Continuous removal of ammonium ion by ion exchange in the presence of organic compounds in packed columns

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Abstract: The removal of ammonia from wastewaters after secondary biological treatment can successfully be achieved by ion exchange. However, the presence of residual organic compounds can impart significant influence on the uptake and their presence may need to be considered during the design of a treatment system. The aim of this work was to determine the effect of the presence of certain organic compounds upon the uptake of ammonium ion and column breakthrough. Two organic contaminants were considered, including citric acid and protein (as whey protein isolate). Three cationic exchangers were used and included the natural zeolite clinoptilolite, the gel resin Dowex 50w-x8, and a macronet resin, Purolite MN-500. The influence of regeneration upon column breakthrough behaviour was also determined. The results showed that the presence of organic compounds had variable effects on ammonium ion uptake. In the case of clinoptilolite the presence of protein appeared to have very little effect upon breakthrough capacity. In the case of the clinoptilolite and the MN500 a substantial reduction of breakthrough capacity was observed in the presence of citric acid. In the case of clinoptilolite a very significant increase in column breakthrough performance was observed after cycles of exhaustion and regeneration. This was not observed in the case of the synthetic resins, which showed a more consistent performance from run to run. Overall the Dowex50w-x8 gave the highest breakthrough capacity for ammonium ion removal of 700 bed volumes. Regenerated clinoptilolite showed a maximum breakthrough capacity of 450 bed volumes, and MN-500 a consistent breakthrough capacity of 300 bed volumes.

Keywords: clinoptilolite; ion exchange; water treatment; zeolites

INTRODUCTION

The polluting potential of ammonia arising from both municipal and industrial wastewaters and in aquaculture is well known.[1–3] The effluent from secondary treatment contains ammonia resulting from the breakdown of proteins and other organic nitrogen, and also residual organic compounds. There are a range of strategies available for the reliable removal of ammonia from treated waters, though traditional biological filtration in trickling filters is perhaps the best known and most widely used. Biological filtration is an effective treatment technique especially where the water volume and ammonia loading are relatively stable, and thus can provide quasi-steady-state conditions. The presence of significant concentrations of pesticides and other xenobiotics which may damage the viability of established cultures of nitrifiers is undesirable. Indeed the occasional presence of such compounds may be a limitation to the reliable application of biological filtration in some cases. Significant fluctuations in temperature, pH, and dissolved oxygen concentration are also undesirable for maintenance of high rates of biological oxidation.

Given the potential limiting features of biological filtration, the need for a physical process such as ion exchange as a back-up is important in order to reduce risk of accidental breach of discharge consent limits. In the case of intensive aquaculture, temporary reduction in ammonia removal capability could be disastrous and could result in major capital loss due to fish stock mortality.

Ammonia removal by ion exchange using natural zeolites such as clinoptilolite is well known and there are a number of papers which describe the relevant capacity, equilibrium and column breakthrough characteristics.[4–9] Clinoptilolite is a silica-rich zeolite, which may have a slightly smaller ion-exchange capacity than other zeolites, but has a very high selectivity for NH_4^+. Clinoptilolite performs well in various environments including those which are slightly acidic. Owing to the high silica-to-aluminium ratio in clinoptilolite it is less susceptible to acidic degradation than other zeolites.

The development of the hypercrosslinked macronets[10] has also stimulated further interest in new applications of ion exchange to wastewater treatment processes. The macronets are resins which exhibit both macroporous and microporous structures and

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therefore show a degree of adsorptive capacity, in addition to ion-exchange capacity. Such resins may thus be suitable for treatment of wastewaters containing a range of contaminants including organic species, proteins and ions.

Ion exchange has a potential advantage over biological treatment in that rapid response to shock loading conditions is possible. Ion exchangers also perform well in the presence of antimicrobial compounds and under conditions of pH and temperature which would not be suitable for biological removal of ammonia.

In earlier work we have focused on the study of the ion-exchange removal of ammonium ion in the presence of contaminants. The equilibrium uptake characteristics of clinoptilolite, the strong acid exchanger Dowex50w-x8 and the cationic macronet exchanger MN-500 have been determined.[9]

EXPERIMENTAL

Scope

The goal of the experimental work was to study the ammonium ion breakthrough characteristics of fixed beds of exchanger resin. In particular, the breakthrough characteristics of beds of clinoptilolite, Dowex50w-x8, and Purolite MN-500 for ammonium ion removal were compared. Secondly, the effect upon ammonium ion breakthrough of the presence of two contaminants was determined. The two contaminants were citric acid and whey protein isolate. Thirdly, the effect of regeneration upon breakthrough performance was determined. Finally, the possible influence of the contaminants upon regeneration performance was studied.

