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# Intensification of ammonia removal in a combined ion-exchange and nitrification column

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**Abstract**

The removal of ammonium ion from wastewater is an important part of tertiary wastewater treatment and is increasingly necessary to meet drinking water and discharge standards being applied in much of the developed world. The use of nitrification filters is an established technology which involves the biological oxidation of ammonium ion to the more benign nitrate ion. An alternative technique for ammonia removal is the use of ion-exchange however the capital costs can be significant and the economics of chemical regeneration may be prohibitive for large volume applications. In this paper we examine the combination of nitrification and ion-exchange in a packed bed system using the natural zeolitic ion-exchangers, clinoptilolite, and mordenite on which colonies of nitrifying bacteria are cultivated. The combined system intensifies ammonia removal and offers the possibility in principle of a more robust technique less sensitive to rapid perturbations in ammonia concentration and less costly than in a single ion-exchange process. One limitation of this approach is the rapid consumption of oxygen in the biologically active column. The paper demonstrates a novel technique for enhancing the oxygen concentration in a combined ion-exchange and nitrification packed column. The performance of fixed beds of clinoptilolite and mordenite in the presence of nitrifying bacteria is compared to that in columns in which only ion-exchange is occurring. Two modes of aeration are compared: (1) external aeration in which the feedwater is aerated conventionally by gas bubbling; (2) in situ aeration in which a membrane-aeration unit is incorporated into the packed bed. The ammonia removal in the presence of the nitrifiers is significantly intensified. Both methods of aeration provided a comparable further enhancement. In the case of the membrane system the air consumption was reduced by a factor of 60.


*Keywords:* Ion-exchange; Water treatment; Nitrification; Zeolites; Aeration

## 1. Introduction

Ammonia is the most commonly occurring nitrogenous pollutant in wastewater [1]. Ammoniacal nitrogen reaches surface or underground water from sewage, agricultural and industrial sources. The industrial context of this problem include: oil refineries, coal gasification plants, slaughterhouses, dairy plants, distilleries, fertilizer plants, pharmaceutical plants, glass production plants and cellulose and paper manufacturing plants [2]. Due to sustainable engineering and strict legislations that control industrial effluents, sewage water is nowadays the major ammonia source in municipal wastewater systems. The problem of ammonia removal is even more important in recirculating systems used in aquaculture. Intensive fish farming is based on usage of protein rich food [3,4]. Ammonia toxicity to fish and other aquatic animals is very significant and concentrations in the range 0.2–0.5 mg/l can be fatal [2]. Some of the problems that ammonia can cause include toxicity to fish and other aquatic animals, depletion of dissolved oxygen levels [5,6], and eutrophication [7].

The guide levels for ammonia released into the receiving water vary in different parts of the world. The Environmental Protection Agency [8] and the American Committee on Water Quality Criteria recommend a value of below 0.02 mg/l N-$NH_3$ [6,9]. The Council of the European Communities suggests a guide level of 0. 05 mg/l N-$NH_3$, with a maximum value of 0.5 mg/l N-$NH_3$ [10].

The classical solution to the problem of ammonia removal is nitrification, which is a component of biological wastewater treatment. Typically ammoniacal nitrogen can be reduced by up to 90% during secondary treatment processes which promotes nitrification by using fixed film biological filters, which include

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trickling filters, rotating biological contactors, and reciprocating biofilters. In each case the maintenance of high dissolved oxygen concentrations is crucial to sustaining effective ammonia removal [11]. These are "attached growth systems" which feature increased surface area available for bacterial growth. There are some limitations to these systems, including sensitivity to toxic shock; pH sensitivity; requirement of high oxygen levels; low temperatures.

With respect to shock loading, Kruner and Rosenthal [12] reported that an increase in total ammonia concentration by up to 80% in the range 0.15–1.8 mg/l reduced nitrification rate in a trickling filter by 60%. Nitrification can also be limited if the dissolved oxygen (DO) concentration is limited for example within the sub-saturation range of 0.5–2.5 mg/l [8]. When dissolved oxygen concentration drops below 1 mg/l, de-nitrification can occur due to the anoxic conditions. Semmens et al. [13] found that the nitrification rate was invariant with respect to DO above 6 mg/l. Below this value the reduction in rate was significant and reached only 33% of maximum effectiveness when the DO concentration was reduced to 2 mg/l.

An alternative to biological treatment is ion-exchange which provides a technique which is responsive to shock loading and can operate at lower (and higher) temperatures. A significant drawback of ion-exchange is the need for regeneration which can incur associated reagent costs. Another possible drawback is that desorption may occur due to shift in the exchange equilibria when the ammonia concentration in the influent drops. This may result in the discharge of ammonia into the eluent stream.

A biological process in combination with ion-exchange might offer some improvements, exploiting the advantages of both techniques. Such a system has the potential to be responsive to shock loading and to yield significantly longer cycle times between regenerations, and offer a reduction in effluent arising because of the conversion of ammonia to nitrate. PH is a critical parameter since ion-exchange efficiency for ammonia removal depends on pH, since the ionized $NH_4^+$ form of ammonia is the entity removed by ion-exchange. Sheng and Chang [14] strongly recommended a pH value below 7 for ion-exchange ammonia removal.

Biological regeneration of an ion-exchanger which is loaded with ammonia is also a possible option and is based on bacterial ammonia oxidation. Demonstration of this approach using ammonia loaded clinoptilolite [1], was partially successful, reducing ammonia loading by approximately 75%. There was clear evidence that oxygen depletion was a key factor in incomplete biological regeneration. In an earlier study Semmens et al. [13,15] performed biological regeneration of columns of clinoptilolite loaded with ammonia and it was concluded that the nitrification rate was the rate limiting step rather than the diffusional release of ammonia.

Sand, plastic media, activated carbon and some ion-exchange materials support bacterial growth. Many natural surfaces, including those of nitrifying bacteria, are negatively charged [16]. Preston and Alleman [17] suggested that negatively charged nitrifying bacteria are electrostatically bound onto a zeolitic crystal surface.

