COMBINED NITRITATION AND CHEMICAL DENITRIFICATION FOR NITROGEN REMOVAL FROM LANDFILL LEACHATES

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ABSTRACT

A new treatment system has been proposed to remove nitrogen from landfill leachates with the combination of partial nitritation (biological oxidation of ammonium to nitrite) followed by chemical denitrification with oxidation of remaining ammonium with nitrite to nitrogen gas. The concentration of nitrite and ammonium plays the most important part for the chemical denitrification, and the use of freezing/thawing and evaporation/drying to concentrate these components were investigated in this paper. Several experiments were performed with high and equal concentrations of ammonium and nitrite (from 200 mg N/l to 3200 mg N/l of each component) at different pH values in water solutions and in leachate. Results showed that the percentage of removed nitrogen increased with increasing initial concentration of solution. During freezing/thawing a maximum removal efficiency of 68% of total nitrogen was obtained for the highest studied initial concentrations of ammonium and nitrite, respectively, in a water solution at pH 4, and about 56 % for leachate with the same concentration. Nearly all nitrogen was transferred to the gas phase at initial neutral pH-values during the evaporation/drying process (somewhere between 95 and 100 % removal of liquid) both for a water solution and leachate with the same initial concentration of ammonium and nitrite nitrogen. Thus, from a technical standpoint a system with partial nitritation to the same amount of ammonium and nitrite nitrogen followed by chemical denitrification has a great potential. The removal of ammonium nitrite was very well correlated with the decrease of conductivity. Before the proposed system can be applied in full-scale, safety risks (crystals of ammonium nitrite may explode when heated above 60-70 °C) must be carefully studied and evaluated as well as possible side reactions forming nitrogen oxides or release of ammonia.

KEYWORDS

Chemical denitrification; conductivity; evaporation/drying; freezing/thawing; leachate; nitrogen removal

INTRODUCTION

Landfill leachates are highly polluted wastewaters that usually have a very high concentration of ammonium-nitrogen. The composition of leachate will vary among all depending on the age of the landfill. Old landfills have too low concentration of biodegradable organic material for biological denitrification. One of possible methods to treat leachate could be a combination of biological pretreatment and physical-chemical treatment as a denitrification step, as described in a previous paper (Nikolić and Hultman, 2003a).

In the first part of proposed treatment system biological nitritation occurs in a SHARON-type reactor, where half of ammonium is oxidised to nitrite. The second part is chemical denitrification of concentrated solution of ammonium and nitrite, where ammonium is oxidized with nitrite to nitrogen gas and water. The pH adjustment is needed before the concentrating step for ensuring

favourable conditions for the reaction between ammonium and nitrite ions. Table 1 shows a short description of proposed steps.

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	Nitritation	Concentrating step	Chemical denitrification					
	$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$	Freezing Evaporation	$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$					

Table 1. Proposed steps in a new treatment system for landfill leachates.

In a previous paper (Nikolić and Hultman, 2003b) it was discussed the possibility to use freezing/thawing as a concentrating step. Another possible method to concentrate the solution is evaporation if the residue is a liquid or drying if the residue is a solid (Nikolić and Hultman, 2003c). In this paper a summary of results of freezing /thawing and evaporation/drying of different water solutions and leachate solutions will be presented. In order to find the easiest way to follow nitrogen removal and in that way to simplify the maintenance of treatment plants, conductivity changes were followed.

MATERIAL AND METHODS

Several series of experiments were performed with different concentrations of ammonium and nitrite nitrogen at different initial pH values, both in water solution (tap water) and in leachate. Solutions of equal and increased concentrations of NH_4^+ -N and NO_2^- -N (from 200 mg N/l up to 3200 mg N/l of each) were prepared. The ratio of ammonium and nitrite nitrogen was about 1:1. Sodium nitrite and ammonium chloride was added to obtain the desired concentration of nitrogen and ratio between ammonium 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 analyzed. In all experiments, the same leachate has been used and it was from Tvetaverket landfill from Södertälje, Sweden and it falls into the category of old landfills. In the freezing experiments 173 mg N/l of ammonium-nitrogen was found in leachate, and in the evaporation experiments 184 mg N/l of ammonium-nitrogen was found, and that is due to the time difference between this two set of experiments. Then, nitrite and ammonium were added in order to reach high and equal concentrations like in the experiments with water solutions.