Materials and methods

Three ion exchangers were evaluated in the study and included the naturally occurring zeolite clinoptilolite (Drydenaqua) with particles classified in the size range 500–1000 μm, the macronet cationic exchanger MN500 (Purolite) 290–840 μm, and the conventional cationic gel resin, Dowex50w-x8 (Dow Chemical), size range 290–840 μm. The influent solutions comprised ammonium chloride solutions and as appropriate these were dosed with the organic contaminant of interest. In this study these included citric acid (Sigma Aldrich) and whey protein isolate (Fonterra). Except in the case of the solutions containing citric acid, the pH of the feed solutions were in the range 7–7.5. In this pH range ammonia is 99.99% ionized at 20 °C.[11,12] In the case of the citric acid dosed solutions, the pH was 3, which corresponded very closely to the calculated value and a high degree of citric acid ionization ($pK_a = 3.08$.[13] At this pH the degree of ammonia ionization is 100 %. Details of the feed solution compositions are shown in Table 1.

Table 1. Feed solution compositions

Component	Influent concentration	
NH_4^+	50 mg L^{-1} (50 ppm)	(NH_4Cl = 148 mg L^{-1})
Citric acid	533 mg L^{-1} (50 ppm)	
Whey protein	20 mg L^{-1}	
Na^+	127 mg L^{-1} (100 ppm)	(NaCl = 324 mg L^{-1})

A single flow rate of 3 bed volumes h^{-1} was used for all the experiments and temperature was maintained at 20 ± 1 °C. Ammonium analyses were conducted using an ion-selective electrode (Hach 50 250) which was contacted with each solution after addition of a standard amount of lithium hydroxide solution. This was part of a standard procedure for the use of the electrode, requiring the sample pH to be raised above a value of 12.0.

The ion-exchange columns were made from Perspex tubing with internal dimensions of 53.5 mm diameter, 400 mm total height and 200 mm in bed height (Fig. 1). The influent solution was fed to each column in upflow mode, using a peristaltic metering pump (Watson Marlowe 502S). A free space was located beneath the supporting grid for the exchanger. This was full of liquid, thus providing an even flow across the whole area of the grid at the lower entry region to the bed. Final eluent samples were taken with a syringe from a sample port at the top of a column. The overflow was regularly sampled to determine the correct flow rate.

Before each experimental run the columns and pipework were sterilized with a weak solution of sodium hypochlorite. The exchangers were sterilized with sodium metabisulphite ($Na_2S_2O_7$) prior to chemical conditioning to minimize biological contamination. To prevent dissolved air from forming bubbles in the tubing, all solutions were subjected to a degassing procedure in which they were warmed to 22–24 °C in a water bath before they were added into the feed tank. The solutions were then cooled to 20 °C in the tubing prior to entering the column. Any gas bubbles that did get trapped in the entrance of the column were removed by a syringe through small sealed holes in the side of the column. Each of the three exchanger resins were preconditioned into the sodium form by contacting with solutions of sodium chloride (10 g L^{-1} NaCl) in a series of batchwise contacts until no further change in composition was observed. The exchangers were rinsed in distilled water to remove traces of free sodium chloride solution. The loading of the column with each exchanger involved initial charging with distilled water. This was followed by addition of the exchanger added as a wet slurry. This was to prevent air bubbles being trapped in the column which might have subsequently affected the breakthrough performance. 10 bed volumes (1 bv = 0.45 L) of a solution of 10 g L^{-1} sodium chloride and 2.0 g L^{-1} NaOH were pumped through each column at a rate of 2 bv h^{-1} as a further preconditioning step. This was followed by pumping through of further batches of distilled water until all traces of NaCl and NaOH were