The study of biologically active ion-exchange has mostly concerned treatment of wastewater from a secondary effluent or some other wastewater with an already established population of nitrifying bacteria. An ion-exchanger might be added into the suspended growth reactor where nitrification already occurred [18], or it could be introduced into the process in the form of packed beds [1,27]. A simple addition to the reactor does not allow regeneration of the exhausted material, which means that if saturation happens, instead of combined ion-exchange and nitrification only the latter will occur. Yang et al. [19] immobilized zeolite particles together with nitrifying bacteria in sodium alginate pellets to improve ammonia transfer to the entrapped bacteria. However, the entrapment method did not show good results since it took 2 days to establish nitrification in the batch reactor due to slow oxygen and ammonia transfer through the pellets. The technique was only effective when initial ammonia concentrations above 50 mg/l were used. The presence of high ammonia/oxygen ratio within the pellets inhibited Nitrobacter activity, limiting nitrification to the production of nitrite which can be significantly toxic.

Beler-Baykal et al. [20] introduced ion-exchanger into an already established biological nitrifying filter in the form of a packed bed and obtained better results in resolving shock loading response, comparing favourably with a single biofilter or an ion-exchange column. In the case of the biofilter a significant lag was observed. The integration of the ion-exchange column demonstrated the ability to enhance the response speed to shock loading. However another issue raised in the work of Beler-Baykal was the problem of ion-exchange uptake of other cations from the wastewater during the post-inoculation conditioning of the biofilter. This suggests that the two systems should be integrated only after the biofilter is conditioned.

Oxygen limitation is a phenomenon associated with fixed bed nitrifying filters and is also an issue in the case of biologically activated ion-exchange. McVeigh [1] observed total oxygen depletion after passing live adapted cultures of nitrifying bacteria through columns of clinoptilolite loaded with ammonium ion. Lahav and Green [21] also observed that oxygen limitation during nitrification in packed columns of the zeolite. In both studies the inlet solutions were saturated with oxygen using intensive aeration.

Another possibility for overcoming oxygen limitation in packed bed nitrification systems is membrane aeration [22]. One option may be in-column membrane aeration, since conventional aeration can significantly modifying hydraulic performance and mass transfer. Kuhlman [23] successfully performed bubble free aeration with a silicone tubing oxygenation system in an aerobic animal cell culture bioreactor.

A further potential limitation of promoting active biological cultures in ion-exchange columns is the obvious problem of fouling. Semmens and Porter [24] advocated a backwashing procedure to prevent. More recently in other work with clinoptilolite, Lahav and Green [21] stated that even the thickest biofilm did not have any influence either on zeolite's removal capacity or on the process kinetics.

From the review of literature it is clear that oxygen depletion in fixed bed nitrification columns is an important factor

and this is also the case for ion-exchange columns which host active nitrifying bacteria. Therefore one of the prime goals of the study described here was to determine options for reducing oxygen limitation in biologically active ion-exchange columns, comparing external aeration of feedwater with in situ aeration using a tubular membrane.

The performance of New Zealand clinoptilolite was compared directly with that of New Zealand mordenite for biologically active ion-exchange removal of ammonia from wastewater. Fixed bed columns of these materials were used for assessing the effectiveness of aeration in enhancing biological activity in each case, and the consequential effects upon ammonia removal from wastewater determined.

## 2. Materials and methods

### 2.1. Design of the columns

Two column designs were evaluated. The first was a simple packed bed of ion-exchanger particles, Fig. 1 [1,6], operated in up-flow mode.

The second was a new design, Fig. 2, which was also a packed bed but was modified to facilitate in-line aeration within the bed in order to improve conditions for nitrification to occur. The major addition comprised a mesh cylinder located coaxially along the center line of the column. Air permeable, peroxide-cured silicon tubing was spiral wound onto the outer surface

