Enhanced removal of ammonium by combined nitrification/adsorption in expanded clay aggregate filters

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Abstract

Long-term experiments were carried out on a nitrifying biofilter with a zeolite-containing expanded clay aggregate filter media (Filtralite ZL) receiving daily peak loads of ammonia. The filter removed ammonium from domestic wastewater by a combination of nitrification and sorption of ammonium. The filter was biologically regenerated continuously and there was no deterioration in performance after 10 months of continuous experiments. Isotherm experiments confirmed that the Filtralite ZL granules that had been used for more than 8 months had about the same capacity as the unused material. Desorption experiments that were carried out indicated that desorption of ammonium from the filter material was mainly caused by an exchange of cations from the wastewater even at low cation concentrations.

Keywords

Ammonium removal; biological regeneration; ion exchange; nitrification; wastewater; zeolite containing expanded clay aggregate filters

Introduction

Many nitrifying treatment plants or N-removal plants have problems in complying with ammonium effluent standards, because of lacking capacity to deal with peak loads of ammonium. This is particularly a problem in nitrifying biofilters. Ammonium in domestic wastewater usually appears with a distinct daily variation, with a peak concentration in the mornings. Such peak-loads are normally dealt with by using considerable peak-load factors in the design. This, of course, leads to larger nitrification reactors than necessary with over-capacity during several hours of the day.

This paper deals with a possible solution to the problem. A special filter medium for the nitrifying biofilter, made of zeolite containing expanded clay aggregates with sorptive capacity with respect to ammonium, has been investigated. The hypothesis was that ammonium peaks would be sorbed to the filter grains in high-load periods and subsequently nitrified in low-load periods. Ideally the process would be able to run continuously without any interruptions for chemical regeneration.

The Norwegian company as Norsk Leca has earlier developed a commercially available filter medium based on expanded clay aggregates (Filtralite). This is widely used in biofilters for water and wastewater treatment. The new zeolite containing product, called Filtralite Zeolite Leca (Filtralite ZL) consists of Filtralite that has been processed and given zeolitic properties, and consequently ion exchange capacity with respect to ammonium (Wendelbo, 1997; US Patent Appl., 1999). The performance of this new Filtralite ZL filter medium has been investigated in batch experiments and in pilot scale filters operated with biological nitrification.

Background

Filtralite ZL may be used as a filter material in any application where removal of ammonium is required. However, regeneration of the material is needed. Natural and synthetic zeolites are most commonly regenerated chemically with a solution of NaOH and NaCl.
Various types of biological regeneration have been suggested as well (Semmens et al., 1977; Lahav and Green, 1998a, 1998b). These authors have mainly been concentrating on a separate sequence for regeneration. Wastewater was first filtered through the zeolite filter until ammonium break-through occurs. Then the filtration cycle was interrupted and the zeolite regenerated biologically by nitrifying bacteria.

In the described experiments described here, it was aimed at more or less continuous biological regeneration of the filter material. Biological regeneration of a zeolite during the nitrification filter cycles has been reported earlier (Oldenburg and Sekulov, 1995; Beler-Baykal et al., 1994, 1996; Beler-Baykal and Guven, 1997; Beler-Baykal, 1998). None of these earlier experiments proved, however, the effect of biological regeneration on a long-term basis. In our experiments Filtralite ZL was used in the whole filter-bed and served the purpose of both biofilm carrier, ammonium exchanger and particle removal filter. The whole filter bed was therefore intended to be effective in terms of sorbing ammonium. This was preferable both with respect to the general removal of ammonium and specifically to the removal at high ammonium peaks.

Initial experiments were run for two months with constant ammonium loading rate for each filter cycle that lasted for 8–10 days (Gisvold et al., 2000). The results demonstrated that Filtralite ZL had the ability to sorb ammonium during periods of high influent concentration. During periods of low influent concentration, ammonium desorbed from the Filtralite ZL and was removed by nitrification.

The removal of ammonium is shown in Figure 1 where ammonium removal rate is given versus ammonium loading rate for Filtralite ZL and a reference material without zeolitic properties (Filtralite). The figure shows a higher maximum removal rate for Filtralite ZL as compared to that of the reference. The amount of ammonium converted into NO\textsubscript{x} by nitrification is shown in Figure 2 where the NO\textsubscript{x} formation rate is given versus the ammonium loading rate. This figure shows that the maximum nitrification rate was the same in both filters, and that at low ammonium loading rates more ammonium was nitrified than actually introduced to the filter.