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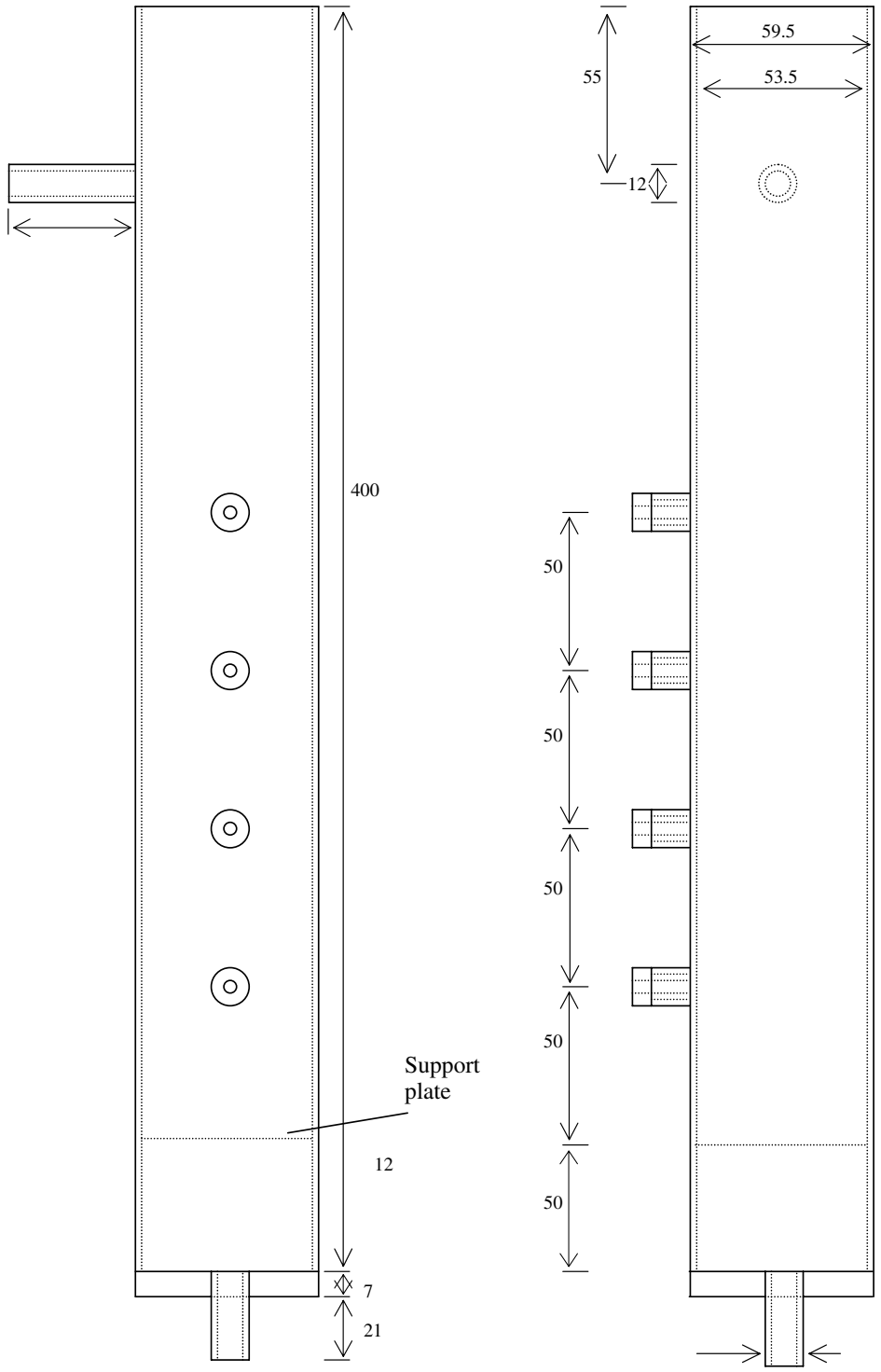

Figure 1. Column design and dimensions.

removed. The preconditioning and regeneration protocols were based on a rigorous procedure developed using clinoptilolite in an earlier study.[14]

At the end of each breakthrough experiment each column of exchanger was regenerated according to the following protocol:

(1) 15 bv of $10\,g\,L^{-1}$ NaCl and $2.0\,g\,L^{-1}$ NaOH pumped at $1.5\,bv\,h^{-1}$;
(2) 5 bv of $2.0\,g\,L^{-1}$ $Na_2S_2O_7$ pumped at $1\,bv\,h^{-1}$;
(3) 10 bv of $10\,g\,L^{-1}$ NaCl and $2.0\,g\,L^{-1}$ NaOH pumped at $2\,bv\,h^{-1}$;
(4) 6 bv of distilled water pumped at $3\,bv\,h^{-1}$ (to remove excess regenerant solution).