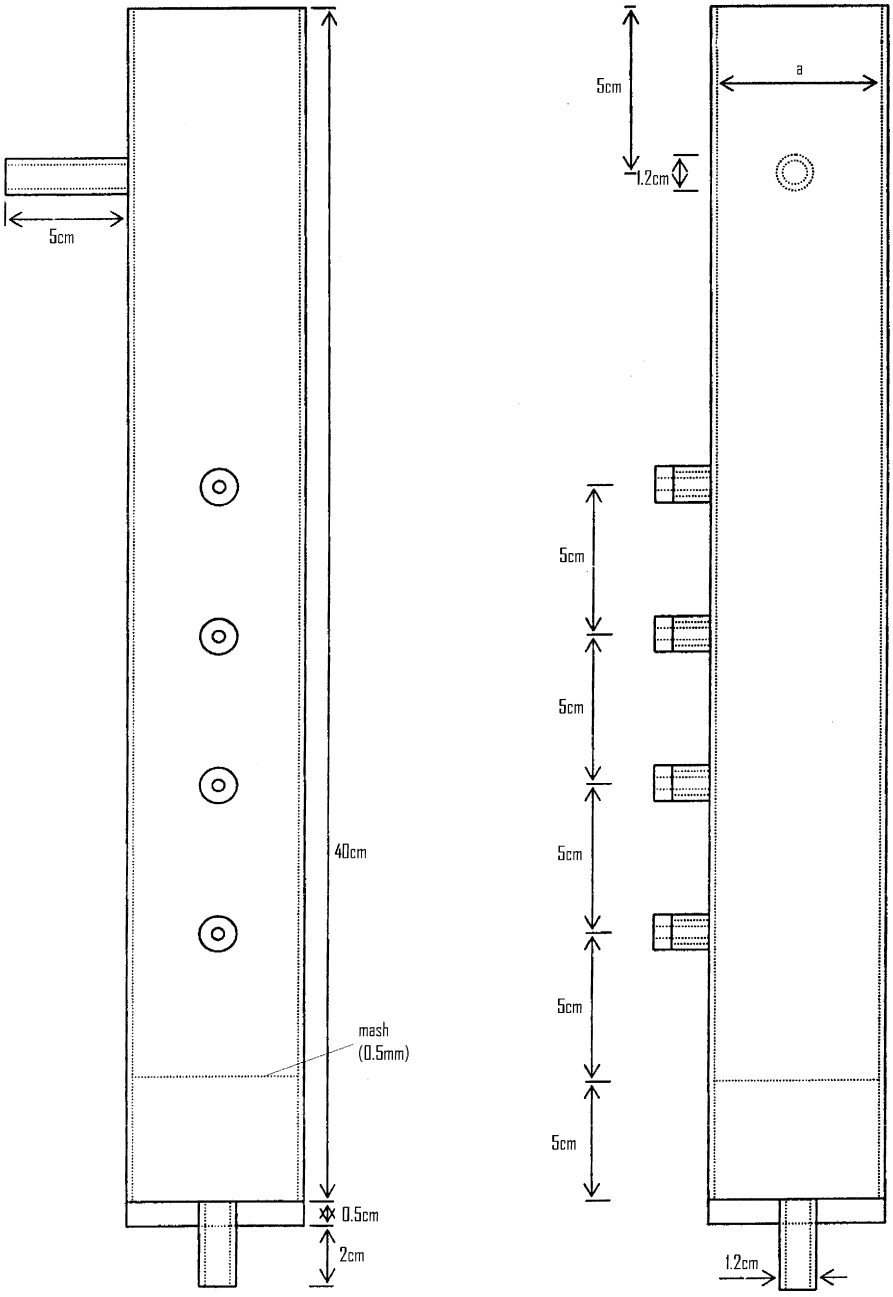


Fig. 1. Packed bed ion-exchange column.

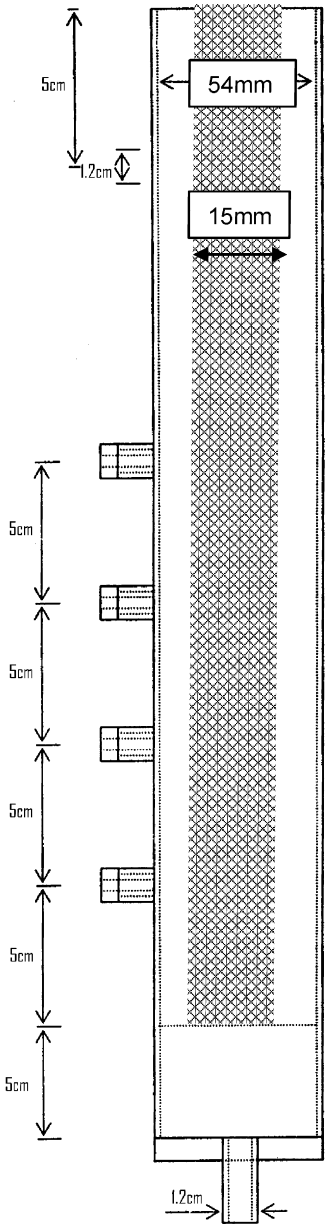


Fig. 2. Packed bed ion-exchange column with intra-bed membrane aeration.

of the mesh cylinder with the goal of continuously introducing air into the bed along its entire length. Permeability of the tubing was $7961 \times 10^{10}$ cm$^3$ s$^{-1}$ cm$^{-2}$ cm Hg$^{-1}$. The internal and external tubing diameters were 2.4 and 4 mm, respectively. The tubing was sealed at one end with a supply of compressed air at the opposite open end of the tube. The ion-exchanger particles were packed around the exterior of cylinder and in the center. Each column was equipped with sampling points along its length. The columns were incorporated into the experimental arrangement shown in Fig. 3.

Prior to loading into the columns, batches of clinoptilolite and mordenite were crushed in a jaw crusher "Retsch BB 50" and classified to a size range of 0.5–0.71, 0.71–1 and 1–1.4 mm. The materials were washed to remove any fines and other undesirable material followed by chemical conditioning in a series of batches of sodium chloride solution (1 M) for periods of approximately 7 days in order to ensure complete conditioning into the sodium form. The materials were washed to remove excess NaCl until a negative reaction for chlorides with $AgNO_3$ was achieved and dried at 65 °C for 24 h. Preconditioned material was maintained in a desiccator prior to use.

In order to prevent air bubbles within the column, water was circulated through each column prior to the addition of wet exchanger. The feed solution was pumped into each column in up-flow mode from a 5 l vessel of stock solution which was made up using standard solutions of ammonium chloride and from the appropriate batch of water. The inlet ammonia concentrations studied were in the range 5–150 mg/l N-$NH_4^+$. The desired flow was maintained using Watson–Marlow and Cole–Palmer peristaltic pumps which were calibrated prior to use and regularly checked during the experiments. Material was packed to a height of 200 mm and the feed flowrate for each column was chosen to ensure that the flow velocity for columns of different diameters was the same. The maximum flow rate was 4 bed volumes/h (note the term bed volumes (BV) refers to the volume of water passed through the bed expressed in terms of the total volume of the packed bed). The pH was regularly checked and if needed, sodium bicarbonate was introduced with the feeding solution to increase the pH value within the column.

Three types of feedwater were used: deionized water, water from a salmon fish farm and water from a local creek. Each batch was analysed and the chemical compositions are shown in Table 1.

In the experiments involving nitrification with external aeration, the feed water aeration was conducted in a separate aeration tank. Air was introduced into the tank using an aquarium air pump type JUN, ACO-5502 and diffuser with a maximum air flow of 3 l/min. The aerated water was transferred to a second tank as shown in Fig. 3 to allow undissolved air bubbles to coalesce and separate to minimize the introduction of gas bubbles into the column. Solutions in both tanks were maintained at 5 °C (Julabo type circulator, F10-C) to minimize significant biological activity. The solutions were preheated to 20 °C immediately prior to introduction to the columns which were maintained at 20 °C. Literature data show that the rate of nitrification stays at 90% of the optimum value over the temperature range 15–30 °C [1]. Experiments on non-biologically active materials were similarly conducted except without aeration.

The aeration rate, the internal diameter of the column, the flow rate of the water treated, the particle size of the material

Table 1
Composition of the water used in the experiment

| (mg/l) | Salmon fish farm water | Creek water |
|---|---|---|
| $Na^+$ | 8 | 7 |
| $K^+$ | 2.19 | 0.9 |
| $Ca^{2+}$ | 22.4 | 18.8 |
| $Mg^{2+}$ | 2.4 | 2.2 |
| TOC[a] | 13.94 | 4.08 |
| N-$NH_4^+$ | 0.97[b] | 0.02 |

[a] Total organic carbon.
[b] Sampling point was just before the biofilter, when the ammonia level was the highest.