Freezing

In the freezing study, all samples were immediately frozen taking the same volume of the sample (about 30 ml) into the plastic bottle. Frozen samples were thawed for 12 h at 4 °C and then concentrations of inorganic nitrogen species like ammonium-nitrogen, nitrite-nitrogen and nitratenitrogen were analysed. No gas composition was analysed. The initial pH value was measured (before freezing). Conductivity changes during the following experiments were observed by measuring conductivity before and after the freezing of samples. An electromagnetic mixer has constantly mixed the solutions. Freezing equipment was used to freeze the samples.

Evaporation

In the evaporation study, 20 or 100 ml of sample were evaporated in a sand bath (if not noted differently). A small volume of the sample was chosen due to safety reasons (crystals of ammonium nitrite may explode when heated at 60 - 70 °C; Lewis, 1996). The evaporation was conducted under the boiling temperature of either water or leachate at different temperatures (25, 50, 60 and 90 °C) as shown in Table 3. pH value of 7 means natural pH value where no acid has been added, and it was around 7.3 for water solutions and around 7.1 for leachate.

In all experiments, evaporation was conducted until the whole volume of the sample (if not noted differently) was evaporated, i.e. until the sample was transferred into a solid state, and then immediately removed from the sand bath. After evaporation the same amount of pure water (20 or 100 ml) was added to the samples and then the concentrations of ammonium-nitrogen, nitrite-nitrogen, nitrate-nitrogen were analysed. Conductivity was measured before and after evaporation in all samples.

In the third set of experiments (Table 2) the evaporation temperature was kept at 60 °C, as in the first set, but the evaporated volume differed and it was from 25 till 95 % from the initial volume of 100 ml. In samples where the evaporated volume was from 25 till 85 %, no pure water was added before the analyses. In sample where 90 and 95 % of the liquid was evaporated, the concentrates were diluted and then measured. The composition of the vapour during evaporation was not studied.

Analytical methods

pH was measured with a pH-meter, Model 210A Meter, which was calibrated with pH 7 and pH 4 buffer solutions. Ammonia nitrogen (NH_4^+-N) was determined by flow injection analysis and gas diffusion, using spectrophotometer Tecator Aquatech Analyzer application ASN 140-03/90 in range: 1.0-100.0 mg/l NH₄-N. Nitrite nitrogen (NO_2^--N) was determined using Aquatech Analyzer application ASN 144-01/90 in range: 25-1000 µg/l NO₂-N. Nitrate + Nitrite $(NO_3^--N+NO_2^--N)$ analyses were performed also by Aquatech Analyzer. In this method, nitrate is reduced to nitrite in a copper-cadmium reduction column and then measured as nitrite. Conductivity was measured by placing the conductivity meter Orion 115 in a sample and recording the electrical resistance.

RESULTS AND DISCUSSION

Influence of pH values and initial nitrogen concentration on removed nitrogen

Freezing. With the goal of studying the optimal conditions for decomposition of ammonium nitrite during freezing several experiments were performed with 200 mg N/l of ammonium-nitrogen and 200 mg N/l of nitrite-nitrogen at pH values between pH 7 and pH 1 and during different time intervals, as shown in Nikolić and Hultman, 2003b. The influence of freezing on the reaction rates was investigated by measuring the concentrations of NH_4^+ , NO_2^- and NO_3^- in samples before and after freezing. It was shown that nitrogen removal was much higher in frozen samples (around 35 % at pH 4) than in samples that were not frozen (around 5 % for samples with pH >3), and this is probably due to a freeze concentration effect. Further, it was shown (see Figure 1) the influence of pH values on removed nitrogen after freezing process. It can be seen that the favorable pH value for the reaction of decomposition of ammonium nitrite is a pH value of 4, which is in an agreement with literature (Smith and Clark, 1960).

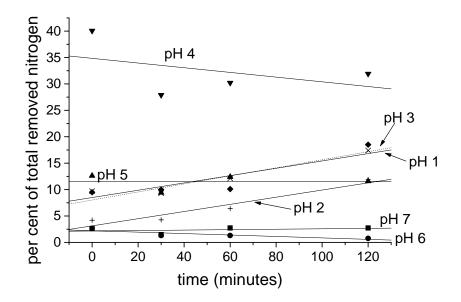


Figure 1. Effect of pH on the reaction of decomposition of 200 mg/l ammonium-nitrogen and 200 mg/l nitrite-nitrogen in water solution after freezing. (Nikolić and Hultman, 2003b)

Since it was shown that freezing of ammonium nitrite water solution accelerates the reaction rate, and that the highest nitrogen removal was observed at the pH value of 4, nitrogen removal during freezing process was further studied only at pH 4 in both water solution and in leachate at higher concentrations.

