Chemical denitrification for nitrogen removal from landfill leachate

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Abstract A new system that removes nitrogen from landfill leachate and other waste waters with similar properties has been proposed with nitritation (i.e. oxidation of ammonium to nitrite) of half of the influent ammonium followed by chemical denitrification with a reaction between equal amounts of ammonium and nitrite to form nitrogen gas. Chemical denitrification occurs at high concentrations and the reactions were studied in combination with a concentration step. Studied concentration methods were freezing/thawing and evaporation/drying. Chemical denitrification is well-known in inorganic chemistry and has been observed in natural systems.

Studies in laboratory were focused on chemical denitrification and showed that nearly complete removal of soluble nitrogen can be obtained in evaporation/drying of water solutions or leachate with equal amounts of ammonium and nitrite. Freezing/drying was less efficient with a removal of about 50–60% at high initial concentrations. Chemical denitrification is much influenced by concentration, pH-value, temperature and some compounds in leachate have an inhibiting effect on the reaction. Factors as safety (ammonium nitrite as a salt is explosive above 60 °C) and possible side-reactions as formation of ammonia and nitrogen oxides must be carefully evaluated before use in full-scale. Conductivity is a suitable parameter to follow-up the chemical denitrification process.

Keywords Chemical denitrification; evaporation; freezing; leachate

Introduction

Leachate and supernatant from dewatering of digested sludge has a high concentration of ammonium but a low concentration of biodegradable organic material. A traditional biological technology for nitrogen removal from these waters with ammonium oxidation to nitrate followed by heterotrophic denitrification uses a high energy due to the needed oxygen supply for nitrification and an external carbon source to accomplish heterotrophic denitrification. Many possibilities have been reported to lessen the energy need and use of organic material, and a newly developed concept is to oxidise half of the ammonium to nitrite by biological means (nitritation) followed by a step with anaerobic oxidation of remaining ammonium with the formed nitrite (Anammox). The first step with nitritation (with formation of only minor amounts of nitrate) is reasonably well-known with possibilities to control the process by use of low or high pH-values, low oxygen concentrations, residence time and temperature. The general principle is to use process conditions that lead to a higher growth rate of Nitrosomonas than Nitrobacter in the reactor and therefore give possibilities of washout of Nitrobacter but remain Nitrosomonas.

Recently, organisms have been identified and process technology has been developed of the Anammox process. As chemical denitrification and Anammox involve the same reaction, i.e. ammonium oxidation with nitrite to nitrogen gas, the aim of this study was to evaluate if chemical denitrification could be seen as an interesting alternative (or complement) to Anammox. The potential of chemical denitrification as a part of a treatment system for leachate or supernatant from dewatering of digested sludge seems to not have been given attention and therefore this study was started. It should, however, be noted that much information on chemical denitrification exists from other areas. Such
studies include general inorganic chemistry (a good compilation of early studies is given in Gmelin, 1936), losses of nitrogen in fertilising during winter time (probably due to partial nitritation in combination with freezing, Christianson et al., 1979; Christianson and Cho, 1983), losses of nitrogen during drying of dew containing ammonium and nitrite (Takenaka et al., 1999), and observations of nitrogen losses in nitrification of urine in combination with drying (Johansson and Hellström, 2002). Different observations are briefly summarised by Nikolić and Hultman (2003a) and Nikolić (2003).

The suggested system (see Figure 1 and Table 1) for the removal of nitrogen from leachate consists of two main parts. The first part entails oxidation of about half of the amount of ammonium to nitrite in a separate biological step. The second part starts with concentrating equal amounts of ammonium and nitrite, followed by chemical denitrification that produces nitrogen gas. The concentration of nitrite and ammonium plays the most important part for the chemical denitrification, and freezing/thawing and evaporation/drying were analysed as concentration methods. Compared with traditional nitrification/denitrification much less oxygen is needed (as only half of the ammonium is oxidised and only to nitrite) and no addition of organic material is necessary for denitrification. In leachate treatment it is common to have a pond for collection of the leachate and part of this pond may be used for partial nitritation. The alkalinity (in mmol hydrogen carbonate) is about the same as the ammonium concentration (in mmol) and therefore nitrification typically stops at oxidation of half of the ammonium to nitrite due to a pH drop that stops nitrification and especially the oxidation of nitrite to nitrate. This gives possibilities of an easy way to control the first part with about 50% nitritation. The concentration part involves some investments but depending on climate conditions freezing/thawing or evaporation/drying may be accomplished with low costs by use of natural methods.