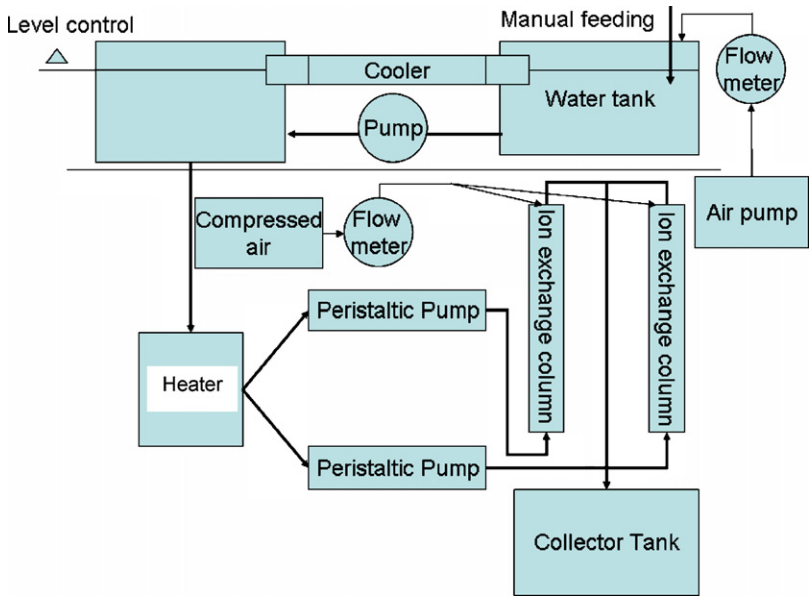


Fig. 3. Flow diagram and experimental arrangement.

used, the temperature and the inlet ammonia concentration were the main variables.

Biological activity was established on the columns of ion-exchanger by passing 48 bed volumes (BV) of bacteria rich and low ammonia concentration solution at a rate of 0.5 BV/h. The live culture solution was an enriched solution of an adapted culture of samples taken from a municipal wastewater treatment plant. Subcultures were prepared by inoculating 50 ml of a fully grown enriched culture into 500 ml of fresh broth. Each column was coated with aluminum foil to prevent light exposure which would have a detrimental effect on the activity. Continuous aeration at a rate of 70 $cm^3$ air $min^{-1}$ was applied. The protein concentration in the solution was checked before and after the solution went through the column to ensure that the column retained biomass.

### 2.2. Analytical methods

#### 2.2.1. Ammonia

Ammonium analyses, as total ammoniacal nitrogen ($NH_4^+$ and $NH_3$) in solution were conducted using an ion selective electrode and ion meter (Orion 95-12, and EA040) and checked by the Nesslerisation technique [25].

#### 2.2.2. Oxygen

Dissolved oxygen concentration was measured using an oxygen probe (YCI model 5739) with a temperature probe built in, attached to a meter YCI model 57.

#### 2.2.3. Metal cation measurements

Metal cation ($K^+$, $Mg^{2+}$, $Ca^{2+}$) concentrations were monitored using a Waters Non-Suppressed Ion Exchange Chromatograph (Dionex DX-120, Millipore Corp.), with Waters baseline 810 software and an Alltech universal cation column with 3 mM methane sulfonic acid like an eluent.

#### 2.2.4. pH measurements

Measurement of pH was conducted using a Hanna meter model pH211 with the glass-body combination pH probe, HI 1131B incorporating a temperature probe and compensation.

#### 2.2.5. Nitrite and nitrate analysis

Nitrite and nitrate were accurately determined using a Hach DR/2000 spectrophotometer after a rapid pre-determination using Merckoquant nitrite and nitrate test strips. They provided us with the information as to whether nitrites and nitrates were present at all and how much to dilute samples so that the results fit into the range of the applied method.

## 3. Results and discussion

The first experiments were designed to check whether aeration within the column would have any impact on the ammonia removal. The performance of the ion-exchange columns in all cases is expressed in terms of the column breakthrough. This is the point at which the exit concentration from the column starts to rise rapidly, indicating that the column is close to full loading with ammonium ion. Fig. 4 presents the comparison between the ammonia uptake in the columns packed with clinoptilolite, with and without aeration. It is concluded that in the absence of inoculated bacteria aeration had negligible impact upon the overall performance of the columns.

Fig. 5 shows that clinoptilolite which was not biologically activated performed well up to the 60 BV of treated solution passed through the bed. By contrast, clinoptilolite with nitrifying bacteria introduced prior to the experiment a 50% increase in breakthrough volume was observed. The introduction of bacteria yielded an apparent increase in uptake capacity 0.15 mequiv./g to an effective value of 0.22 mequiv./g. The slope of the breakthrough curves remained the same for both of the columns, and the presence of the bacteria appears to postpone the break-

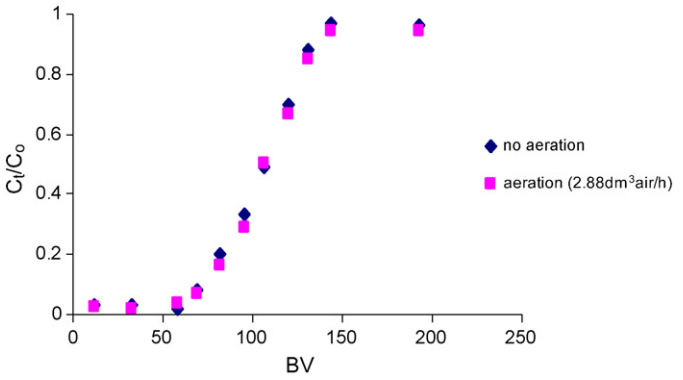


Fig. 4. The uptake values for the packed bed of clinoptilolite—the effect of aeration. Particle size: 0.7–1.4 mm, initial ammonia concentration: 40 mg/l N-$NH_4^+$, flow rate: 2 BV/h, salmon fish farm. $C_t$ = ammonia concentration in the exit stream from the column (mg/l); $C_0$ = ammonia concentration in the feed stream to the column (mg/l).