These experiments proved that Filtralite ZL adsorbed ammonium at high ammonium loading rates and desorbed ammonium at low ammonium loading rates. The combined effect of ion exchange and nitrification in the Filtralite ZL filters was, however, demonstrated in experiments with an almost constant ammonium loading rate for each filter cycle. Constant loading rates for filter cycles up to 10 days would not be optimal with respect to taking advantage of the sorption capacity of the material.

At more frequent fluctuations of ammonium loading rate, one would expect the advantage of ion exchange and removal of ammonium by sorption to be even higher than demonstrated in the previous experiments. In practice conditions are alternating quite frequently.
Most domestic wastewater treatment plants experience one distinct peak of ammonium every day. Therefore, long-term experiments with daily ammonium peaks were carried out. In addition, isotherm experiments were carried on used and unused material to see whether there was any deterioration in the sorptive capacity of the material after extensive use. Desorption experiments were also carried out.

**Methods**

**Batch experiments**
The isotherm experiments were run at 15°C in a water-shaking bath (120 rpm) for 48 hours. The pH was kept at pH 7 by addition of 0.1 M NaOH and 0.1 M HCl. Two different solutions were used; NH₄Cl in distilled water with a NaHPO₄ buffer (alkalinity 3.7 mmol/l) and a constructed wastewater (94 mg COD/l, 44 mg SCOD/l, 90 mg SS/l, pH 7, alkalinity 3.7 mmol/l, turbidity 50 NTU and conductivity 0.65–0.9 mS/cm).

Both test waters were made with ammonium concentrations of 10 and 35 mg NH₄-N/l. Unused Filtralite ZL and material removed from the filter just after backwashing (for removal of suspended solids) were used. The used material had experienced more than eight months of continuous use. Both materials were used in granular (grain size: 2.5–5 mm) and in powdered (grain size <70 μm) form. Different amounts of Filtralite ZL (0.5, 0.75, 1.5, 2.5, 4, and 6 g) were placed in 100 ml of test water.

Desorption experiments were carried out at the same conditions as the isotherm experiments. Used and unused filter material was first saturated in NH₄Cl solutions of high and low concentration (35 and 10 mg NH₄-N/l) for a period of one week. The saturated material (4 g to 200 ml) was placed into solutions of de-ionised water and constructed wastewater without ammonium. Samples were taken at certain intervals for 48 hours and analysed for the ammonia content.

**Pilot plant experiments**
The pilot experiments were carried out in two identical up-flow filters fed with biologically treated domestic wastewater. A flow-scheme for the pilot plant is given in Figure 3. The filters were aerated to enhance biological nitrification. One filter was filled with the filter material Filtralite ZL and the other one with normal Filtralite, the basis material for Filtralite ZL. Filtralite, without ion exchange capacity, served as the reference filter with nitrification as the only process for ammonium removal. Pilot plant characteristics are given in Table 1.

The filters had been operated for four months before the long-term experiments, that lasted for seven months, were started. The pilot plant experiments were operated at a constant hydraulic loading rate. During four hours every day an ammonium peak of 3–5 times the normal influent concentration was added. Each filter cycle lasted for one week. The filter was backwashed (50% filter expansion) between the filter cycles with tap water in order to remove suspended solids accumulated in the filter. Sampling of a daily cycle was carried out approximately once a month with an automatic sampler taking samples from the influent and the two effluents every hour. All samples were analysed for ammonium, while some samples were analysed for alkalinity, nitrate and nitrite as well.

