INFLUENCE OF DISSOLV ED OXYGEN CONCENTRATION ON DEAMMONIFICATION PROCESS PERFORMANCE

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ABSTRACT
Partial nitrification together with Anammox process (deammonification) is a new method for nitrogen removal from wastewater, which nowadays is widely studied in Europe. Compared to conventional nitrification/denitrification, this method saves 100% of the required organic carbon source and over 60% of the required oxygen. This leads to a reduction of operational costs of 90%. The deammonification process was successfully tested on a laboratory-scale pilot plant at Royal Institute of Technology (KTH) in Sweden for over 2 years. Two reactors of pilot plant were filled with Kaldnes rings as a biofilm carrier and supplied with a supernatant from dewatering of the digested sludge at the Bromma Wastewater Treatment Plant (WWTP). For the stable and efficient process performance a suitable values of many parameters as dissolved oxygen, pH, temperature, NO2-N and NO3-N concentration should be assured. This article presents an evaluation of the influence of dissolved oxygen (DO) on the deammonification process efficiency. Analysis of eight months operation of pilot plant proved that high N-removal efficiency of second reactor (Anammox) is assured by proper NO2-N/NH4-N ratio in the effluent from the first reactor depending on DO concentration. To estimate influence of DO concentration on reaction rates during the Anammox process several batch tests were performed. The highest ammonium and nitrite removal rates were obtained for DO concentration amounted to 0.2÷0.4 mg O2/l. This is in agreement with the observations from laboratory-scale pilot plant, when the best results for Anammox process efficiency took place under similar oxygen conditions. A linear correlation between inorganic nitrogen removal and conductivity in the batch tests proved that conductivity could be a suitable parameter for a nitrogen removal process control.

KEYWORDS
ammonium removal rate; Anammox; batch test; conductivity; deammonification; dissolved oxygen

INTRODUCTION
The deammonification process for treatment of ammonium rich waste streams can reduce the costs of plant operation due to less aeration demand. However, DO concentration is one of the most important and sensitive parameters affecting the deammonification process.

In the first step of the deammonification process nitrite can be produced from ammonia by aerobic autotrophic ammonia-oxidizing bacteria, according to reaction:

\[ \text{NH}_3 + 1.5 \text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + \text{H}^+ \]
In the second step, ammonia together with nitrite is converted to nitrogen gas. This process can be described by reaction:

\[ \text{NH}_4^+ + 1.32 \text{NO}_2^- + \text{H}^+ \rightarrow 1.02 \text{N}_2 + 0.26 \text{NO}_3^- + 2 \text{H}_2\text{O} \]

Bacteria oxidizing ammonia to nitrite need oxygen, whereas bacteria converting ammonia and nitrite to dinitrogen gas are anaerobic and their activity is only reversibly inhibited by oxygen.

DO is a key factor in both the first step of deammonification process – nitritation and in the second one – Anammox. Therefore many authors investigate influence of DO concentration on both processes. Ruiz et al. (2002) proved that at DO of 1.7 mg O\textsubscript{2}/l there was a temporal accumulation of nitrite and at DO of 1.4 and 0.7 mg O\textsubscript{2}/l accumulation increased with the same ammonia consumption. At a DO of 0.5 mg O\textsubscript{2}/l, both nitrite accumulation and ammonia consumption decreased. Similar value is given by Bae et al. (2002), who proved that DO at around 1.5 mg O\textsubscript{2}/l gave the highest nitrite accumulation and these were favour conditions for nitrite production. The results reported by Pollice et al. (2002) indicate dissolved oxygen as an alternative parameter for controlling nitrification to nitrite and that under limited oxygen supply complete and stable conversion of ammonium into nitrite was obtained, independent of the sludge age.