Evaporation. Figure 2 shows the influence of initial concentration on the removal efficiency of nitrogen for water and leachate, respectively, and at two different pH ranges. For solutions in the pH range between 4 and 7 approximate average values for nitrogen removal were calculated because it was shown (Nikolić and Hultman, 2003c) that there is a big similarity in behaviour (i.e. nitrogen removal efficiency) among those solutions. However, in the experiments only initial pH values were measured and during the evaporation process large changes will occur of the pH values for the remaining liquid. Furthermore, the difference between removed nitrogen at pH 4 -7and pH 3 is lower in leachate than in water solutions, i.e. the pH dependence of the leachate is lower than for water. This is probably due to the reason that the hydrogen carbonate concentration is much higher in a leachate than in the water. Hydrogen carbonate has a buffering effect on pH value changes during the evaporation process. Figure 2 shows the less dependence of pH value for leachate compared with water solution, the very high removal efficiency of nitrogen in water solutions with pH values between 4 and 7, and the important role of initial concentration on removal efficiency of nitrogen from leachate during evaporation. Since it was shown a clear difference between removal efficiency at two pH ranges, for both water solutions and for leachate, further comparison of results between freezing and evaporation will deal only with one of solutions in the pH range from 4 to 7.

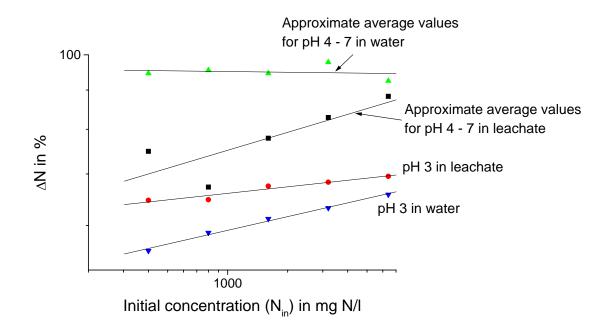


Figure 2. Comparison of influence of pH values on removed nitrogen between leachate and water solutions after evaporation at 90 °C. (Nikolić and Hultman, 2003c)

Freezing and evaporation - comparison. Figures 3 and 4 show the influences of initial concentration and inhibitory behaviours of leachate on removed nitrogen after freezing and evaporation processes. From Figures 3 and 4 it could also be seen that with the same concentration of ammonium and nitrite the percentage of removed ammonium and total nitrogen was much higher after evaporation than after freezing. Figure 3 shows a comparison of removed ammonium-nitrogen in the NH_4NO_2 water solution and in the solution of leachate- NO_2 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 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 removed ammonium, which is in an agreement with literature (Smith and Clark, 1960).

According to Figure 4, the percentage of removed total inorganic nitrogen in water solution sharply increases with increasing values of initial concentration, and in the highest studied concentration (3200 mg N/l of each component) 4347 mg N/l of total inorganic nitrogen was removed after freezing, whereas 6334 mg N/l of total inorganic nitrogen was removed after evaporation at pH 7. Due to the leachate's inhibitory behavior, there is less removed total inorganic nitrogen in leachate than in water solution. Leachate consists of different cations and ions 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 behavior decreases with increasing initial concentration and for the highest concentration is almost equalized with results in water solution (3549 mg N/l after freezing and 5311 mg N/l at pH 7 after evaporation).

Furthermore, results from freezing study (Nikolić and Hultman, 2003b) showed that a lot of nitrite is being oxidized to nitrate. The reason lies in fact (Takenaka et al. 1996) that the reaction of nitrous acid with dissolved oxygen under acid conditions is accelerated about 10^5 times by freezing of the

aqueous solution (2HNO₂ + O₂ \leftrightarrow 2HNO₃). In the absence of dissolved oxygen, a small percent of nitrate can also be formed due to freezing: 3HNO₂ \rightarrow NO₃⁻ + 2NO + H⁺ + H₂O.