**Wastewater analysis**
A Flow Injection Analyser (FIA) was used to determine ammonium, nitrate and nitrite. Ammonium was determined after FIA application note ASN 151-01/92, nitrate after FIA application note ASN 110-01/92 and nitrite after FIA application note ASN 112-01/02. Alkalinity and pH were determined by a Methrom 726 Titroprocessor. Alkalinity was determined by using end point titration with 0.1 M HCl (end point set at pH 4.5).
Results and discussion

Batch experiments

The results from the isotherm experiments were fitted to the Freundlich isotherm equation:

\[ Q = \frac{q}{M} = K_f^* C^{1/n} \]

where \( q \) is the amount of sorbate (ammonium), \( M \) is the amount of sorbent (Filtralite ZL), \( K_f \) is related to the capacity of the adsorbent for the adsorbate and \( 1/n \) is a function of the strength of adsorption. The data from most experiments were well correlated to the Freundlich equation and gave regression coefficients from 0.96 to 1.0. Some of the experiments, however, gave \( 1/n \) values above 1 demonstrating that the equation could not describe the sorption well. This was probably caused by insufficient data range. Generally the results demonstrated, however, that the Filtralite ZL material has a capacity which is slightly lower than most natural zeolites (for example clinoptilolite) that have been reported in wastewater treatment projects. It also gives a \( 1/n \)-value that is relatively high, meaning a not-favoured adsorption isotherm. Such an isotherm is representative for a sorbent that is best at a high equilibrium ammonium concentration and poorest at lower equilibrium ammonium concentrations.

Powder versus granular material. A comparison between experiments with granular and powdered material for the unused material, showed almost identical results. Figure 4 compares the results from unused granular and unused powdered material, confirming that equilibrium was reached also when Filtralite ZL was used on granular form. When comparing used material on powdered and granular form, the powdered material gave much poorer adsorption. The differences were most pronounced at the lowest initial ammonium concentration as demonstrated in Figure 5 where the results from the used granular and used powdered material are compared. One possible explanation for this difference is that the relatively high amount of ammonium that is stored in the sorbent is more easily released when the material is in the powdered form because of more exposed adsorption area.

Comparing used versus unused material. For the granular material no major decrease in capacity was found for the used material in general as compared to the unused, as demonstrated in Figure 6. The comparison of used and unused powdered material in both test waters, demonstrated much lower capacities for the used material at all concentrations, as shown in Figure 7. One possible explanation for this is that ammonium may be more strongly bound to the inner pores. This ammonium is made available to the solution when the material is powdered, thereby influencing the equilibrium concentration with a decrease of the measured capacity of the used powdered material as the result.

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<th>Table 1 Pilot plant characteristics</th>
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<td>Parameter</td>
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<tr>
<td>Filter diameter</td>
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<td>Influent NH₄–N (no peak)</td>
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<td>NH₄–N loading (no peak)</td>
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<td>Average influent COD</td>
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Figure 3 Flow-scheme for the pilot plant
Affinity towards competing ions. The capacity of unused granular material was 35% to 65% lower in wastewater as compared to a pure NH₄Cl solution, as shown in Figure 8. These experiments confirmed that competing cations in wastewater decrease the capacity of Filtralite ZL. This has also been observed to be the case for other zeolites (Jørgensen et al., 1975; Komarowski and Yu, 1997).

Changes in sorption capacity caused by continuously biological regeneration. The experiments showed that adsorption capacity of used granular material was kept almost constant while the capacity of used powdered material decreased dramatically over time of use in the continuous filters. If the decrease in the capacity of the used powdered material was caused by a release of ammonium bound strongly to the inner pores, the capacity would also be expected to decrease for the used granular material. Since this was not the case, one explanation can be that more pores are available in the “outer” area of the used grains as compared to the unused grains. More pores may have been made available by an activation of the material through the continuous biological regeneration.

Desorption experiments. In these experiments desorption is describing a reverse exchange process. No air was present and thereby no nitrification found place on the used grains. The desorption experiments showed much lower desorption of ammonium in the de-ionised water as compared to the constructed wastewater, only 7–15% of the value. The results given in Figure 9 are from the material saturated in 35 mg NH₄-N/l. This experiment was carried out in order to see if the used material had the same ability to desorb ammonium as the unused material. The higher desorption in the constructed wastewater was caused by exchange with other cations present. The cation concentration in the constructed wastewater was within the normal range of domestic wastewater: 110 mg Na⁺/l, 20 mg Ca²⁺/l and...
The results also demonstrated that there was no deterioration in desorption capacity for the used material as compared to the unused material.