After regeneration the resin was removed and repacked to ensure even distribution for each run.

RESULTS AND DISCUSSION

The first set of breakthrough results is shown in Fig. 2 and compares the column exchange performance for clinoptilolite, MN-500 and Dowex 50w-x8 in the individual presence of ammonium ion, sodium ion (the initial form of each exchanger) and chloride. Dowex 50w-x8 shows the best breakthrough performance in terms of overall breakthrough capacity. The MN-500 shows the sharpest breakthrough though the overall capacity is the least of the three exchangers.

Figure 3 shows the breakthrough curves of three separate experiments using fresh clinoptilolite in the presence of ammonium ion only, ammonium ion and citric acid, and, ammonium ion and whey protein. In each case only the ammonium ion in the eluent was determined. Freshly conditioned exchanger was used in each case. The presence of citric acid appeared to cause earlier breakthrough of ammonium ion. This can be readily explained by the fact that although citric acid is a weak acid, it would still provide a degree of competing protons for the cationic sites on the exchanger, thus reducing the availability of sites for ammonium ion uptake. In the presence of whey protein concentrate, the opposite effect is observed and small but significant enhancement of approximately 10 % in ammonium ion breakthrough capacity is observed.

Earlier ion-exchange equilibrium studies[9] showed that the presence of whey protein significantly enhanced the batch uptake of the NH_4^+ ion. It can be seen in Fig. 3 that the enhanced breakthrough performance is consistent with the higher selectivity for ammonium ion reported in the earlier study in the presence of whey protein. This could be explained by the amphoteric nature of the protein, which may enhance the ionization equilibria of the ammonia, thus increasing the availability of free ammonium ion for uptake. Another interesting point to note is that the breakthrough characteristic appears to plateau at a concentration corresponding to less than full exhaustion of the exchanger.

In the case of the MN500 (Fig. 4), the effect of the presence of the citric acid is even more marked compared with the clinoptilolite, with a very significant reduction in bed volumes of water fed prior to breakthrough, from just over 300 bv to around 200 bv. This suggests that the clinoptilolite may better adsorb some of the citric acid, in undissociated form,

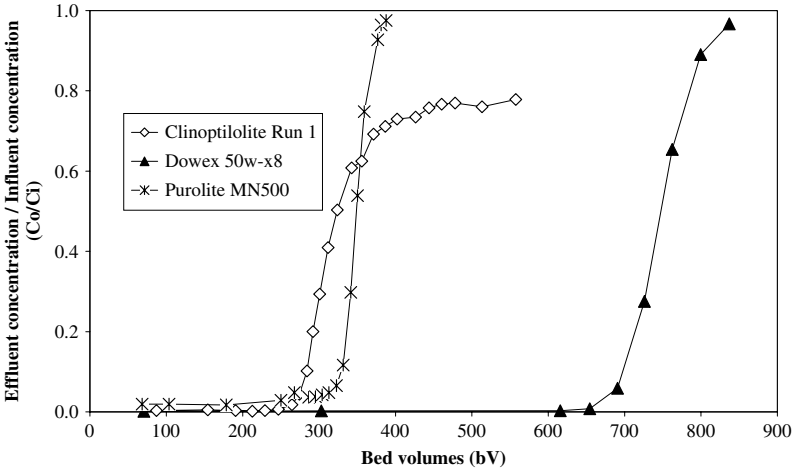

Figure 2. Comparison of NH_4^+ breakthrough onto various exchanger resins.

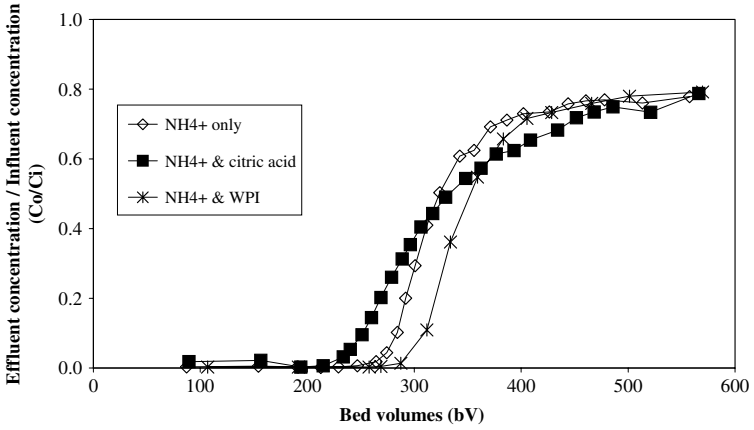

Figure 3. NH_4^+ breakthrough with various organics onto fresh clinoptilolite.