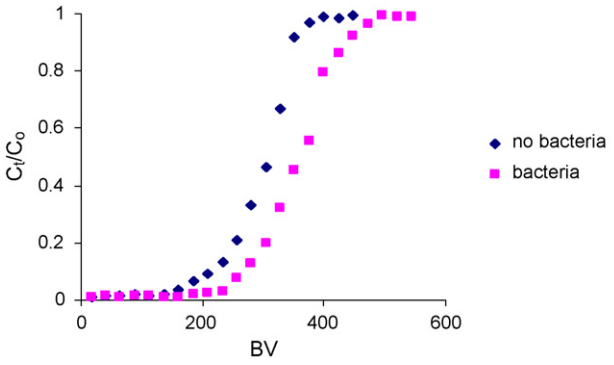


Fig. 6. The uptake onto biologically active and non-active mordenite. Particle size: 0.7–1.4 mm, initial ammonia concentration: 40 mg/l N-$NH_4^+$, flow rate: 1 BV/h, creek water. $C_t$ = ammonia concentration in the exit stream from the column (mg/l); $C_0$ = ammonia concentration in the feed stream to the column (mg/l).

through with no significant effect upon the kinetics. McVeigh [1] also obtained breakthrough curves with very similar slope when comparing sterile and biologically active beds, for the removal of wastewater which itself exhibited low levels of biological activity. McVeigh obtained a different slope of the curves only when wastewater with already established bacteria activity was passed through the biologically active bed. This suggested that the breakthrough performance can be significantly improved if nitrification is already established in the treated wastewater. The current results were with a column mean retention time of 30 min. These compare with data for trickling filters [28], in which 95% nitrification was observed at a retention time of 1 h and at a temperature of 22 °C.

Other work [26] showed that ammonia concentrations were reduced from 27 to 3 mg/l $NH_3$-N—at a retention time of 38 min. However in this latter work, the growth time prior to the experiment was 10 weeks, contrasting with the current research in which a period of 3 weeks from inoculation into the growth media was used followed by a period of 96 h after inoculation

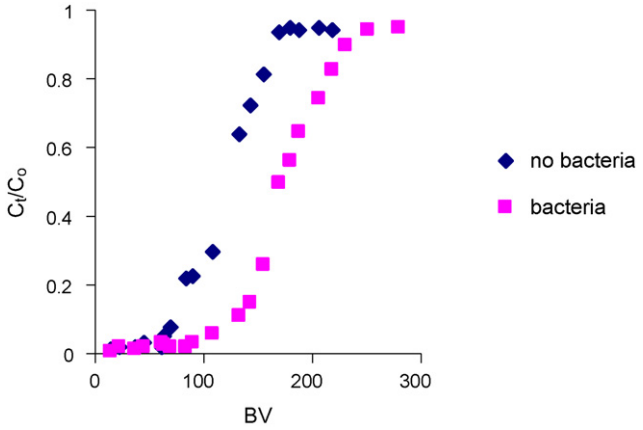


Fig. 5. The uptake onto biologically active and non-active clinoptilolite. Particle size: 0.7–1.4 mm, initial ammonia concentration: 40 mg/l N-$NH_4^+$, flow rate: 1 BV/h, creek water. $C_t$ = ammonia concentration in the exit stream from the column (mg/l); $C_0$ = ammonia concentration in the feed stream to the column (mg/l).

on the ion-exchanger. In the case of ion-exchangers, extended periods of bacterial growth on the packed bed may cause significant capacity loss due to the adsorption of ions present in the bacteria broth.

Fig. 6 shows that bacteria introduced into the column packed with biologically active mordenite prolonged the bed service time from 161 to 233 BV; increasing the effective breakthrough capacity from a value of 0.30 mequiv./g without bacterial activity, to a value of 0.41 mequiv./g when bacteria were active. Nitrifying bacteria only appear to enhance the ammonia removal performance prior to breakthrough as reflected by the similar slopes of the breakthrough profiles.

Although no detailed results are presented here, one unusual observation was the apparent retention of some biological activity after chemical regeneration. Regenerated columns were used for a new set of experiments with bacteria being introduced only in one, presuming that the other column would not exhibit bacteria activity any more. However, biological activity was present in both of the columns, leading to the conclusion that some of the bacteria can survive a regeneration procedure. Retention of some biological activity after alkaline regeneration may actually improve overall performance of the column, since established colonies of nitrifying bacteria proved to perform better compared to newly established ones.

Since all the experiments involving bacteria and real wastewater did not allow creation of identical experimental conditions, the only way to compare the performance of biologically active clinoptilolite and mordenite was to study the columns simultaneously.

Inlet ammonia concentrations of 40 mg/l were used initially to strongly promote establishment of adapted cultures of nitrifiers. The concentration then was progressively reduced from 40 to 20 mg/l and then to 5 mg/l. Shock loading response was determined by sudden increase of inlet ammonia to 40 and 80 mg/l in two separate tests. The air flowrate to each column was varied across the range 0–2.88 $dm^3$/h air. Fig. 7 shows the variation of the outlet ammonia concentrations for each of the columns with respect to volume of water treated (expressed as bed volumes—BV). Fig. 8 shows the corresponding varia-

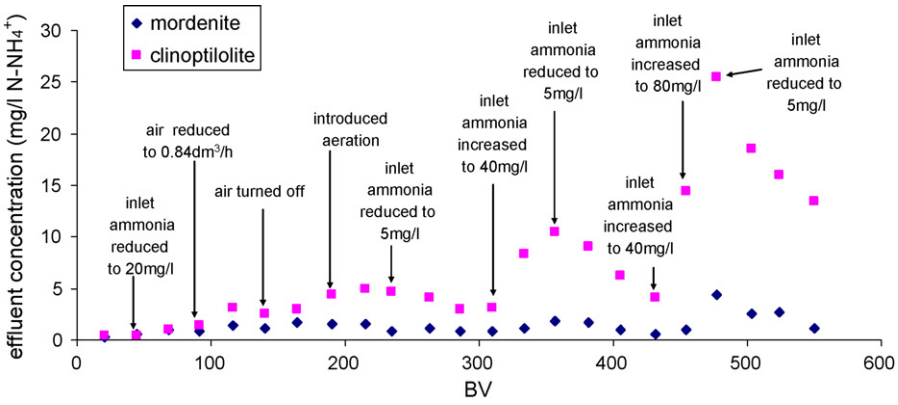


Fig. 7. Ammonia uptake onto the biologically activated columns. If not indicated differently, particle size: 0.7–1.4 mm, number of regenerations: 2, initial ammonia concentration: 40 mg/l N-$NH_4^+$, flow rate: 1 BV/h, aeration: 2.88 $dm^3$/h, creek water (Table 1).

tion of the nitrate concentrations in both columns during the experiment.

