LIMITED BIOLOGICAL NITRITATION AND DENITRIFICATION

A.Machnicka, J. Suschka and S. Popławski

University of Bielsko-Biała, Institute of Environmental Protection and Engineering,
ul. Willowa 2, 43-309 Bielsko-Biała, Poland
(E-mail: amachnicka@ath.bielsko.pl; jsuschka@ath.bielsko.pl; spoplawski@ath.bielsko.pl)

ABSTRACT
Nitrification and denitrification are traditional ways of nitrogen removal from sewage. Performed studies, however, confirm from supernatant with high concentration of ammonia nitrogen in one-step process of "limited nitrification".
"Limited nitrification" method was used in present study with addition of external source of organic carbon in reduced amounts as well as process achievement in real sewage temperature.

KEYWORDS
nitrogen removal, nitrification, denitryfication, anammox

INTRODUCTION

Three physiologically different processes are known to contribute to the disappearance of nitrate in the environment; the reduction of nitrate to dinitrogen (denitrification), the use of nitrate as a source (assimilation), and the dissimilatory reduction of nitrate to ammonia – sometimes referred as to "ammonification". Only denitrification contribute to the elimination of nitrogen from ecosystems. Denitrification can also lead to production of another gas - N_2O (Sliekers et al. 2002; Kester et al., 1997).
The classical approach of ammonia oxidation and consecutive denitrification is widely introduced in full technical scale all over the world. There are several alternatives possible in configuration of the steps comprising aerobic, anoxic and anaerobic stages. The aim of the various configurations used is the intention to avoid addition of external sources of carbon, essential if denitrification (the anaerobic stage) is put after nitrification (aerobic stage), and/or upgrade the overall effect of nitrogen removal. Even so, the stringent nitrogen requirements are not meet in many cases. Extending these treatment plants, where achievement of adequate nitrogen removal effects are the bottleneck, will often mean high investment costs.
Treatment of sludge liquor – the effluent produced from sludge dewatering (also called the reject water, filtrate or centrate) – could be one option to reduce the nitrogen load to be removed in the sewage main stream. The load of returned nitrogen, as ammonia nitrogen , varies between 10 to 25 % of the total load of the inflowing (raw) sewage.
To totally innovative concept of simultaneous limited nitrification and denitrification was investigated and preliminary results presented in this paper.

EXPERIMENTAL

A full technical scale municipal sewage treatment plant with a flow of about 60 000 m^3/d was the source of substrates and the base for evaluation of results. Supernatant of anaerobically digested surplus activated sludge was the main substrate used for experiments on ammonia nitrogen biological removal.. The quality of the supernatant varied, maintaining however, the concentration of ammonia and phosphates within a relatively narrow range. The concentration of ammonia varied between 1000 to 1600 mg $N\text{-}NH_4$/l, while the concentration of phosphates was mainly in the range of 180 to 220 mg PO_4/l. The average concentration of ammonia nitrogen was about1150 mg $N\text{-}NH_4$/l. The quality of sludge supernatant is given in Table 1.

Table 1. Characteristic of centrate used for experiments

Parameter	Units	Measured range	Average
Temperature	^oC	24 – 27	26
pH	-	7,49 – 7,84	7,7
COD	mg O_2/l	280 - 350	315
Ammonia nitrogen	mg $N\text{-}NH_4$/l	1000 – 1600	1150
Phosphates	mg PO_4/l	180 – 220	200
Total phosphorous	mg P/l	46 – 111	75
Magnsium	mg Mg/l	13 – 18	14
Potassium	mg K/l	152 – 195	160
Calcium	mg Ca/l	62 - 89	65

The biological process of limited nitrification and denitrification was carried out in laboratory scale. A batch reactor of a volume of 20 litres was filled with recirculated sludge and sludge supernantant. At the beginning 12 litres of recirculated sludge was added, plus 3 litres of sludge supernatant. The total active volume was therefore 15 litres. After 24 hours of aeration, 3.6 litres of decanted sludge and also 3 litres of liquid was withdrawn. The same amount was substituted with activated sludge – 3.6 litres,(taken from the recirculation stream) and a new portion of sludge supernatant.