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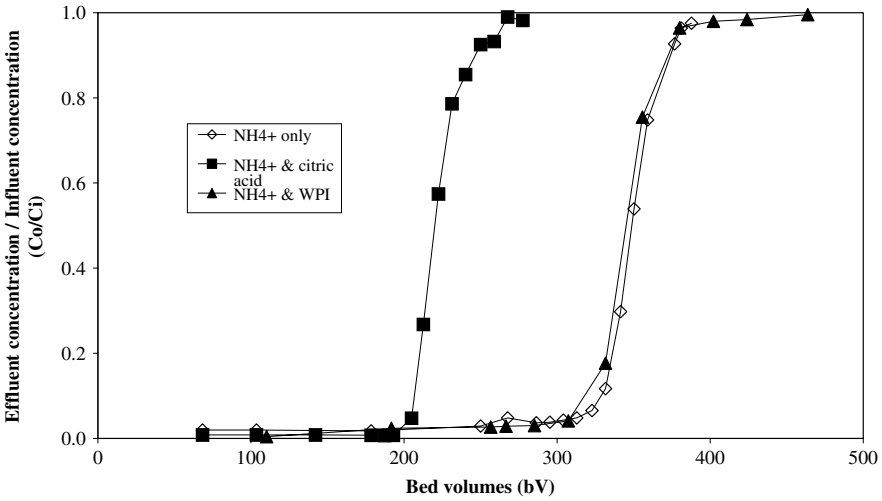

Figure 4. NH_4^+ breakthrough with various organics onto fresh Purolite MN500.

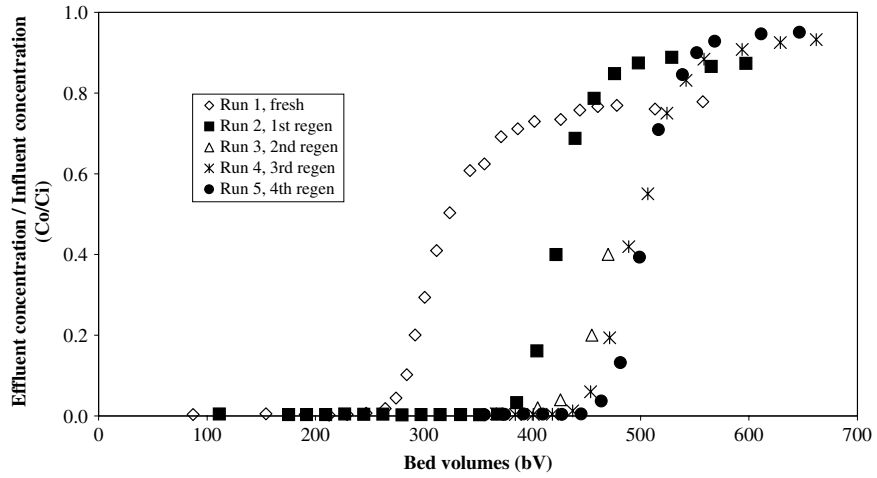

Figure 5. NH_4^+ breakthrough and regeneration onto clinoptilolite.

compared with the MN500. The release of competing hydrogen ions would therefore be at a lower level. An alternative explanation is that the citric acid produces a degree of enhancement of the performance of clinoptilolite, perhaps due to acid leaching and beneficial structural modification.

After the first breakthrough experiment involving ammonium ion uptake onto clinoptilolite (Fig. 2), the zeolite was regenerated and then subjected to four further cycles of breakthrough and regeneration. The successive breakthrough curves are compared in Fig. 5. There are three significant points of interest here. First, there is an apparent increase in breakthrough capacity at each cycle, reaching a maximum of 460 bv after the fourth regeneration. Second, the attainment of equilibrium appears to be more clear-cut with respect to succeeding cycles of uptake and regeneration and the breakthrough is sharper. This could be explained by changes in the internal structure of the zeolite, which enhanced the kinetics of uptake and thus the shape of the breakthrough curve. Third, in the case of run 5, the final eluent ammonium ion concentration approaches closely that of the feed solution, reflecting near-attainment of equilibrium.