Takenata et al. (1996) state that if the freezing potential of the ice is negative then nitrate formation can be prevented. They showed that this could be achieved by the addition of salts like NaCl and KCl, or some organic compounds like methanol or acetate. They also pointed out that the oxidation reaction with dissolved oxygen involves the HNO₂ molecule rather than the NO₂⁻ ion and as a result is highly pH dependent. As shown in literature (Reuss and Smith, 1965), the equilibrium constant K_a for the equation HNO₂ \leftrightarrow H⁺ + NO₂⁻ is 6.0 x 10⁻⁴ (pKa = 3.2), and that at pH 4 and pH 3 the amounts of nitrite-N existing as HNO₂ are 14 and 63 %, respectively. In all experiments, only the initial pH value was measured, so the possible decrease of pH due to freezing (Takenaka et al. 1996), and therefore the increase of HNO₂ concentration was not measured. But, for the reaction of decomposition of ammonium nitrite concentration of molecular HNO₂ also plays an important role. As the concentration of HNO₂ increases the reaction rate increases too (Dusenbury and Powel, 1951). This means that increasing of pH value in order to avoid nitrate formation may practically decrease available concentration of nitrite for chemical denitrification.

As a pre-concentration process before freezing and evaporation concentrates components that might inhibit the chemical denitrification process, the concentration effects should be further studied. It is possible that the suggested biological step before chemical denitrification with partial nitritation may remove some of the inhibitory substances and also most of the alkalinity and the treated leachate before chemical denitrification may have properties coming closer to the studied with water solutions compared with leachate with added chemicals.

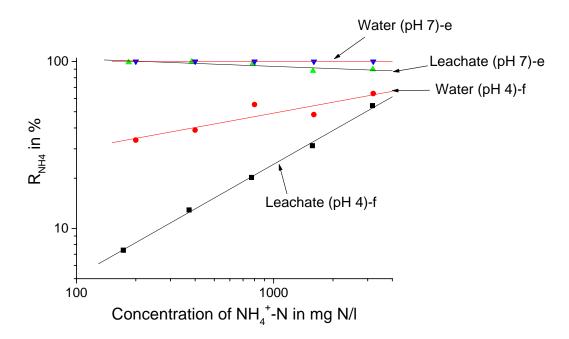


Figure 3. Dependence of removed ammonium (R_{NH4}) with increasing concentration of ammonium in initial water solutions and in leachate after freezing (-f) and evaporation at 90 °C (-e).

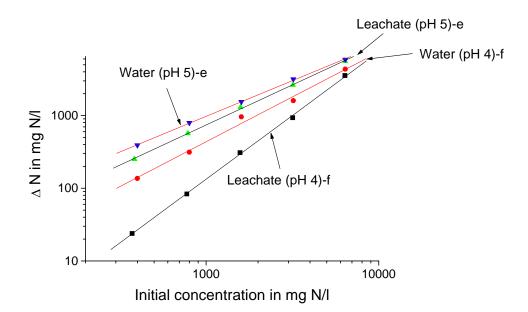


Figure 4. Influence of increasing the initial concentration (N_{in}) on removed nitrogen (ΔN) in water solutions and in leachate after freezing (-f) and evaporation at 90 °C (-e).

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

Figures 5 and 6 show the influence of the initial pH values on the ratio of removed ammonium and nitrite nitrogen after evaporation and freezing. If decomposition of ammonium nitrite proceeds according to reaction $NH_3 + HNO_2 \rightarrow N_2 + 2H_2O$, then concentrations of removed ammonium and nitrite should be the same, and the ratio $\Delta N_{NH4} / \Delta N_{NO2}$ should be equal to 1. Since a lot of nitrite is being oxidized to nitrate during freezing, the concentration of removed ammonium should be equal with the difference between removed concentrations of nitrite and produced nitrate. From Figures 5 and 6 it can be seen that the ratio of removed nitrogen species after evaporation differs much from 1 (specially in leachate) and the difference depends on the initial pH values. The ratio of removed nitrogen after freezing in water solutions is almost 1 but it decreases with increasing initial concentration. In leachate the ratio is higher than 1 and with increasing concentration it reaches 1. Therefore, it seems that during evaporation some other reactions as ammonia stripping and formation of NO_x , are involved into nitrogen removal. Crystals of ammonium nitrite during heating can also be decomposed into ammonia and NO_x (Lewis, 1996). Since gaseous products of ammonium nitrite decomposition were not measured, it is difficult to evaluate the mechanisms of reaction. Side-reactions during freezing might be that some of the nitrogen is released as NO and NH₃ (Allison, 1963). The Figures indicate that the most favorable initial pH values for the nitrogen gas formation after evaporation are between pH 7 and 5 for water solutions and about pH 5 for leachate.

