly in the second experimental run (see Table 3) and the regenerated clinoptilolite does not appear to have lost any capacity. Future work will involve quantifying the capacities to establish the efficiency losses, if any, due to regeneration.

In the packed beds used in the first experimental run (Figure 3), column 1 and column 2 show a gradual increase in NH_4^+ until they stabilise. This suggests that the nitrifying bacteria have had time to establish and colonise, on the solid surfaces of the packed bed, to the maximum that conditions allow. It can also be noted

that there was at no time full nitrogen removal and typical concentrations broken down in each column were 2-3 mg/l.

Table 2. Media used for packing first experimental run

	Packing
Col 1	Fresh Clinoptilolite
Col 2	Washed Clinoptilolite
Col 3	Regenerated Clinoptilolite
Col 4	Filter Sand

Table 3. Media used for packing second experimental run

	Packing
Col 1	Exhausted Clinoptilolite (from first run)
Col 2	Regenerated Clinoptilolite
Col 3	Fresh Clinoptilolite
Col 4	Filter Sand (from first run)

Table 4 shows a sample of concentration changes during the second experimental run after 200 bed volumes of processing. There is a decrease in NH_4^+ concentration through each of the columns. If we take column 4, where no ion-exchange has occurred, it can be assumed that all concentration changes are due to biological activity. A fall in NH_4^+, alkalinity and dissolved oxygen with a rise in NO_2^- and Total Oxidised Nitrogen (T.O.N.) concentrations, signifies the process of nitrification through the column. These concentration changes are true for each column and therefore in column 2 and column 3 the processes of nitrification and ion-exchange are taking place together. Calculations of nitrification, de-nitrification and ion-exchange kinetics of ammonia removal in these columns become complex.

Table 4. Samples taken after 200 bed volumes of processing, inlet and outlet to the experimental rig

Determinand	Inlet	Column 1 Exhausted clinoptilolite	Column 2 Regenerated clinoptilolite	Column 3 Fresh clinoptilolite	Column 4 Filter sand
NH_4 as N mg/l	5.00	2.10	3.90	0.30	2.60
T.O.N. mg/l	27.60	27.80	26.70	27.40	27.70
NO_2^- mg/l	0.90	2.70	2.50	2.20	5.40
NO_3^- mg/l	26.70	25.10	24.20	25.20	22.30
Alkalinity $CaCO_3$ mg/l	86.00	73.00	83.00	100.00	77.00
Dissolved O_2 mg/l	8.80	0-0.3	0-0.3	0-0.3	0-0.3

From the previous two experimental runs it can be seen that the processes of ion-exchange and nitrification occurred together. But due to the dissolved oxygen limitations the process of denitrification also takes place in the upper half of each column. The final run was established to investigate the effect of aerobic biological activity on the cycle life of the clinoptilolite packed bed. Two columns with identical packed bed characteristics were set up: bed volume – 255 cm³; packing – fresh clinoptilolite; flow rate - 4 bed volumes per hour. One column was supplied with aerated secondary wastewater providing an environment for biological activity. The other was supplied with synthetic wastewater with similar cation concentrations and conditions unsuitable for nitrification. Cation concentrations in the influents are presented in Table 5.

From Figure 5 we can see that the cycle life of the clinoptilolite being used with wastewater was considerably longer. The packed bed treating the synthetic water reached equilibrium close to 900 bed volumes whereas the other was still removing 40% of the influent ammonium. Initial conclusions would be that extended cycle life must be due to biological activity occurring within the packed bed. By taking a