The reasons for the changes in uptake behaviour with successive cycles of uptake/breakthrough/regeneration are unclear. Incomplete preconditioning of the zeolite might be suggested but this is considered to be unlikely, since the preconditioning protocol was a tried and tested method.[14] It should be noted that the ionic strength of the conditioning solutions was much higher than that in any of the feed solutions ($10\,g\,L^{-1}$ NaCl compared with an ammonium ion concentration in the feed of $50\,mg\,L^{-1}$) and would provide a very significant driving force to achieve a fully conditioned zeolite. It is also clear that there was no suggestion of incomplete preconditioning in the case of either the Purolite MN500 or the Dowex 50w-8x.

The presence of magnesium ion Mg^{2+} in clinoptilolite could play a role. Other work[15] with clinoptilolite has shown that the zeolite has a strong affinity for

Mg^{2+} ions, which are only very weakly displaced in the presence of sodium ions. However, the affinity of the zeolite for ammonium ions appears to be significantly strong as to allow significant replacement of magnesium in the presence of ammonium. Therefore it is possible that preconditioning using sodium chloride solution would not displace Mg^{2+}. However, displacement of magnesium ion may occur during ammonium ion uptake because of the greater affinity of NH_4^+ for the zeolite. The maximum capacity appears to be reached by the fifth run, which is the point when most of the Mg^{2+} would have been removed. In this case, the presence of Mg^{2+} was checked by placing a batch of the clinoptilolite in contact with an ammonium solution for five days, after which analysis of the solution by ion-exchange chromatography revealed the presence of small amounts of Mg^{2+} ions, thus suggesting exchange of Mg^{2+} and ammonium ion.

The same general procedure was adopted in the case of the Purolite MN500 after the first breakthrough. In this case only one further cycle of uptake and breakthrough was studied and the results are shown in Fig. 6. There is no discernible change in the breakthrough behaviour after the first cycle of regeneration and uptake.

Clinoptilolite which was exhausted with ammonium ion in the presence of citric acid after one cycle (Fig. 3) was regenerated and its breakthrough performance determined for a number of successive cycles of uptake–breakthrough–regeneration, in the presence of citric acid. The results of this comparison are shown in Fig. 7. Similar behaviour was observed, although the slow breakthrough in run 1 was replaced by much sharper breakthrough in subsequent runs, as was similarly observed in the absence of citric acid (Fig. 5). Comparison of Figs 5 and 7 shows that the overall removal capacity for ammonium ion appears to be reduced in the presence of citric acid, possibly due to competition from H^+ ions. Typically the reduction is reflected in a reduction of breakthrough capacity

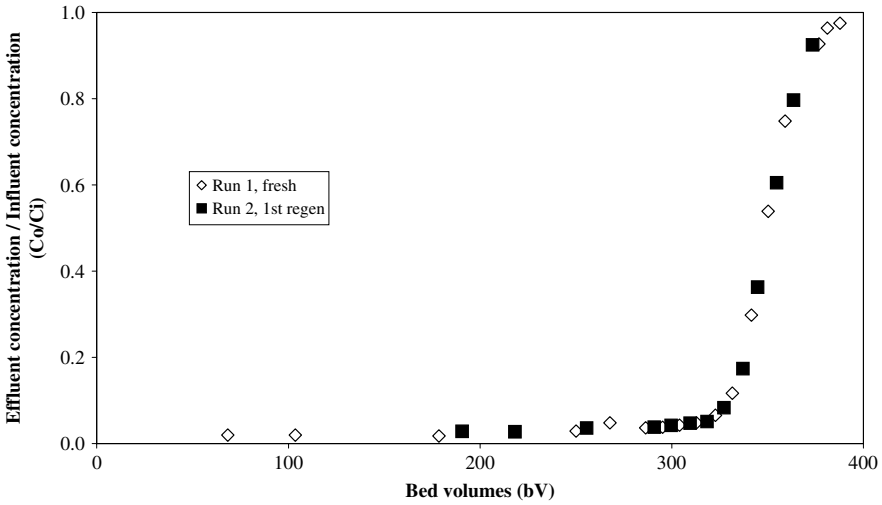

Figure 6. NH_4^+ breakthrough and regeneration onto Purolite MN500.