**Pilot plant experiments.** In Figure 10 the ammonium concentrations in the inlet and in the filter effluents for two following daily cycles are shown. The fluctuations in the influent ammonium concentration can be seen also in the effluent from the reference filter (Filtralite) that remove ammonium by nitrification only. In the effluent from the Filtralite ZL filter, however, no response to the influent ammonium peak is found. The nitrogen that was not removed by nitrification, was obviously removed by sorption onto the Filtralite ZL material. In Figure 11, the nitrification activity on the same days can be seen from the NOX formed in the filter. In the reference filter, a response to the increased influent ammonium concentration is demonstrated by the increased amount of NOX that is produced by nitrification. The Filtralite ZL column, on the contrary, has a relatively constant nitrification activity while it sorbs ammonium at high influent concentrations.

Ideally, one would expect to find a higher average nitrification activity in the Filtralite ZL filter than in the reference filter, since more ammonium is removed overall. This was the case most of the time, but there were also times when there was mainly sorption of ammonium and still good effluent values, as well as times when there was mainly desorption and high effluent values of ammonium. Some examples of the various operating situations that occurred are given in Figure 12 to 15.

In Figure 12 results from a daily cycle at the beginning of the experimental period is given. Effluent ammonium from the Filtralite ZL filter increased slowly as filter run time proceeded and the effluent concentration was rather high (just below 20 mg NH4-N/l). Investigations demonstrated that this was caused by lack of alkalinity needed for the nitrification. After that alkalinity addition (NaHCO3 to the influent) was implemented, the nitrification activity in the Filtralite ZL filter increased.
Figure 13 shows results from a daily cycle just after starting alkalinity addition. In addition to inlet and effluent ammonium, this figure also shows the amount removed from the Filtralite ZL filter by nitrification. These values are calculated from the alkalinity consumption. Figure 13 shows high ammonium concentration in the Filtralite ZL effluent caused by build-up of ammonium in the filter during the period with lack of alkalinity. The figure also shows a high nitrification activity that exceeds the amount of ammonium entering the filter. This lead to a gradually filter recovering.

Figure 14 shows results from a daily cycle where the overall amount of ammonium that is nitrified in the Filtralite ZL filter is the same as the overall amount of ammonium that is loaded to the filter. Ideally, this cycle should show no ammonium in the effluent from the Filtralite ZL filter. Still, about 5 mg NH₄⁻N/l is found in the effluent. This must originate from the previously stored ammonium.

Figure 15 shows results from a daily cycle without ammonium in Filtralite ZL effluent. The amount of ammonium nitrified is lower than the total amount of ammonium removed, indicating some ammonium storage. This is a demonstration of good operation of the filter that normally took place.

These figures are shown to illustrate different experiences with the filter during the experimental period. However, most of the time the filter performed well and the problems experienced can be explained by lack of alkalinity and/or overloading of ammonium for a longer period.

**Process evaluation**

Continuous biological regeneration of Filtralite ZL was observed during the whole experimental period of 10 months. Isotherm experiments with granular Filtralite ZL used for about 8 months demonstrated no deterioration in capacity. Desorption experiments
demonstrated that the ability to desorb ammonium (from the grain into the solution), was the same in both used and unused material. Biological activity of the filter might also influence regeneration (desorption of ammonium) of the material, but this was not investigated. From both batch and pilot plant experiments we can draw the conclusion that continuous biological regeneration was still present after 10 months of experiments.

The process requires less volume since it can be dimensioned for a lower average ammonium load than the peak load. The process also provides a constant loading rate on the denitrification step, which may reduce the volume needed for that step as well. The process will need good operation and surveillance, however. The operator needs to know the mass balance situation at any time. Influent loads higher than designed for, will lead to high amounts of ammonium stored. On the contrary, extreme, unpredicted peak loads of ammonium can be captured in the filter. In practice, also this filter will have to be designed with a safety factor, but the safety factor can be smaller than when designing for the peak load in a normal nitrification filter.

Conclusion
Long-term experiments have proven that Filtralite ZL can be used as a combined nitrification/adsorption filter medium for ammonium removal. Peak loads of ammonium were sorbed to the material and later desorbed and nitrified when the influent ammonium concentration became lower. The effect was still present after 10 months of continuous operation. At a base filter loading rate of 0.4 kg NH4-N/m3·d, 4 hour peaks of 3–5 times the influent concentration were removed successfully.

The process requires less volume than a conventional nitrification reactor. In order to avoid too high storage of ammonium, which could subsequently be released at higher amounts than the biomass can cope with, this process has to be designed with a safety factor, which can, however, be smaller than for conventional nitrification in biofilters.

References