During batch tests performed by Egli et al. (2001), at low oxygen concentration (below 1% of oxygen saturation) reversible inhibition of the Anammox process was recorded. However, higher dissolved oxygen concentration (18% of oxygen saturation) caused irreversible inhibition. According to Helmer et al. (1999) during batch tests inoculated with biofilm material nitrogen loss of almost 60% occurred at a DO concentration of 1 mg/l.

Sensitivity of DO parameter and its influence on nitrogen removal efficiency in CANON process performance was investigated by Hao et al. (2002). According to his simulations DO range for the maximal nitrogen removal efficiency is narrow. A DO deviation of ±0.2 mg O\textsubscript{2}/l from the optimal level could easily reduce the nitrogen removal efficiency by about 5-15%. Modelling trials proved also that DO depends on ammonium surface load (ASL) and it is necessary to adjust DO concentration to the variable ASL. Absence of balance between required and applied DO can lead to the decreased nitrogen removal efficiency.

**MATERIAL AND METHODS**

**Pilot plant description**

The laboratory-scale pilot plant (Figure 1) consisted of two reactors, which were filled with Kaldnes rings as carrier material for fixed biofilm growth. Each reactor was equipped with heater to keep temperature stable (at a level of 31°C) and with mixer to assure proper mixing and oxygen conditions. The pH level was corrected with a continuous dosage of Na\textsubscript{2}CO\textsubscript{3} solution to the first reactor (to keep pH around 8.2). The pilot plant was continuously fed with supernatant from dewatering of the digested sludge from Bromma WWTP, which receives municipal wastewater from central and western part of the Stockholm region. To obtain the required concentration, supernatant was diluted with tap water. Detailed description can be found in earlier publications (Plaza et al., 2003; Szatkowska et al., 2003).
Batch test description

During eight-month operational period of the pilot plant three batch tests with different DO concentration were performed. Each batch test was run in three parallel bottles of 1 litre working volume. On test days, the carriers were taken from the second reactor of the continuously working pilot plant (described above) and put into the bottles to fill 50% of their volume. Then, the liquid from the reactors was poured over the Kaldnes rings up to 1 litre volume. The temperature in each test was kept stable at about 31°C by water bath.

To shorten the reaction time it was decided to increase the amount of Kaldnes rings up to 50% of the working volume, instead of 40% used in the pilot plant. It was planned to reach three different DO concentrations inside of these bottles. In the bottle where conditions should be about 0.2÷0.3 mg O₂/l magnetic stirrers were placed to assure an adequate mixing of medium throughout the test. Compressed air was used to obtain condition of about 1 mg O₂/l in the second bottle and nitrogen gas was used in the third one to obtain as low dissolved oxygen concentration as possible. Figure 2 presents batch test equipment.

The initial concentrations of ammonium, nitrite and nitrate nitrogen were set for each test. To obtain the required concentrations NaNO₂ and NH₄Cl solutions were used (2 mg/ml both for NO₂-N or NH₄-N). The solution of 1M Na₂CO₃ and 0.5M HCl was prepared for pH correction.

Figure 1. Laboratory-scale pilot plant scheme.

Figure 2. Batch test equipment scheme.
MEASUREMENT AND SAMPLING PROCEDURE

Pilot plant
Samples were collected twice a week, both from the inlet and outlet of each reactor of the laboratory-scale pilot plant. They were analysed for ammonium nitrogen (NH₄-N), nitrate nitrogen (NO₃-N) and nitrite nitrogen (NO₂-N) with TECATOR – AQUATEC 5400 ANALYZER (flow-injection system based on VIS spectrophotometry). The parameters such as dissolved oxygen concentration, temperature and pH value were measured every day.

Batch test
Each of the batch tests lasted 8 hours. The proposed sampling strategy enabled very accurate control during the test - every hour 10 ml sample was taken from the bottle by syringe. The samples were filtrated with a pre-filter and a 0.45 µm filter and then stored at -10°C. Samples were analysed for NH₄-N, NO₂-N and NO₃-N like pilot plant’s samples. Moreover, pH, dissolved oxygen concentration and conductivity were measured.