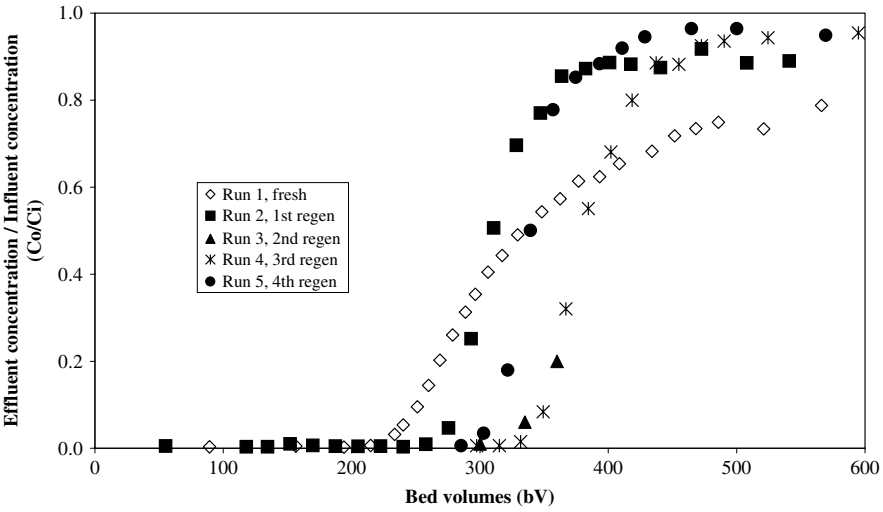

Figure 7. NH_4^+ breakthrough and regeneration onto clinoptilolite with citric acid present.

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from 400 to approximately 300 bv. The capacity in run 5 is observed to be less than that for run 4, which might be on account of some degradation of the zeolite by the acid. Clinoptilolite is likely only to suffer a minor capacity loss due to its high silica to aluminium ratio, unlike other zeolites with higher aluminium ratios, which can be totally degraded.[15–17]

Similar measurements were made using regenerated batches of clinoptilolite in the presence of WPI (Fig. 8) and for MN500 in the presence of citric acid and WPI, respectively. The results for the MN500 are shown in Figs 9 and 10, respectively. The breakthrough data presented in Fig. 10 showed that the presence of whey protein had no effect on the uptake of NH_4^+ by the MN500 even after three regenerations This contrasts with the enhancement observed during the analogous experiments involving clinoptilolite.

In the case of ammonium ion uptake on to MN500 in the presence of citric acid the breakthrough capacity is significantly reduced, from 320 bv to 220 bv (Fig. 4). This was also true the case of the clinoptilolite in the presence of citric acid, with the difference becoming more marked after the first and subsequent regenerations. However, the data in Fig. 9 show that virtually no further reduction in breakthrough capacity of MN500 in the presence of citric acid is observed after the first regeneration.

CONCLUSIONS

In each case NH_4^+ was successfully removed by the three exchangers. Dowex 50w-x8 showed the highest capacity. Purolite MN500 showed the sharpest breakthrough characteristics.

In the case of clinoptilolite, the regeneration of the zeolite after breakthrough increased the breakthrough capacity each time up to and including the fourth regeneration. The regeneration also led to sharper breakthrough in the case of clinoptilolite. The presence of organic compounds had a significant effect on the total uptake of ammonium ion by clinoptilolite. The presence of citric acid exerted a negative influence