The results in Fig. 7 show that mordenite performed significantly better than clinoptilolite. This is consistent with the higher capacities observed in both batch and continuous column experiments reported above. The overall fluctuations in ammonia concentration showed the same general trend for both columns, but with the clinoptilolite column exhibiting fluctuations of greater magnitude.

The change in the inlet ammonia concentration showed a significant influence upon nitrification rate, see Fig. 8 where the variation in exit nitrate concentration is presented for each column. The initial decrease in nitrate concentration may be explained by wash-out of the nitrates which were present in the column as a result of the bacterial immobilization procedure. The reduction of inlet ammonia concentration to 20 mg/l initiated a temporary reduction in bacteria activity which is reflected in a short-term reduction in nitrate levels. The nitrate levels are observed to increase again at 110 BV as the nitrifiers adapted to the new substrate concentration. The next decrease in nitrate concentration was observed when inlet ammonia concentration was reduced to 5 mg/l at 350 BV. This change had a significant impact on the nitrification in the case of the clinoptilolite since an adaptation time of 48 h (24 BV) was observed. Subsequent increase of inlet ammonia concentration to 40 mg/l produced only a slightly negative response with respect to nitrification, showing less effect compared with the response upon reduction of ammonia feed concentration to biological activity, but the biological part of the reactor suffered less than in the case when inlet ammonia was reduced to 5 mg/l.

Higher levels of bacterial activity and greater ion-exchange capacity would explain why mordenite responded to sharp increases in ammonia levels significantly better than clinoptilolite. In the final part of the experiment at 450 BV (Figs. 7 and 8), the inlet ammonium ion concentration was increased to a value of 80 mg/l. In the case of the mordenite the response in respect of outlet ammonia concentration is much more favourable compared with that of the clinoptilolite. In the case of the mordenite the maximum outlet ammonia concentration observed was 5 mg/l, compared to 25 mg/l in the case of clinoptilolite. In the former case the concentration was reduced to 1 mg/l within 72 h. The second shock loading had a greater effect on the nitrification process within both columns. After the inlet ammonia was readjusted, it took the approximately 48 h for the nitrification process to readjust (increase in nitrate levels after 524 BV). The reason for this larger effect was probably capacity loss due to partial exhaustion of the exchanger. Biological activity within the bed would only regenerate sites occupied by ammonium

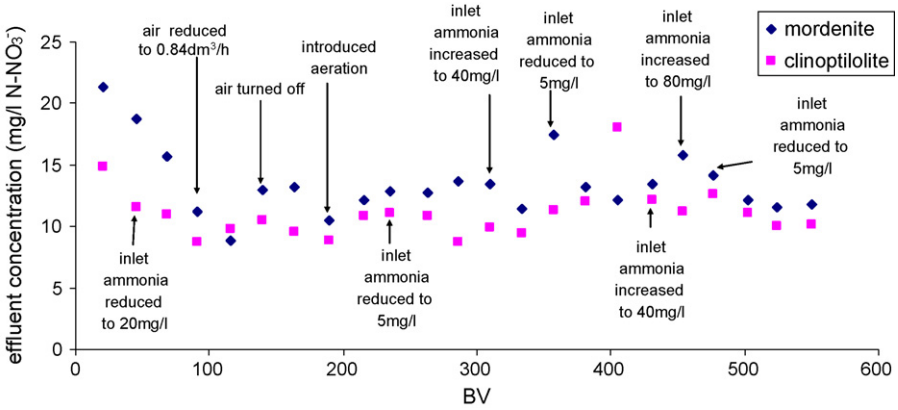


Fig. 8. Nitrate concentration within the biologically activated columns. If not indicated differently, particle size: 0.7–1.4 mm, number of regenerations: 2, initial ammonia concentration: 40 mg/l N-$NH_4^+$, flow rate: 1 BV/h, aeration: 2.88 $dm^3$/h, creek water (Table 1).

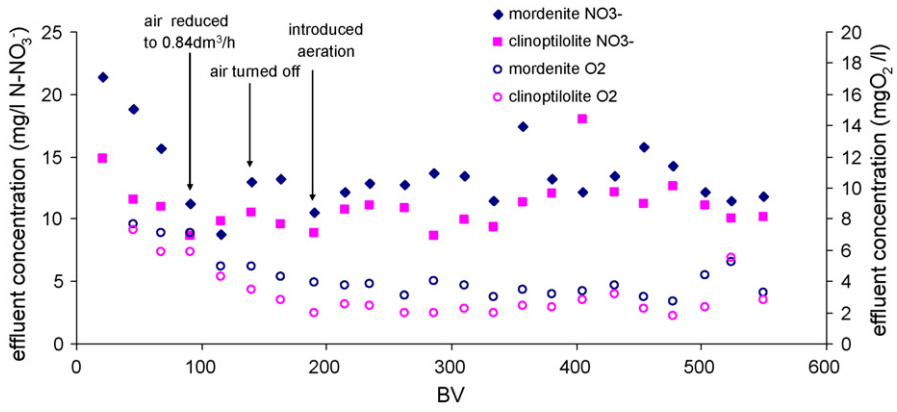


Fig. 9. Nitrate and oxygen concentrations within the biologically activated columns. If not indicated differently, particle size: 0.7–1.4 mm, number of regenerations: 2, initial ammonia concentration: 40 mg/l N-$NH_4^+$, flow rate: BV/h, aeration: 2.88 $dm^3$/h, creek water.

cations. Thus loss of exchange capacity per se would reduce the buffering capacity of the system, leaving nitrifying organisms more exposed to a change in the inlet ammonia concentration, which lead to short-term reductions in biological activity.