Material and methods
Several series of experiments were performed with different concentrations of ammonium and nitrite at different initial pH values, both in water (tap water) and in leachate solutions. In the series, solutions of equal and increased concentrations of NH$_4$+ -N and NO$_2$–-N (200, 400, 800, 1600 and 3200 mg N/l of each component) were prepared. The ratio of ammonium and nitrite was about 1:1. Sodium nitrite and ammonium chloride were added to obtain the desired concentration of nitrogen and ratio between ammonium

<table>
<thead>
<tr>
<th>Nitritation</th>
<th>Concentration step</th>
<th>Chemical denitrification</th>
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</thead>
<tbody>
<tr>
<td>NH$_4$+ + 1.5O$_2$ → NO$_2$ + 2H$_2$O + H$_2$O</td>
<td>Freezing evaporation</td>
<td>NH$_4$+ + NO$_2$ → N$_2$ + 2H$_2$O</td>
</tr>
</tbody>
</table>
and nitrite. Hydrochloric acid was used for adjusting the pH value of the solutions. In the experiments where leachate was used as a source of ammonium, before adding nitrite, the concentration of ammonium in leachate was analysed and it was from 173 to 184 mg N/l. In all experiments, the same leachate has been used and it falls into the category of leachate from old landfills.

In the first series, freezing was investigated; the samples were immediately frozen into the plastic bottle and then thawed for 12 h at 4 °C. Freezing equipment was used to freeze the samples. In the second series, evaporation was investigated; the samples (20 or 100 ml) were evaporated in a sand bath until the whole volume of the sample (if not noted differently) was evaporated, and then immediately removed from the sand bath. After complete evaporation the same amount of pure water (20 or 100 ml) was added to the samples.

The concentration of inorganic nitrogen species like ammonium-nitrogen, nitrite-nitrogen and nitrate-nitrogen was analyzed after freezing/thawing and evaporation/drying. The composition of the gas phase during freezing and evaporation was not analyzed. Conductivity changes during the following experiments were observed by measuring conductivity before and after freezing or evaporation. The initial pH value was measured (before freezing or evaporation).

Analytical methods. pH was measured with a pH-meter, Model 210A Meter. Ammonium-nitrogen (NH₄⁺-N), nitrite-nitrogen (NO₂⁻-N) and nitrate + nitrite nitrogen (NO₃⁻-N + NO₂⁻-N) were determined by flow injection analysis and gas diffusion, using spectrophotometer Tecator Aquatech Analyzer. Conductivity was measured by placing the conductivity meter Orion 115 in the sample and recording the electrical resistance.

Results and discussion
Influence of pH values and initial nitrogen concentrations on nitrogen removed
In the freezing study (Nikolić and Hultman, 2003b) it was shown that freezing of ammonium nitrite water solution accelerates the reaction rate and not thawing, and that the highest nitrogen removal was observed at a pH value of 4. Furthermore, it was shown that freezing also accelerated the oxidation of nitrite to nitrate in both water and leachate solutions, which can be prevented (Takenaka et al., 1996) by stirring of solution during the freezing, by adding salts like NaCl and KCl, or some organic compounds like methanol or acetate. Nitrogen removal during the freezing process was further studied only at pH 4 in both water and leachate solutions at higher concentrations. In the evaporation study (Nikolić and Hultman, 2003c) the highest removal efficiency was obtained in the pH range from 4 to 7, and the lowest at pH 3, for both water and leachate solutions. Further comparison of results between freezing and evaporation will deal only with one of solutions in the pH range from 4 to 7.