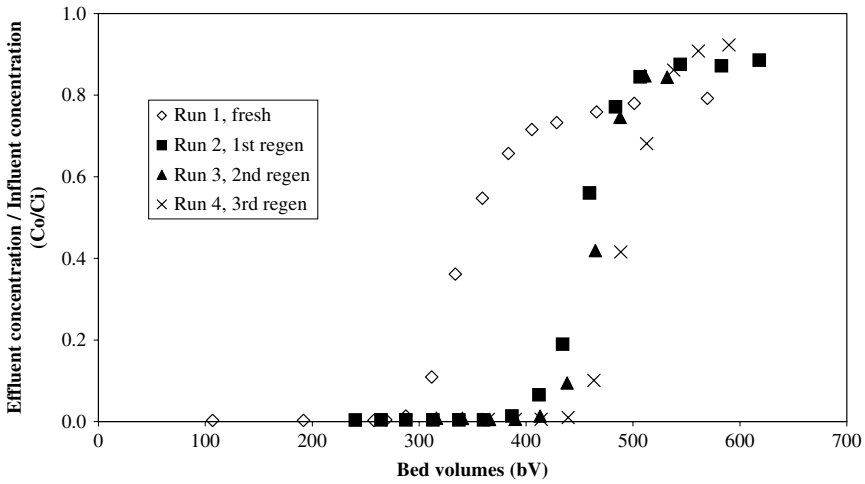

Figure 8. NH_4^+ breakthrough and regeneration onto clinoptilolite with whey protein present.

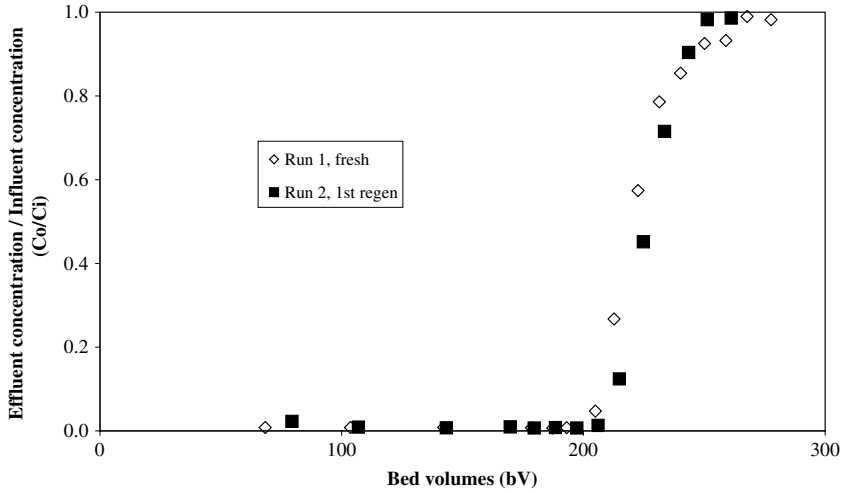

Figure 9. NH_4^+ breakthrough and regeneration onto Purolite MN500 with citric acid present.

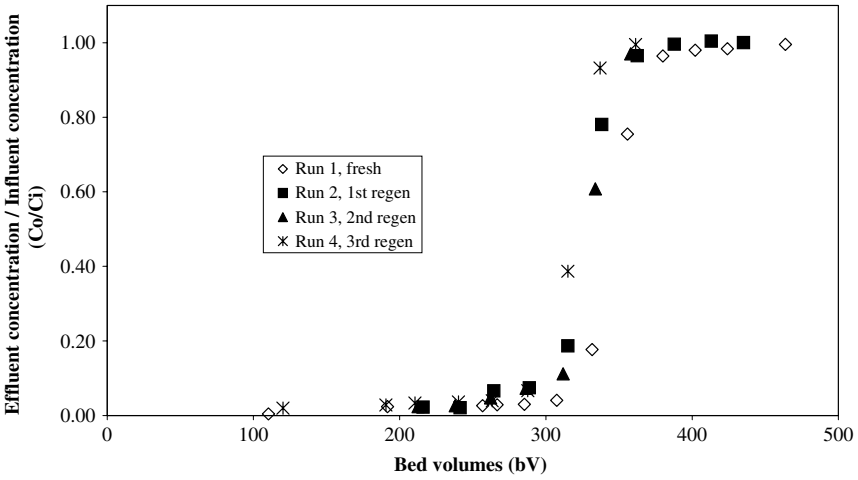

Figure 10. NH_4^+ breakthrough and regeneration onto Purolite MN500 with whey protein present.

on breakthrough capacity. The presence of whey protein isolate increased the breakthrough capacity by approximately 10 %.

In the case of the Purolite MN500, the presence of citric acid had a significant effect, reducing breakthrough capacity by approximately 50 %. In contrast, the presence of whey protein isolate showed no significant influence.

The presence of Mg^{2+} in fresh clinoptilolite may not be removed by sodium ion conditioning but may be displaced by ammonium during uptake. The displacement of magnesium from fresh clinoptilolite by ammonium ion was detected and could partly explain the increase in breakthrough capacity of the clinoptilolite after each of the first four regenerations.

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