Introduction of some new materials for combined biological and ion-exchange wastewater treatment for ammonia removal

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Abstract

Ammonia is a water pollutant that causes serious problems in terrestrial and saline receiving waters. The classical solution to the problem of ammonia removal is biological waste treatment that can be easily inhibited by toxic shock, pH change, low dissolved oxygen concentration and low temperatures. Ion-exchange materials have been used as an alternative to the biological process. However, chemical regeneration of ion-exchangers can be expensive and if ammonia concentration in the influent drops, desorption may occur resulting in increased ammonia concentration in the effluent. When ion-exchange and biological oxidation processes are combined some drawbacks can be overcome. Literature review suggests that only clinoptilolite (natural zeolite), has been investigated in terms of biological regeneration. In the research described in this paper some new materials have been evaluated in terms of biological activation. Those materials include: mordenite (natural zeolite); MN 500 (belonging to the group of materials known as Macronets), as well as chemically modified zeolite for ammonia removal from saline waste water. Enriched cultures of nitrifying bacteria in a growth medium were established and have been used for obtaining the batch adsorption results on biologically active materials. Uptake onto biologically active and bacteria free materials was compared. The same experiments have been done in terrestrial and saline wastewater. In the case of non saline media, natural materials, zeolites, have overall better ammonia uptake and experience highly biological regeneration when compared to the synthetic MN 500. In saline media, synthetic material MN 500 showed better ammonia removal compared with modified zeolite ZZ.
1 Introduction

Nitrogen exists in many forms in the environment. Before it can be assimilated by higher plants and animals nitrogen gas must be combined with oxygen or nitrogen to form organic nitrogen compounds, nitrate or ammonia. Before humans interfered nature had maintained the nitrogen cycle in which the fixation process is followed by oxidation of ammonia and denitrification to recover free nitrogen. Human action through industrial nitrogen fixation processes and the large-scale growing of nitrogen-fixing plants has played a significant role in disturbing the nitrogen cycle. Therefore, the permanent increase in the concentration of nitrogen compounds in ground and surface waters has become a common problem during recent years. Nitrogen compounds are also contributing to serious water pollution problems in seawater due to ammoniacal nitrogen arising from river flows into the sea and due to intensive fish farming operations. Ammonia is the major end-product of protein metabolism in most aquatic animals. Nitrogen compounds also accumulate in seawater aquaria, aquacultural ponds and disposal sites.

Ammonia-nitrogen is the nitrogenous compound most responsible for toxicity effects in aquatic life. Ammoniacal nitrogen is present in two forms when in water; ammonia (NH₃) or ammonium (NH₄⁺), according to equations (1) and (2).

\[
\begin{align*}
\text{NH}_4^+ + \text{OH}^- & \Leftrightarrow \text{NH}_3 + \text{H}_2\text{O} \\
\text{NH}_3 + \text{H}_2\text{O}^+ & \Leftrightarrow \text{NH}_4^+ + \text{H}_2\text{O}
\end{align*}
\]

The conditions that control this equilibrium are pH, temperature and ionic strength. At given pH and temperature, the concentration of un-ionized ammonia is approximately 40% less in seawater [1] but its toxicity is increased by the generally higher pH in seawater, which displaces the equilibrium towards the NH₃ form.

The discharge of effluent waters containing ammonia and ammonium ion has to be according to strict concentration limits for discharge. The Council of the European Community [2] has set a guide level of 0.05mg/l and a maximum level of 0.5mg/l of ammonia. The American Committee on Water Quality recommended a limit of 0.02mg/l of ammonia [3]. New Zealand discharge standards vary from 0.22mg/L to 0.77mg/L when being released into receiving waters [4]. Ammonia toxicity to fish and other aquatic animals is very significant and concentrations in the range 0.2mg/l to 0.5mg/l can be fatal [5].

The classical solution to the problem of ammonia removal is nitrification, which is a component of biological waste treatment, whose effectiveness depends on the ability of nitrifying organisms to oxidise ammonia to nitrate. Species belonging to the genera *Nitrosomonas* and *Nitrobacter* are responsible for most of the naturally occurring nitrification. For the ammonium and nitrite oxidation the following equations can be written:
Problems with biological ammonia removal include the sensitivity of nitrifying bacteria to toxic shock, pH, a low dissolved oxygen concentration and low temperatures. Nitrifying bacteria also have a relatively slow growth rate, which is about one tenth of the growth rate of many carbon oxidising bacteria.