RESULTS – PILOT PLANT
After experiment on the influence of increase in ammonium surface load on deammonification process, pilot plant with 20% volume filled with Kaldnes rings has been operated with high initial ammonium concentration equal to 400 mg/l for three months. System worked with the average overall efficiency amounted to 45.5%. It was decided to increase the volume filled with Kaldnes rings to 40%. Eight-month investigation period started on the 6th January 2003 and lasted until the 28th August. After addition of new Kaldnes rings, initial NH₄-N concentration which amounted to 200 mg NH₄-N/l was gradually increasing to reach the value of 300 mg NH₄-N/l on the 10th February. The process was performed at the average temperature equal to 31.5 ± 0.7 °C and the average pH amounted to 8.1 ± 0.2 for both reactors. These parameters were stable and easy to maintain in optimal range for the deammonification process. DO concentration was very important and sensitive for the process performance and development of new layer of biofilm. DO variations in both reactors are presented in Figure 3.

![Figure 3. Dissolved oxygen in the laboratory-scale pilot plant.](image)

From Figure 3 it can be seen that bigger fluctuations took place in the first reactor than in the second one due to variability in influent ammonium concentration. It can be also observed that after the installation of a new stirrer in the first reactor (22nd of June), which assured better mixing of
Kaldnes rings and proper adjustment of DO concentration, smaller fluctuations were recorded. During the first month, when supernatant with the lower ammonium concentration (about 200 mg NH$_4$-N/l) was supplied to the first reactor good conversion of ammonium to the nitrite nitrogen was recorded. After increasing influent ammonium concentration, smaller amount of removed ammonium together with very low nitrite and nitrate production was observed. From the end of June increasing tendency in nitrite production could be observed, what proved that proper DO conditions were assured for biofilm developed on new Kaldnes rings and that new bacterial culture started to exhibit activity (Figure 4).

![Figure 4](image-url) Nitrogen variations in the first reactor.

At the beginning of the analysing period in the second reactor the process proceeded with high nitrogen removal as it can be observed in Figure 5. After increase of ASL, similar like in the first reactor, efficiency of nitrogen removal dropped and fluctuated in small degree until the end of June.

![Figure 5](image-url) Nitrogen variations in the second reactor.

After that time, improved value of nitrite to ammonium ratio in effluent from the first reactor caused that efficiency in the second reactor was increasing. Almost complete utilization of ammonium nitrogen together with nitrite nitrogen can be observed at that time. Nitrate nitrogen concentration increased only insignificantly. As it can be seen from the above presented figures, DO
concentration has a big influence on process efficiency in both reactors. The first reactor requires higher DO concentration to oxidize ammonium to nitrite while the second reactor should work under anaerobic condition to convert ammonium and nitrite to nitrogen gas.

RESULTS – BATCH TESTS

Process parameters
During batch test temperature in the bottles was kept constant at 31°C. The pH level was corrected to maintain it in the optimal, similar to pilot plant level, when necessary. It occurred that it was difficult to reach the DO concentration within planned ranges of 0.2÷0.3; 1 mg O₂/l and especially for the bottle where DO should be equal to 0 mg O₂/l. The average value of DO during all three batch tests amounted to 0.18 mg O₂/l for the first bottle (DO~0), 1.07 mg O₂/l for second (DO~1) and 0.27 mg O₂/l for the third one (DO~0.2÷0.4). Table 1 presents average values of DO, temperature and pH during three batch tests.

Table 1. Average values of DO, temperature and pH during batch tests.

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<th>Test No</th>
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<th>Bottle 3</th>
<th>Bottle 1 T [°C]</th>
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Nitrogen conversion
Analysis of nitrogen forms variation during the batch tests enabled to calculate removal rates of ammonium, nitrite and inorganic nitrogen. All results of removal rates calculations are presented in Figure 6.

Figure 6. Removal rates obtained during batch tests.