The results obtained for equalization of the inlet ammonia peaks on biologically active mordenite are very good when compared to the results available from the literature. Beler-Baykal et al. [20] increased the inlet ammonia concentration from 5 to 15 mg/l for the time period of 4 h and the outlet ammonia concentration increased to the value of more than 2 mg/l. They used a bed packed with clinoptilolite and secondary wastewater with already established biological activity. In our experiments, in the case of the mordenite, with the inlet ammonia concentration of 40 mg/l during the initial period of 24 h, the effluent ammonia concentration was maintained below the value of 2 mg/l, theoretical residence time within the columns was almost the same.

The results in Fig. 9 show that the oxygen levels within the clinoptilolite column were consistently lower compared with those for the mordenite column. Nitrate levels were also lower for the clinoptilolite, which strongly suggests that the drop in oxygen level was not accounted for by enhancements in nitrification rate. One possible explanation is that the air distribution within the clinoptilolite column is less effective. This would be possible since the brittle nature of clinoptilolite makes it more susceptible to in-column comminution leading to reductions in free space through which air is effectively transported and absorbed. Fluid phase residence time measurements for each column showed a lower mean residence time in the case of clinoptilolte which would be consistent with lower bed voidage and less accessibility for gas/liquid contact.

Reduction of the air rate from 2.88 to 0.84 $dm^3$/h at 95 BV (Fig. 9) initiated slower nitrification in the mordenite's bed as evidenced by the reduction in nitrate level. However, this change in inlet air rate did not have the same effect on the nitrification process within the clinoptilolite. A complete shut down of aeration caused a drop in nitrate level in both columns, which increased once again when the level of aeration was resumed at 2.88 $dm^3$/h. As mentioned above, these variations in bacterial activity due to variations in the oxygen concentration did not cause significant change in the effluent ammonia concentration within the column packed with mordenite. This contrasts with the case of the clinoptilolite where decrease or shutting off of aeration increased effluent ammonia concentration, Fig. 7.

Overall, comparing the performance of clinoptilolite with that of mordenite over the various conditions indicated in Figs. 8 and 9, shows that the mordenite columns were on the whole more effective than the columns of clinoptilolite. However towards the later stages of the experiment, the nitrate production levels and the oxygen depletion levels of the two columns converge. In this case this suggests that the ammonia removal capacity of the clinoptilolite by means of nitrification becomes more effective. This could be explained by longer adapation and colonization times in the case of the clinoptilolite compared with mordenite. Another possibility is that the ammonia uptake kinetics are slower in the case of mordenite, resulting in a greater role for nitrification during ammonia removal in the earlier stages of the experiment, compared with the clinoptilolite. Direct comparison of the ion-exchange kinetics for the two materials in the absence of nitrification would be necessary to confirm this possible explanation.

Fig. 10 shows the ammonia uptake onto the mordenite column of the modified design incorporating intra-bed membrane

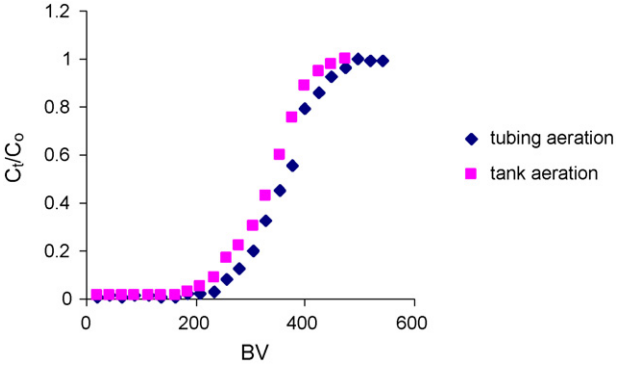


Fig. 10. Ammonia uptake onto the biologically activated columns of mordenite. Particle size: 0.7–1.4 mm, initial ammonia concentration: 40 mg/l N-$NH_4^+$, flow rate: 1 BV/h, aeration: 2.88 $dm^3$/h (tubing) and 180 $dm^3$/h, creek water. $C_t$ = ammonia concentration in the exit stream from the column (mg/l); $C_0$ = ammonia concentration in the feed stream to the column (mg/l).

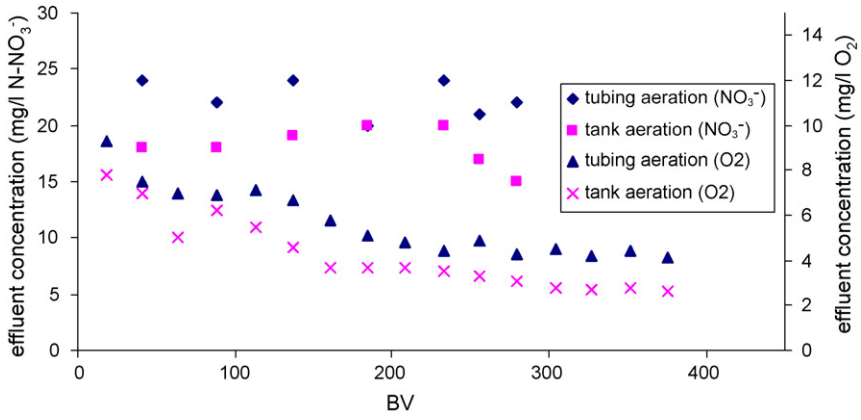


Fig. 11. Nitrate and oxygen levels within the biologically activated columns of mordenite. If not indicated differently, particle size: 0.7–1.4 mm, initial ammonia concentration: 40 mg/l N-$NH_4^+$, flow rate: 1 BV/h, aeration: 2.88 $dm^3$/h (tubing) and 180 $dm^3$/h, creek water.

aeration. The performance is compared with that of a control column in which no air was supplied to the tubular membrane but rather operating with external pre-aeration of the feed water as described earlier.

The nitrate and oxygen concentrations in the exit solutions from these columns are shown in Fig. 11.

There is clear evidence from this preliminary experiment that intra-bed membrane aeration showed significant enhancement relative to the control. This is not so obvious from the breakthrough data shown in Fig. 10, but in terms of oxygen level, and nitrate ion production, Fig. 11 shows significant enhancement with higher levels in both cases. This strongly suggests improved oxygenation and faster nitrification in the case of the membrane-aeration system.

## 4. Conclusions

The ion-exchange breakthrough behaviour of the natural zeolites, clinoptilolite and mordenite, in the presence of nitrifying bacteria was compared. The mordenite was shown to exhibit higher breakthrough capacity in all cases.