An alternative to biological treatment is ion-exchange. Ion exchange materials which are highly selective for ammonia have been used; natural zeolites clinoptilolite and mordenite [4], [6], [7], [8] synthetic zeolite [9] or other synthetic ion exchange resin [10]. The main drawbacks in using ion-exchangers for ammonia removal are the following:

- adsorbent quickly becomes saturated with ammonia and chemical regeneration can prove expensive;
- when ammonia concentration in the influent drops, desorption may occur from the adsorbent resulting in ammonia being discharged into the effluent.

When the biological process is combined with ion exchange [11], [12], [13], [14] some improvements may be obtained:

- the ion-exchanger responds to loading ammonia peaks;
- at low ammonia level nitrifying bacteria serve to oxidise the desorbed ammonia;
- nitrifiers serve to extend the ion-exchanger’s usage which results in less frequent regeneration;
- the ion-exchanger can serve as a solid surface to which bacteria can be attached, since it has been proved that nitrifying organisms prefer being attached to a solid surface rather than freely swimming.

From literature data it can be seen that only clinoptilolite, natural zeolite, has been investigated in terms of biological regeneration for application in terrestrial waste water, while cellulose carriers were used for similar processes in saline water. In this paper we tried to introduce some new materials that might be more suitable for the combination of biological and ion-exchange removal of ammonia from wastewaters.

2 Materials and methods

The materials being used in this research are the natural zeolites, clinoptilolite and mordenite, MN 500 (that belongs to the group of material known as Macronets, which are hypercrosslinked polyvinyl styrenes) as well as a product called ZZ, which is the chemically modified zeolite. Modified zeolite (ZZ) was developed and identified by a research group at the University of Cadiz in Spain.

\[
\begin{align*}
\text{NH}_4^+ + 3/2\text{O}_2 & \Leftrightarrow \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O} \\
\text{NO}_2^- + 1/2\text{O}_2 & \Leftrightarrow \text{NO}_3^-
\end{align*}
\]
Zeolites are common in their possessing a three dimensional frame work which arises from an open frame work of SiO₄ and AlO₄ tetrahedra linked together and they are known to have a high affinity for ammonium ions. The precise mechanism by which ammonia is adsorbed by the modified zeolite ZZ is not yet understood. The clinoptilolite and the mordenite were sourced from deposits in New Zealand.

Clinoptilolite, mordenite and MN 500 were pre-treated by washing with deionised water and contacting with batches of 1% sodium chloride solution for sufficient time to ensure the zeolite became homoionic. The material was then washed with distilled water until a negative reaction for chloride unions was obtained, dried at 30°C for 24 hours and placed in the desiccator. ZZ was just washed and dried before usage since it has already been treated with the sodium hydroxide solution during the preparation process, so it can be presumed that all the available sites already had sodium ions attached. The material was sieved so as to retain batches of material with a particle size of 500-1000 microns.

The capacity of the resulting material to adsorb ammonia from synthetic wastewater was measured as follows. 0.5g of the material was placed in a 100ml conical flask with 50 ml of ammonia solution with concentrations ranging from 10-200 mg/l N-NH₄⁺. Ammonia solutions were made in a sterile broth that was made according to the literature procedure [15]. In each flask, 1ml of the bacteria seed was added and the flasks were placed on an orbital shaker with the speed adjusted to 200rpm. Bacteria seed was obtained by taking a sample from the municipal wastewater treatment plant and enriching the ammonia oxidisers by adding broth for the growth of the nitrifying organisms. Subcultures were prepared by inoculation of 50ml of a fully grown enriched culture into 500ml of fresh broth. After the seed was added, artificial aeration was introduced to improve the nitrification process in the flasks and each flask was coated with aluminium foil to exclude light. In order to compare adsorption on biologically active and non-active materials, we prepared the flasks with the same ammonia concentration, in which 1ml of sterile seed was added, and put them under the same conditions on the orbital shaker. In that way, we had the same medium for adsorption, however, bacteria were not present. Each day the pH was checked and adjusted to a level of 7.5 by adding sodium carbonate solution. To make up for evaporated water, sterile water was added when it was necessary. After 13 days of shaking at a constant temperature of 22°C, samples were filtered into the 50ml volumetric flasks and each sample was filled up to 50ml with sterile water. Ammonia concentrations were measured in each flask. The ammonia concentration was also measured in seed solution and this value was taken into calculation (the initial ammonia concentrations were therefore slightly increased).

To determine the extent to which bacterial colonies influenced ammonia adsorption (not overall removal), material in each flask was washed and shaken with 1% potassium chloride solution to release all adsorbed ammonia, which was
then measured. Adsorption on biologically active and bacteria free materials was compared.