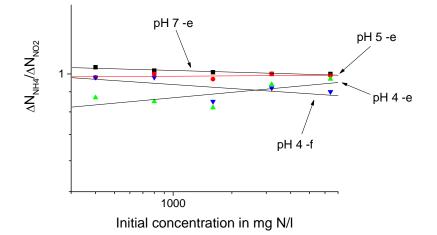


Figure 5. Influence of increasing of initial concentration on the ratio between removed ammonium nitrogen and nitrite nitrogen ($\Delta N_{NH4}/\Delta N_{NO2}$) in water solutions after evaporation at 90 °C (-e) and freezing (-f).

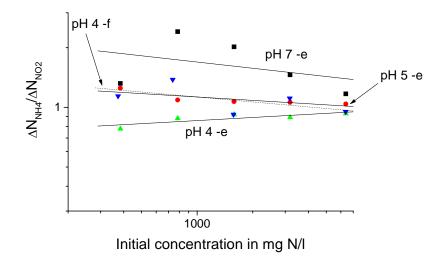


Figure 6. Influence of increasing of initial concentration on the ratio between removed ammonium and nitrite nitrogen ($\Delta N_{NH4}/\Delta N_{NO2}$) in leachate after evaporation at 90 °C (-e) and freezing (-f).

Influence of removed concentration of inorganic nitrogen on removed conductivity

Figures 7 and 8 show measurements of electrical conductivity. It can be seen that the mentioned increase of total inorganic nitrogen removed from solutions after evaporation and freezing with increasing of initial concentration could be followed also with the difference in conductivity measured before and after evaporation or freezing (ΔC). Figure 7 shows that with an increase of the initial concentration the removed nitrogen increases, electrical conductivity decreases and ΔC increases. ΔC for water solutions after evaporation is larger than for leachate and that is due to the fact that the percentage of removed nitrogen is higher in water solutions than in leachate. Furthermore, as can be seen from Figure 7, a difference between measured conductivities (ΔC) for leachate after freezing is larger than ΔC for water solution, and this is because besides nitrogen removal alkalinity is also removed. But, in a full-scale process scheme for leachate treatment, after

nitritation alkalinity will already be reduced. So, the composition of leachate, as mentioned before, will be different compared to the leachate used in these experiments. Figure 8 shows that the correlation between removed conductivity ΔC and total inorganic nitrogen removed from solution could be written as linear equation $\Delta C = a * \Delta N + b$, with a high correlation coefficient ($R^2 = 0.99$). The value of *a* varied between 0.003 and 0.005, and is probably due to removed alkalinity but also due to the influence of ionic strength of the salt concentration on conductivity, and the value of *b* refers to the influence of initial salts and added chemicals. The leachate nitrite line shows a sharper rise than the ammonium nitrite line due to removed alkalinity during both freezing and evaporation processes.

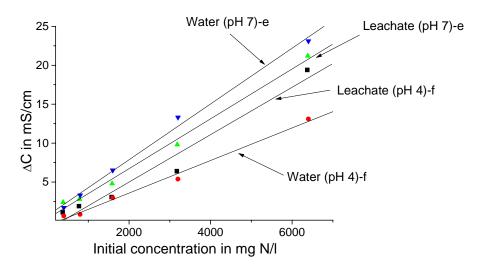


Figure 7. Dependence of removed conductivity (ΔC) on increasing initial concentration in water solutions and in leachate after evaporation at 90 °C (-e) and freezing (-f).

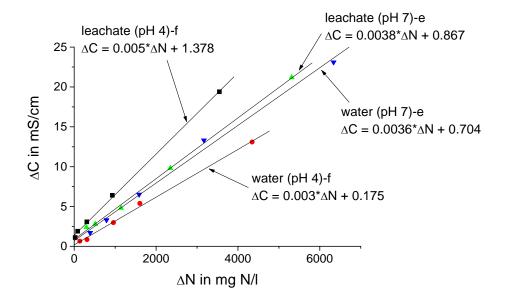


Figure 8. Dependence of removed conductivity (ΔC) on total inorganic N removed from solution in water solutions and in leachate after evaporation at 90 °C (-e) and freezing (-f). (R² for all curves = 0.99)

Influence of evaporated volume and temperature of evaporation on nitrogen removal