Figures 2 and 3 show the comparison of influences of increasing initial concentrations and inhibitory behaviour of leachate on nitrogen removed after the freezing and evaporation processes, respectively. It could also be seen that with the same initial concentrations of ammonium and nitrite the percentage of ammonium and total nitrogen removed was much higher after evaporation than after freezing. Figure 2 shows a comparison of ammonium-nitrogen removed in NH₄NO₂ water and leachate solutions after freezing (-f) and evaporation (-e). The initial pH value of 7.3 for water and 100% removal of ammonium after evaporation indicate some ammonium stripping due to high temperature, while minor amounts of nitrite and nitrate are left in the residue. Furthermore, the rate of ammonium nitrite decomposition increases with concentration, showing
a linear increase of ammonium removed, which is in an agreement with literature (Smith and Clark, 1960).

According to Figure 3, the percentage of total inorganic nitrogen removed from the water solution sharply increases with increasing values of initial concentrations, and in the highest studied concentration (3200 mg N/l of each component) 4350 mg N/l of total inorganic nitrogen was removed after freezing at pH 4, whereas 5890 mg N/l of total inorganic nitrogen was removed after evaporation at pH 5. Due to the leachate’s inhibitory behavior, there is less total inorganic nitrogen removed in the leachate than in the water solution. Leachate consists of different cations and anions that can act as inhibitors for both freezing and evaporation, for example nitrite ion may be combined with cations other than ammonium and therefore causing the decrease of available nitrite for denitrification (Allison, 1963). This inhibitory behaviour decreases with increasing initial concentrations and for the highest concentration it is almost equal to results in the water solutions.

**Influence of the initial nitrogen concentration and pH value on the quotient of ammonium and nitrite nitrogen removed**

During all experiments, both in freezing and evaporation studies, gaseous products of ammonium nitrite decomposition and possible side reactions forming nitrogen oxides were not measured. In order to follow the influence of the initial pH values on nitrogen removed, the quotient of ammonium and nitrite nitrogen removed after evaporation and freezing was calculated (Nikolić, 2003). If decomposition of ammonium nitrite proceeds according to the reaction \( \text{NH}_3 + \text{HNO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \), then concentrations of ammonium and nitrite removed should be the same, and the ratio \( \Delta\text{N}_{\text{NH}_4}/\Delta\text{N}_{\text{NO}_2} \) should
be equal to 1. Since a lot of nitrite is being oxidized to nitrate during freezing, the concentration of ammonium removed should be equal to the difference between concentrations of nitrite removed and nitrate produced. Figure 4 shows the ratio between ammonium and nitrite removed in water and leachate solutions at pH 5 and 4 after evaporation, and at pH 4 after freezing. The ratio of nitrogen removed after freezing in water solutions is almost 1 but it decreases with increasing initial concentrations. In leachate the ratio is higher than 1 and with increasing concentrations it reaches 1. The Figure indicate that the most favourable initial pH value for the nitrogen gas formation after evaporation is pH 5 for both water and leachate solutions.

**Influence of removed concentration of inorganic nitrogen on conductivity removed**

One of the objectives of this research was to investigate the possibility to follow chemical denitrification, i.e. nitrogen removal, with measuring of electrical conductivity before and after the reaction took place. Since the conductivity value is proportional to the concentrations of ions in the solution, a possible decrease of conductivity as the reactions proceeds will mean that ions are transformed into molecules, in this case into nitrogen gas.

With an increase of the initial concentration the nitrogen removed increases, electrical conductivity decreases and therefore $\Delta C$ increases. Figure 5 shows that the correlation between conductivity removed $\Delta C$ and total inorganic nitrogen removed from solutions could be written as a linear equation $\Delta C = a \times \Delta N + b$, with a high correlation coefficient for all curves ($R^2 = 0.99$). The value of $a$ varied between 0.003 and 0.005, and is probably due to alkalinity removed, but also due to the influence of ionic strength of the salt concentration on conductivity. The value of $b$ refers to the influence of initial salts (in leachate due to the present cations and anions some other salts could be precipitated and cause a decrease of conductivity when there is no nitrogen removed) and added chemicals. The leachate nitrite line shows a sharper rise than the ammonium nitrite line due to alkalinity removed during both freezing and evaporation processes.