Aeration of the feed solution to the columns of clinoptilolite had no effect upon breakthrough in the absence of nitrifying bacteria. In the presence of nitrifying bacteria the breakthrough capacities of columns of both mordenite and of clinoptilolite were enhanced in both cases. In the case of the clinoptilolite, the fractional enhancement of breakthrough capacity in the presence of nitrifying bacteria was greater than in the case of the mordenite, 50% in the case of the clinoptilolite compared to 36% in the case of the mordenite. This is a reflection of the better ion-exchange performance of the mordenite.

The rates of nitrification in columns of the mordenite showed a significant sensitivity to the aeration rate. The clinoptilolite used in the study appeared to exhibit less effective oxygen distribution compared to the mordenite. This was attributed to lower bed voidage in the case of the clinoptilolite and shorter mean residence time.

The intra-column membrane-based aeration system within each column appeared to provide higher degrees of aeration and oxygen availability compared with that observed when aeration of the feed water was conducted externally.

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## References

[1] R.J. McVeigh, The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria, PhD research dissertation, Department of Chemical Engineering, The Queens University of Belfast, 1999.
[2] U. Wiesmann, Biological nitrogen removal from wastewater, Adv. Biochem. Eng. Biotechnol. 51 (1994) 114–153.
[3] R.T. Lovel, Nutrition and Feeding Fish, Van Nostrand Rainhold, USA, 1989.
[4] A. Gross, A. Nemirovsky, D. Zilberg, A. Khaimov, A. Brenner, E. Snir, Z. Ronen, A. Nejidat, Soil nitrifying enrichments as biofilter starters in intensive recirculating saline water aquaculture, Aquaculture 223 (1–4) (2003) 51–62.
[5] J.E. Huguenin, J. Colt, Design and Operating Guide for Aquaculture Seawater Systems, Elsevier, 1989.
[6] T.C. Jorgensen, Removal of ammonia from wastewater by ion exchange in the presence of organic compounds, MSc research dissertation, Department of Chemical Engineering, University of Canterbury, 2002.
[7] G. Tchobanoglous, E. Schroeder, Water Quality: Characteristics, Modeling Modification, Addison-Wesley, 1985.
[8] USEPA, 2000 United States Environmental Protection Agency, "Manual, Nitrogen Control", EPA-625-R-93-010, Office of Research and Development, Risk Reduction Engineering Laboratory, Cincinnati, 1993.
[9] H.T. Dryden, Ammonium ion removal from dilute solutions and fish culture water by ion exchange, PhD research dissertation, Department of Chemical Engineering, Heriot-Watt University, Edinburgh, 1984.
[10] N. Woods, The removal of ammonia from industrial wastewater, MSc research dissertation, Department of Chemical Engineering, The Queen's University of Belfast, 1997.
[11] C. Bryant, W. Barkley, R. Garret, D. Gardner, Biological nitrification of kraft wastewater, Water Sci. Technol. 35 (1–2) (1996) 147–153.
[12] G. Kruner, H. Rosenthal, Efficiency of nitrification in trickling filters using different substrates, Aquacult. Eng. 2 (1983) 49–67.
[13] M.J. Semmens, J.T. Wang, A.C. Booth, Nitrogen removal by ion exchange biological regeneration of clinoptilolite, J. Water Pollut. Control Fed. 49 (12) (1977) 2431–2444.
[14] H.L. Sheng, L.W. Chang, Removal of nitrogenous compounds from aqueous solution by ozonation and ion exchange, Water Res. 30 (8) (1996) 1851–1857.

[15] M.J. Semmens, J.T. Wang, A.C. Booth, Biological regeneration of ammonium saturated clinoptilolite. Mechanism of regeneration and influence of salt concentration, Environ. Sci. Technol. 11 (1977) 260–265.
[16] M.C.M. Van Loosdrecht, J. Lyklema, W. Norde, G. Chraa, J.B. Zehnder, Electrophoretic mobility and hydrophobicity as a measure to predict the initial steps of bacterial adhesion, Appl. Environ. Microbiol. 53 (8) (1987) 1898–1901.
[17] K.T. Preston, J.E. Alleman, Co-immobilization of nitrifying bacteria and clinoptilolite for enhanced control of nitrification, in: Proceedings of the 48th Industrial Waste Conference, 1994, pp. 407–412.
[18] R.C. Sims, L.W. Little, Enhanced nitrification by addition of clinoptilolite to tertiary activated sludge, Environ. Lett. 4 (1) (1973) 27–34.
[19] P.P. Yang, S. Nitisoravut, J.Y.S. Wu, Nitrate removal using a mixed culture entrapped microbial cell immobilization process under high salt condition, Water Res. 29 (6) (1994) 1525–1532.
[20] B. Beler-Baykal, M. Oldenburg, L. Sekoulov, Post equalization of ammonia peaks, Water Res. 28 (9) (1994) 2039–2042.
[21] O. Lahav, M. Green, Ammonium removal using ion exchange and biological regeneration, Water Res. 32 (7) (1998) 2019–2028.
[22] k. Kanokwaree, P.M. Doran, Application of membrane tubing aeration and perfluorocarbon to improve oxygen delivery to hairy root cultures, Biotechnol. Programme 14 (3) (1998) 479–486.
[23] W. Kuhlman, Optimisation of a membrane oxygenation system for cell culture in stirred tank reactors, Dev. Biol. Stand. 66 (1987) 263–268.
[24] M.J. Semmens, P.S. Porter, Ammonium removal by ion exchange using biologically restored regenerant, J. Water Pollut. Control Fed. 51 (12) (1979) 2928–2940.
[25] A.D. Eaton, L.S. Cleceri, A.E. Greenberg, Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, USA, 1995.
[26] P.F. Cooper, S.C. Williams, High-rate nitrification in a biological fluidized bed, Water Sci. Technol. 22 (1–2) (1990) 431–442.
[27] Y.C. Chung, D.H. Son, D.H. Ahn, Nitrogen and organics removal from industrial wastewater using natural zeolite media, Water Sci. Technol. 42 (5–6) (2000) 127–134.
[28] R.T. Haug, P.L. McCarty, Nitrification with submerged filters, J. Water Pollut. Control Fed. 44 (1972) 2086–2102.