From previous experiments (Nikolić and Hultman, 2003c) it was shown that chemical denitrification occurred when more than 75% of liquid was evaporated in both water solution and in leachate. It was also shown that as the volume of the sample decreased concentrations of remained ammonium and nitrite increased rapidly. In order to investigate at which evaporated volume chemical denitrification occurs and how the pH value is changing during evaporation new experiments were conducted. Table 2 shows the influence of evaporated volume of the samples on the change in composition in the residue followed with conductivity. Chemical denitrification occurred somewhere between when 95% of liquid was evaporated and when all liquid was evaporated. Furthermore, it was shown that as the volume of the sample decreased the pH value of the remaining liquid also decreased (in samples were 100% of liquid was evaporated pure water was added and therefore the pH value increased). Additional drying of the residue showed that conductivity decreased very little comparing with samples that were not dried additionally, but it also showed an increase concerning a pH value.

Table 2 . Evaporation of 100 ml of 200 mg/l NH ₄ ⁺ -N and 200 mg/l NO ₂ ⁻ -N water solutions with	i
different evaporated volume at 60 °C	

Sample ID		C _{before}	Cafter	pН	Time
		(mS/cm)	(mS/cm)		(hours)
	25 % evaporated	3.59	4.81	6.47	8.14
	50 % evaporated	3.59	7.20	6.10	13.48
	75 % evaporated	3.59	13.10	6.06	15.42
	85 % evaporated	3.59	22.8	6.10	17.37
pH 7	90 % evaporated	3.59	30.8	6.20	19.20
	95 % evaporated	3.59	59.64	6.28	19.36
	100 % evaporated	3.59	1.98	8.54	12.28
	$100 \% + 30 \min^{(1)}$	3.59	1.93	9.00	13.01
	$100 \% + 60 \min^{(1)}$	3.59	1.94	8.84	14.14

Where:

(1) the residue was dried additionally 30 and 60 minutes.

Table 3 shows the influence of different evaporation technologies, different temperatures of evaporation and the evaporation speed on chemical denitrification followed with the decrease of conductivity. The difference in duration of evaporation in a sand bath between samples evaporated at 90 ° and at 65 °C was around 5 hours. The percentage of removed ammonium-nitrogen decreased around 7% for samples at pH 7, and around 14% for samples at pH 5. The total removal of inorganic nitrogen varied between 88 and 91% for samples at pH 7, which is about 9% less than at evaporation at 90 °C. Samples evaporated at 25 °C were not evaporated in a sand bath but were left at room temperature for necessary period of time (three weeks). Samples evaporated at 50 °C were first heated up to 50 °C and then were left in an incubator (that keeps constant temperature) until complete evaporation occurred. From Table 3 it can be seen that the highest removal efficiency (or ΔC) was achieved when samples were evaporated in a sand bath and lowest in an incubator. Furthermore, the influence of the evaporation technology seems to affect results more than the influence of both an evaporation temperature and evaporation speed, but this require more investigation.

Therefore, the proposed evaporation/drying method for chemical denitrification should in the same time enable complete or almost complete evaporation and operate at low temperature due to safety

aspects (crystals of ammonium nitrite may explode at 60 - 70 °C; Lewis, 1996). One of possible methods could be natural evaporation/drying during the summer period. Another possibility is to combine adequate technical methods (like a new evaporation technology that operate at low temperature as described by Ettala, 1997) with natural methods, where technical methods could evaporate solutions up to 95% and then if necessary such concentrated solutions can be transported to ponds where drying can take place, but the whole process should be maintained with precautions.

Sample ID	C _{before}	Cafter	Time	ΔC	Evaporation
Sample ID	(mS/cm)	(mS/cm)	(hours)	(mS/cm)	technology
pH 7 at 25 °C	3.64	3.01	511.12	0.63	Room temperature
pH 5 at 25 °C	3.70	2.90	505.0	0.80	Room temperature
pH 7 at 50 °C	2.81	2.48	36.54	0.33	Incubator
pH 5 at 50 °C	2.92	2.69	36.54	0.23	Incubator
pH 7 at 65 °C	3.29	1.80	7.02	1.49	Sand bath
pH 5 at 65 °C	3.32	1.96	7.57	1.36	Sand bath
pH 7 at 90 °C	3.40	1.73	2.12	1.67	Sand bath
pH 5 at 90 °C	3.44	1.81	2.32	1.63	Sand bath