For three different DO concentrations dissimilar nitrogen conversion paths were recorded. It can be observed from Figure 7 where the results from batch test no 3 (as an example) are presented.
Figures 7-A and 7-B present similar utilization of nitrogen compounds. In these both figures the curves representing NH$_4$-N and NO$_2$-N concentration run almost parallel what indicates that ammonium and nitrite are removed simultaneously. After 7 hours, nitrite nitrogen in bottle with the lowest DO concentration was almost completely utilized. Utilisation in the bottle with DO between 0.2÷0.4 mg O$_2$/l lasted one hour shorter. In both bottles a considerable decrease in the NH$_4$-N concentration without production of nitrate (only insignificant increase after NO$_2$-N consumption) could be observed during the 8-hour test period. Amount of nitrate did not exceed 13 mg NO$_3$-N/l what corresponds below to 10% of initial ammonium concentration. The slope of utilization curve was bigger for nitrite than for ammonium. It means that nitrite removal rates are higher than ammonium removal rates. It also can be seen that after utilization of nitrite, ammonium utilisation is slower. For the bottle with the lowest value of DO concentration ammonium removal rates amounted to 0.49÷0.93 g NH$_4$-N/m$^2$d and nitrite removal rates fluctuated between 0.51÷0.91 g NO$_2$-N/m$^2$d. For the bottles with DO~0.2÷0.4 mg O$_2$/l they amounted to 0.67÷1.04 g NH$_4$-N/m$^2$d and 0.72÷1.26 g NO$_2$-N/m$^2$d for ammonium and nitrite respectively. Achieved values of ammonium removal rates for the bottle with DO concentration in the range of 0.2÷0.4 mg O$_2$/l are comparable with results reported by many others authors like Johansson et al. (1998); Siegrist et al. (1998); Szatkowska et al. (2002).
Figure 7-C representing nitrogen conversion in the bottle with the highest DO concentration indicated different reactions. Ammonium is utilized with parallel growth of nitrite and at a higher than in the bottles A and B but constant nitrate concentration. After 6 hour of tests the concentration of ammonium and nitrite nitrogen reach almost the same value and in the next hour nitrite exceed ammonium concentration. Ammonium removal rates varied in the range from 0.94 to 1.06 g NH₄-N/m²d. Under this condition (about 1 mg O₂/l) the Anammox process was inhibited and only ammonium oxidation to nitrite took place.

To estimate the influence of DO on total nitrogen removal, apart from ammonium and nitrite removal rates, total inorganic removal rates were also calculated. Nitrogen removal rate for bottle with the lowest DO concentration was estimated as 80% of the rate obtained for the test with oxygen values 0.2÷0.4 mg O₂/l, while as 52% for the bottle with DO~1 mg O₂/l. These calculations confirm previous conclusions that the best results were achieved under DO concentration within the range of 0.2÷0.4 mg O₂/l. Under these conditions during batch test no 2 and 3 inorganic nitrogen removal rate reach the maximum value over 2 g N/m²d.

**Conductivity**

During all batch tests parallel with DO, pH, and T every hour conductivity measurements were performed. Analysing correlation between inorganic nitrogen utilization and conductivity, it was possible to find a linear equations and correlation coefficients. This is illustrated in Figure 8, where correlation for analysed test no 3 is presented as an example.

![Figure 8](image)

**Figure 8.** Correlation between inorganic nitrogen and conductivity values. Batch test no 3. A) DO~0.14÷0.18 mg O₂/l; B) DO~0.2÷0.4 mg O₂/l; C) DO~1 mg O₂/l

Correlation coefficients were relatively high and exceed 0.8. To conclude conductivity measurements can be used as a control parameter for the nitrogen removal process.