Conductivity changes of ammonium nitrite water solutions were calculated according to Eaton *et al.* (1995) after both evaporation and freezing. Table 2 shows calculations of conductivity for water solutions ($k_{\text{calc}}$) at different pH values and its comparison with measured conductivity ($k_{\text{meas}}$). The acceptable ratio is $0.9 < k_{\text{calc}}/k_{\text{meas}} < 1.1$. From calculations of conductivity for NaCl (only for samples after evaporation) it can be seen that after evaporation sodium and chloride ions are present in the highest concentration in comparison with other ions. Furthermore, within the same solution conductivity increases with decreasing pH values due to an increase of the concentration of chloride ions (because HCl was used for regulation of the pH value). The differences between

![Figure 4](https://iwaponline.com/wst/article-pdf/52/10-11/509/433749/509.pdf)

**Figure 4** Influence of initial concentrations on the ratio between ammonium and nitrite removed ($\Delta N_{\text{NH}_4}/\Delta N_{\text{NO}_2}$) in water and leachate solutions after evaporation at 90°C (-e) and freezing (-f).
measured and calculated values were in the acceptable ratio. It can also be seen that ammonium nitrite decomposition could be followed by measurements of the conductivity and in that way the control of the treatment system could be simplified.

**Influence of evaporated volume on nitrogen removal**

In order to investigate how chemical denitrification is influenced by evaporated volume new experiments were performed at 60 °C with ammonium nitrite water solutions at the initial pH-value of 7.2 (see Table 3). The experiment was followed-up only with conductivity. Measurements of the conductivity were done directly in the samples where 25 to 85% of the initial volume was evaporated, while dilution was necessary in the samples where 90 and 95% was evaporated. Table 3 shows that chemical denitrification occurred somewhere between 95% evaporated volume and complete evaporation, but it could not be established if a solid phase of ammonium nitrite was formed before decomposition.

**Discussion**

Two different methods were investigated for concentration in combination with chemical denitrification. Evaporation/drying was much more efficient than freezing/thawing for transfer of the ammonium nitrite into nitrogen gases. Freezing/thawing could therefore be seen as a pre-treatment step for nitrogen removal, while evaporation/drying has the poten-

**Table 2** Difference between measured and calculated conductivities

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>pH value</th>
<th>$k_{\text{meas}}$ (mS/cm)</th>
<th>$k_{\text{calc}}$ (mS/cm)</th>
<th>$K_{\text{NaCl}}$ (mS/cm)</th>
<th>$\Delta$ (mS/cm)</th>
<th>Ratio $k_{\text{meas}}/k_{\text{calc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 mg/l NH$_4$-N + 200 mg/l NO$_2$-N (before evaporation)</td>
<td>7</td>
<td>3.5</td>
<td>3.0</td>
<td>1.6</td>
<td>0.5</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.6</td>
<td>3.1</td>
<td>1.7</td>
<td>0.5</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.5</td>
<td>3.1</td>
<td>1.7</td>
<td>0.4</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.8</td>
<td>3.5</td>
<td>2.1</td>
<td>0.3</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.0</td>
<td>2.6</td>
<td>1.9</td>
<td>0.4</td>
<td>0.87</td>
</tr>
<tr>
<td>200 mg/l NH$_4$-N + 200 mg/l NO$_2$-N (after evaporation)</td>
<td>7</td>
<td>1.8</td>
<td>1.5</td>
<td>1.4</td>
<td>0.3</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.8</td>
<td>1.5</td>
<td>1.5</td>
<td>0.3</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>4</td>
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<td></td>
<td>3</td>
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<td>2.6</td>
<td>1.9</td>
<td>0.4</td>
<td>0.87</td>
</tr>
<tr>
<td>200 mg/l NH$_4$-N + 200 mg/l NO$_2$-N (before freezing)</td>
<td>4</td>
<td>3.3</td>
<td>3.1</td>
<td>-</td>
<td>0.2</td>
<td>0.95</td>
</tr>
<tr>
<td>200 mg/l NH$_4$-N + 200 mg/l NO$_2$-N (after freezing)</td>
<td>4</td>
<td>2.7</td>
<td>2.6</td>
<td>-</td>
<td>0.1</td>
<td>0.96</td>
</tr>
</tbody>
</table>

$^1$Calculated conductivity assuming that there is only NaCl in the solution

![Figure 5](https://iwaponline.com/wst/article-pdf/52/10-11/509/433749/509.pdf)
tial for complete nitrogen removal. Safety aspects are very important in use of evaporation/drying due to risks for explosion as ammonium nitrite in a crystal state may explode when heated up to 60–70°C (Lewis, 1996). It is possible that ammonium nitrite decomposes at very high concentration in the liquid and will not form a solid phase and that thereby safety aspects can be controlled. Natural evaporation/drying in open areas may also be a suitable solution.