Table 3. Evaporation of 20 ml of 200 mg/l NH_4^+ -N and 200 mg/l NO_2^- -N water solutions at different temperatures

CONCLUSIONS

Chemical denitrification was investigated during freezing/thawing and evaporation/drying processes and it was shown that:

• With the same initial concentration of ammonium and nitrite nitrogen the percentage of removed ammonium and total inorganic nitrogen was much higher after evaporation than after freezing. Furthermore, almost all inorganic nitrogen (97 - 99 %) was removed at all concentrations from the water solution during evaporation at natural initial pH value (about 7). In leachate solutions, the percentage of removed total inorganic nitrogen varied between 64 and 94 % and increased with increasing of initial concentration. During freezing 64 % of ammonium nitrogen was removed from the water solution of ammonium nitrite in the highest concentration (3200 mg/l of ammonium nitrogen), and about 54 % in leachate solution with the same concentration. It was shown that leachate acts as inhibitor to chemical denitrification, but this behavior decreases with increasing concentration;

• The influence of initial pH values on the quotient of removed ammonium and nitrite nitrogen showed that the most favorable initial pH values for the ammonium nitrite decomposition according to reaction $NH_4^+ + NO_2^- = N_2 + 2H_2O$ during evaporation are between pH 5 and 7 for water solutions and about pH 5 for leachate, and during freezing pH 4 for both water solutions and leachate;

• It was shown that ammonium nitrite decomposition during evaporation occurs when more than 95% of liquid was evaporated, i.e. somewhere between 95% and 100%;

• Ammonium nitrite decomposition i.e. nitrogen removal during both evaporation and freezing was very well correlated with the decrease of electrical conductivity. The conductivity measurements showed a decrease as the reaction proceeds. Conductivity changes of ammonium nitrite water solution were calculated and it was shown that the differences between measured and calculated values were in the acceptable ratio (Nikolić and Hultman, 2003b; Nikolić and Hultman, 2003c).

Therefore, one of possible methods to remove nitrogen from leachate could be chemical denitrification during evaporation (where different technical methods that operates at low temperatures, below 60 °C, should be considered) and, if necessary, natural drying of the concentrate. Furthermore, before this treatment system can be applied in full scale one should be aware of ammonium nitrite explosive properties in a crystal state when heated up to 60-70 °C and possible side reactions of nitrogen oxides and ammonium release.

REFERENCES

- Allison F.E. (1963) Losses of gaseous nitrogen from soils by chemical mechanisms involving nitrous acid and nitrites. *Soil Sci.*, **96**, 404-409.
- Dusenbury H.J. and Powell E.R. (1951) Reactions of nitrous acid -ammonium nitrite decomposition. J. Am. Chem. Soc., 73, 3266-3270.
- Ettala M. (1997). Full-scale leachate treatment using new evaporation technology. *Proceedings* Sardinia 97, Sixth International Landfill Symposium, Cagliari, Italy, 423-426.
- Lewis R.J. (1996) Sax's dangerous properties of industrial materials. A division of Internal Thomson Publishing, Inc., USA.
- Nikolić A. and Hultman B. (2003a) Combined nitritation and chemical denitrification a new treatment system for nitrogen removal from landfill leachates. *Vatten*, **59**(1), 39-45.
- Nikolić A. and Hultman B. (2003b) Chemical denitrification of landfill leachates under freezing/thawing conditions. *Vatten*, **59**(2), 89-97.
- Nikolić A. and Hultman B. (2003c) Chemical denitrification of landfill leachates during evaporation/drying. *Vatten*, **59**(3), 183-190.
- Reuss J.O. and Smith R.L. (1965) Chemical reaction of nitrites in acid soils. *Soil Sci. Soc. Proc.*, **29**, 267-270.
- Smith D.H. and Clark F.E. (1960) Volatile losses of nitrogen from acid or neutral soils or solutions containing nitrite and ammonium ions. *Soil Sci.*, **90**, 86-92.
- Takenaka N., Suzue T., Ohira K., Morikawa T., Bandow H. and Maede Y. (1999) Natural denitrification in drying process of dew. *Environ. Sci. Technol.*, **33**(9), 1444-1447.
- Takenaka N., Ueda A., Diamon T., Bandow H., Dohmaru T. and Maeda Y. (1996) Acceleration mechanism of chemical reaction by freezing: the reaction of nitrous acid with dissolved oxygen. *J. Phys. Chem.* 100, 13874-13884.