For experiments in the saline medium the same procedure was followed with the only difference being that broth in artificial sea water was used like a growth medium for nitrifying organisms. To avoid an adaptation period in saline water, the seed solution of nitrifying bacteria was obtained by enrichment of ammonia oxidisers in saline broth using a sample taken from a waste water treatment plant. Seawater was made according to the procedure given in the literature [16].

3 Results and discussion

The obtained results for the non saline medium are presented in Table 1. The results of each batch experiment were calculated using aqueous phase analysis for ammonium ion concentrations. The uptake of the ammonium ion onto the exchanger was calculated from the initial and final solution concentrations, the amount of exchanger added and the solution volume. The solid phase concentrations ($Q_e$) are expressed in mg N-$\text{NH}_4^+/g$ of exchanger.

Table 1. Ammonia removal on biologically free and active materials in non saline water.

| Initial amm. conc. (mg/l N-$\text{NH}_4^+$) | Clinoptilolite | | Mordenite | |
|----------------------------------------|---------------|----------------|----------------|
|                                        | without bacteria | with bacteria | without bacteria | with bacteria |
|                                        | % removed | Qe(mg/g) | % removed | Qe(mg/g) | % removed | Qe(mg/g) |
| 10.08 | 84.69 | 0.85 | | 97.73 | 0.02 | |
| 40.08 | 78.51 | 3.15 | | 98.72 | 0.05 | |
| 70.08 | 70.23 | 4.92 | | 98.48 | 0.14 | |
| 90.08 | 59.86 | 5.39 | | 83.30 | 1.84 | |
| 150.08 | 51.73 | 7.76 | | 84.17 | 2.41 | |
| 200.08 | 48.46 | 9.70 | | 86.72 | 2.35 | |
The results show that removal of ammonia is generally better on natural materials (clinoptilolite and mordenite) when compared to the synthetic ion exchanger MN 500. This can be noticed on biologically free materials as well as on the materials that had bacteria attached. Therefore, natural zeolites not only have higher ammonia capacity but also are better media for bacteria growth.

If mordenite is compared to clinoptilolite, first we can notice that without bacteria mordenite has better ammonia removal for higher initial ammonia concentrations, which is in agreement with our previous results [17]. In terms of biological regeneration both materials show similar results, which suggest that the nitrifiers perform more effectively on the clinoptilolite compared to the mordenite. According to the literature data [18] high ammonia concentration (over 80mg/l) will cause very significant nitrification inhibition, which did not happen in our experiments probably because the ion exchange materials served as a buffer to protect the bacteria population from fatal initial ammonia concentrations. Once that ammonia from the solution was oxidized by bacteria, more ions were released from the material and the process continued.

Results obtained for the MN 500 and ZZ in a saline medium are presented in the Table 2. ZZ exhibited better removal than MN 500 when the medium was bacteria free. While in non saline water MN 500 did not show good biological regeneration, it served like a good medium for bacteria growth in saline water. Since better nitrification was obtained with MN 500 we had less ammonia remaining on this material compared to the ZZ once when the process was finished (Qe values from the Table 2). A possible reason for this is that during the process of modification of the natural material the structure has been changed so that surface is not suitable for bacteria growth any more. It might also be that the desorption of ammonium ions from MN 500 in saline water is easier than from ZZ, so that ions consumed by bacteria are not replaced in the solution. Although both materials used have significantly less capacity for ammonia removal in sea water due to the high concentrations of other salts, the buffering
effect in solutions with high initial ammonia concentrations still exists to protect bacteria from ammonia inhibition.

Table 2. Ammonia removal on biologically free and active materials in saline water.

<table>
<thead>
<tr>
<th>Innit. amm. conc. (mg/l N-NH₄)</th>
<th>MN 500</th>
<th>ZZ</th>
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<tr>
<td></td>
<td>without bacteria</td>
<td>with bacteria</td>
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<tr>
<td></td>
<td>% removed</td>
<td>Qe(mg/g)</td>
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4 Conclusion

Mordenite has better ammonia uptake than clinoptilolite when initial ammonia concentrations are higher than 50mg/l. This material will be considered for application in a combined biological and ion exchange process for non saline wastewaters, particularly for the treatment of the effluent where variations in ammonia concentrations could be expected.

In the case of non saline media, natural materials, zeolites, have overall better ammonia uptake and experience highly biological regeneration when compared to the synthetic MN 500.
A combined process could also be considered for ammonia removal from saline medium. Synthetic material MN 500 showed better ammonia removal performance in sea water compared with modified zeolite ZZ.

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References