**DISCUSSION**

The average DO concentration in the first reactor for period until the 22nd June (period I) amounted to 0.46±0.28 mg O₂/l. During last two months (period II) the average DO concentration was lower and equal to 0.38±0.14 mg O₂/l. For the second reactor DO concentration did not change significantly during the whole experimental period and the average value amounted to 0.30±0.15 mg O₂/l. Moreover, the stable DO condition in the first reactor during the last two months assured
proper ratio between NO$_2$-N and NH$_4$-N. The average value of this ratio for period I was lower than for period II and amounted to 0.22 while for period II it was equal to 0.7. The proper NO$_2$-N/NH$_4$-N ratio is a condition for high efficiency of Anammox process in the second reactor, as it can be seen from Figure 9.

$$y = 14.223 \ln(x) + 75.159$$

$$R^2 = 0.6138$$

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{N-removal efficiency in the second reactor of the pilot plant as a function of NO$_2$-N/NH$_4$-N ratio in the first reactor.}
\end{figure}

In period I the lower average value of NO$_2$-N/NH$_4$-N ratio in the first reactor responds to the lower average value of nitrogen removal efficiency in the second reactor, which is equal to 50.7%. Higher efficiency with the average value of 70.5% can be observed parallel with higher value of NO$_2$-N/NH$_4$-N ratio for the period II.

Stoichiometrical reaction for Anammox process gives NO$_2$/NH$_4^{+}$ ratio equal to 1.3 as suitable value for efficient process performance. From calculated equation for value \(x = 1.3\), value \(y = 78.9\) is obtained. It means that the maximal process efficiency that can be reached for ratio equal to 1.3, amounts to 78.9%. The residual 21.1% shows that another factors than NO$_2$-N/NH$_4$-N ratio are responsible for the Anammox process inhibition.

Recorded values of nitrogen removal efficiency for period I and II for the second reactor and corresponded to them DO concentrations are presented in Figure 10. The most points concentrated area with the highest efficiency was obtained within the range of 0.2÷0.4 mg O$_2$/l. Points show that the highest efficiency from this range belongs to period II. It should be emphasized that in the same range (0.2÷0.4 mg O$_2$/l) the highest ammonium and nitrite removal rates were obtained during batch tests. It proved that second reactor of pilot plant had suitable conditions of DO (kept in optimal range) for bacterial culture growth and biofilm development and it also resulted in high efficiency of the Anammox process.

Summarising, stable DO concentration positively affect ammonium oxidation in the first reactor what assures proper NO$_2$-N/NH$_4$-N ratio in the influent to the second reactor. DO within the range of 0.2÷0.4 mg O$_2$/l together with suitable NO$_2$-N/NH$_4$-N ratio is the condition for a high efficiency of Anammox process in the second reactor.
Figure 10. N-removal efficiency in the second reactor as a function of DO.

CONCLUSIONS

- Results obtained during eight-month operation of pilot plant and three series of batch tests proved that DO concentration is a very sensitive parameter, which affect the deammonification process.
- Proper NO$_2$-N/NH$_4$-N ratio in the first reactor assures very good course of Anammox reaction in the second reactor.
- The bacterial culture from reactor 2 was utilising ammonium at required level only with a surplus of nitrite. At low level of nitrite the deammonification process was much slower.
- The optimal range of DO varies between 0.2÷0.4 mg O$_2$/l for the second reactor. Those conditions enabled bacterial culture growth in the system.
- Ammonium removal rates achieved during all batch tests were in the range of 0.5÷1.1 g NH$_4$-N/m$^2$.d.
- The highest value of ammonium and nitrite removal rates was obtained under oxygen condition of 0.2÷0.4 mg O$_2$/l.
- Increase and decrease in DO concentration from the optimal range had a negative effect on the Anammox process efficiency. Both ammonium and nitrite removal rates were slower.
- Second reactor of the pilot plant worked with the highest efficiency under the similar oxygen conditions of 0.2÷0.4 mg O$_2$/l as during the batch tests.
- The inorganic nitrogen concentration decrease was proportional to the conductivity and therefore this parameter can be used as a controlling parameter of the nitrogen removal process.

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