closer look at the inlet cation concentrations in Table 5, it can be seen that although the total cation concentrations are equal individual cation concentrations differ. Therefore showing that some of the enhancement of cycle life seen in Figure 5 could be caused by competition for ion-exchange sites due to higher calcium cation concentrations in the synthetic wastewater. Previous uptake work has shown that clinoptilolite removes calcium, magnesium and potassium cations as well as ammonium (Ames, 1967).
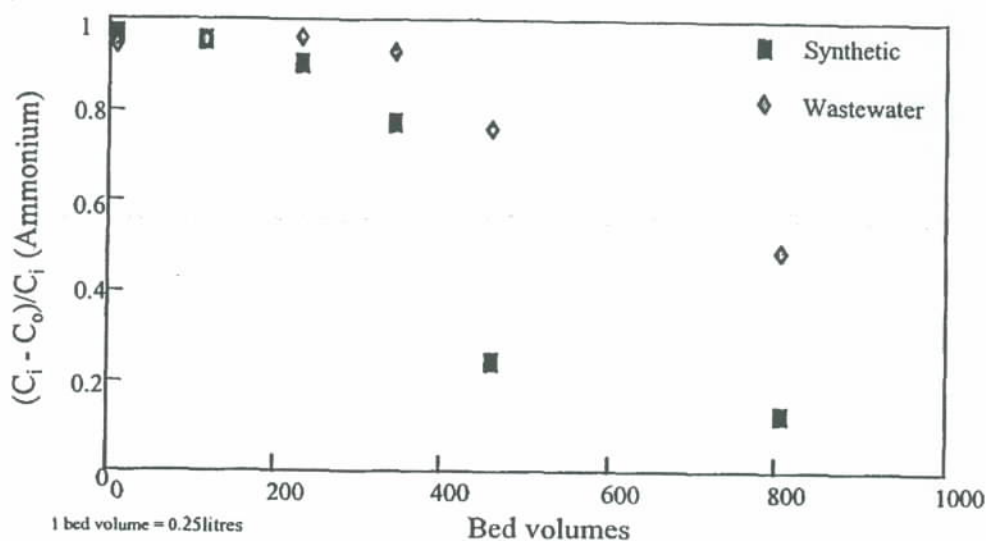

Figure 5. Effect of biological nitrification on clinoptilolite cycle life.

Table 5. Cation concentrations in each influent

meq/l	Synthetic	Wastewater
NH_4^+	0.80	0.70
Ca^{++}	1.30	0.90
Mg^{++}	0.40	0.30
Na^+	5.60	6.40
K^+	0.90	0.70
Total	9.00	9.00

CONCLUSIONS AND FURTHER WORK

Results found through this experimental work are very promising as it has been indicated in the column studies how the two processes of ion-exchange and nitrification can operate together when treating secondary effluent. Work of this type has also been carried out with variable shock loadings (Beler-Baykal et al., 1996). This secondary treatment effluent contained high concentrations of nitrifying bacteria and alkalinity and a bacterial culture became established on the packed bed soon after processing was started. Theory would suggest that if these cations, taken up by clinoptilolite, are oxidised to anions they will relieve the ion-exchange sites and therefore the cycle life will be extended. The experimental work with the modified rig comparing water suitable and unsuitable for nitrification was devised to investigate this theory and estimate the overall effect on exchange resin cycle life. Calculations of ion-exchange and nitrification become extremely complex as both processes are occurring at the same time and a definite ammonium concentration between samples is unknown. As the nitrification reactions are limited by dissolved oxygen levels in the upflow columns, maximum nitrification rates in terms of ammonium reduction were 2-3 mg/l (50-70 mg/day).

Questions have been raised from this work as to how processing with wastewater will affect packed bed performance. Do the Ca^{++} and Mg^{++} cations take up these exchange sites permanently (shortening the cycle life) or temporarily (having no long term effect)? How does biological activity, seen in Table 4, affect the uptake process and zeolite capacity? Does the beneficial effect of nitrification outweigh the inhibition

caused by other cations within wastewater? Further work is needed to investigate these questions in more detail.

As was previously stated the process of nitrification is highly dependent on dissolved oxygen concentrations. Some of the results gathered in this work suggest that denitrification occurs towards the top of each packed bed where the environment becomes anoxic. Further work will involve providing the packed bed with oxygen throughout, by the use of bubbleless membranes for example, which would provide an environment where maximum nitrification rates could be obtained as dissolved oxygen is no longer the rate limiting step.

NOTATION

C_i Inlet ammonium concentrations meq/l,
C_o Outlet ammonium concentrations meq/l
meq   Milliequivalents
Alkalinity $CaCO_3$ concentration mg/l (pH buffer)

ACKNOWLEDGEMENTS

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