The type of gases formed in chemical denitrification was not investigated. It seems, however, possible that if the quotient $\frac{D_{\text{NH}_4}}{D_{\text{NO}_2}}$ is higher than 1 that some ammonia will be released, while if the quotient is less than 1 some nitrogen oxides will be formed. In this case treatment of the gas phase may be necessary. Use of a suitable initial pH value before freezing/thawing or evaporation/drying is an important way to transfer most of the ammonium nitrite removed to nitrogen gas.

The transfer of ammonium and nitrite ions to nitrogen gas (molecule) means that the salt concentration diminishes (and thereby the conductivity) as nitrogen is removed from the water phase. Conductivity is easy to measure and therefore an important parameter to follow-up the chemical denitrification process.

Many countries will forbid the use of landfilling of organic biodegradable materials and by that reason ammonium generation will decrease successively. However, release of ammonium-rich leachate will occur for a long period ahead. Supernatant from dewatering of digested sludge is an important side-stream in wastewater treatment and has similar composition as leachate. For these streams chemical denitrification may have a future role as main or complementary treatment method for nitrogen removal.

### Conclusions

A process scheme has been proposed for nitrogen removal from landfill leachate and similar waters based on partial nitritation (biological oxidation of about 50% of the influent ammonium nitrogen to nitrite nitrogen) followed by chemical denitrification (chemical reaction between ammonium and nitrite to nitrogen gas) in a step with concentrating conditions. Studied methods for concentration were freezing/thawing and evaporation/drying. Results from chemical denitrification show the following.

- More than 90% of ammonium nitrite in water or leachate can be transferred to gaseous components in evaporation/drying, while the removal efficiency was less for freezing/thawing (50–60% at high initial concentrations).
- Chemical denitrification is much influenced by initial concentration of ammonium and nitrite, pH-value, temperature, and leachate components have an inhibiting effect on the process.

### Table 3

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$C_{\text{before}}$ (mS/cm)</th>
<th>$C_{\text{after}}$ (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25% evaporated</td>
<td>3.59</td>
<td>4.81</td>
</tr>
<tr>
<td>50% evaporated</td>
<td>3.59</td>
<td>7.20</td>
</tr>
<tr>
<td>75% evaporated</td>
<td>3.59</td>
<td>13.10</td>
</tr>
<tr>
<td>85% evaporated</td>
<td>3.59</td>
<td>22.80</td>
</tr>
<tr>
<td>90% evaporated</td>
<td>3.59</td>
<td>30.80</td>
</tr>
<tr>
<td>95% evaporated</td>
<td>3.59</td>
<td>45.64</td>
</tr>
<tr>
<td>100% evaporated</td>
<td>3.59</td>
<td>1.98</td>
</tr>
<tr>
<td>100% + 30 min$^1$</td>
<td>3.59</td>
<td>1.93</td>
</tr>
<tr>
<td>100% + 60 min$^1$</td>
<td>3.59</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Where: (1) the residue was dried additionally 30 and 60 minutes.
• Ammonium nitrite decomposition during evaporation occurs when more than 95% of the liquid is evaporated and if ammonium nitrite is formed in solid phase the explosion risks must be carefully considered.

• The chemical denitrification process with the reaction between ammonium and nitrite assumes equal amounts of ammonium and nitrite nitrogen to form nitrogen gas and deviations from this ratio may form gaseous side products as ammonia or nitrogen oxides that may be necessary to be minimised/treated to avoid negative environmental effects.

• Removal of ammonium nitrite from a solution can be followed in chemical denitrification by use of conductivity measurements as ions are transferred into molecules.

• Compared with other solutions the proposed system for nitrogen removal from leachate has many advantages based on the technology (use of existing ponds, low use of chemicals and oxygen, control by use of conductivity etc.), but safety aspects, the need for a concentration step, and possibilities to minimize formation of other gaseous components than nitrogen gas must be further evaluated and are crucial questions for applying the process scheme in full-scale.

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References