At the beginning the content of the batch reactor was aerated with pressured air. The necessary amount of supplied air, in order to the keep the sludge in suspension, resulted in dissolved oxygen concnetration above 1.0 mg O_2/l. Such condition have been maintained for several days with the intentions to increase the number of nitrifies adapted to much higher ammonia concentration in comparison to that in the sewage main stream bioreactors. For dissolved oxygen concentrations bellow 1.0 mg O_2/l, additional mechanical mixing was necessary. The rpm of the mixer was kept at slow rates, sufficient only for maintaining the sludge in suspension.

Determinations of ammonia, nitrates, nitrites and other parameters were done according to Standard Methods .

RESULTS AND DISCUSSION

The main feature of the introduced and investigated treatment system – the **S**imultaneous **Li**mited **N**itrification and **D**enitrification (SLIND) is taking advantage of nitrifying bacteria present in recirculated activated sludge with developing denitrifiers, elevated temperature of sludge liquor (centrate) in the order of 28 to 30 ^oC. The high biomass content in the recirculate is also a limited source of organic carbon, apart from the sludge liquor itself.

Keeping the dissolved oxygen on a low level, close to 1,0 mg O_2/l ammonia nitrification to the final form of nitrates is hindered and only a partial effect could be expected (Mulder et al., 1995; Jetten et al., 1999, Siegrist et al., 1998, Kuai and Verstraete, 1998; Helmer et al., 2001). The higher temperature most probable enables the growth of nitritation bacteria denominated as annamox microorganisms and ammonia oxidation to nitrites. Simultaneous loss of nitrogen could be the result of dinitrogen formation (N_2) and/or N_2O.

As given before in Table 1, the ammonia nitrogen concentration in the digested sludge supernatant, varied most often in the range between 1000 and 1600 mg N-NH_4/l. Some measured concentrations of ammonia nitrogen in the liquor are presented in Fig. 1. The average, and most often measured value was close to 1150 mg N-NH_4/l.

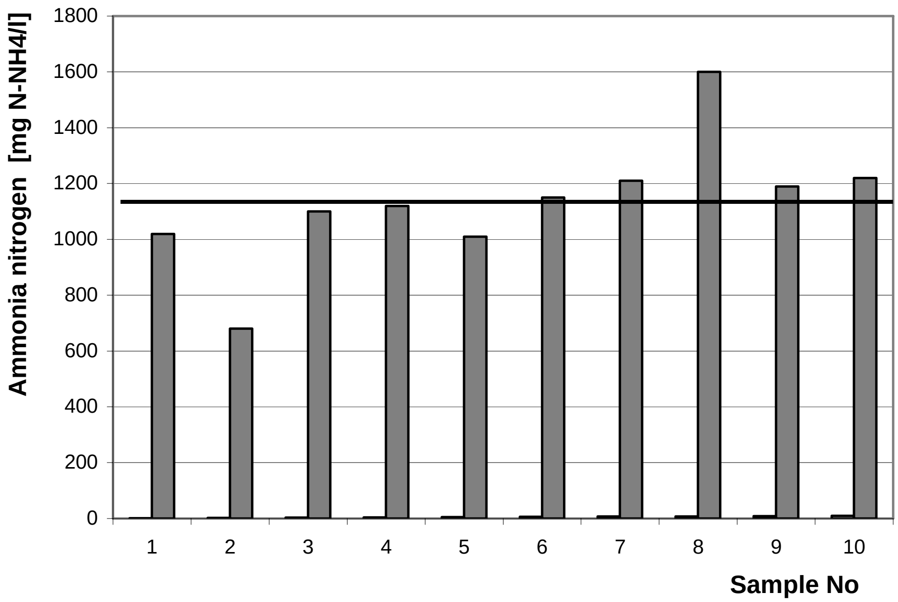

Figure 1. Ammonia nitrogen concentration in digested sludge supernatant.

According to the aforementioned methodology, the sludge liquor (centrate) after mixing with activated sludge recirculateted from the secondary treatment tanks and the remaining in the reactor mixture the concentration of ammonia nitrogen at the beginning of the daily cycle was in the order of 400 mg N-NH_4. The samples for analytical determinations were taken after several minutes and a immediate diminution of the ammonia concentration was measured. A difference of about 10 % from the calculated values could be found.

Under low dissolved oxygen concentrations in the bioreactor, below 1,0 mg O_2/l only a partial nitrification was measured. There was a difference between ammonia concentration decrease and nitrates nitrogen increase. The correlation between the ammonia concentration at the beginning of the experiments and after 24 hours is demonstrated by example results in Fig. 2.

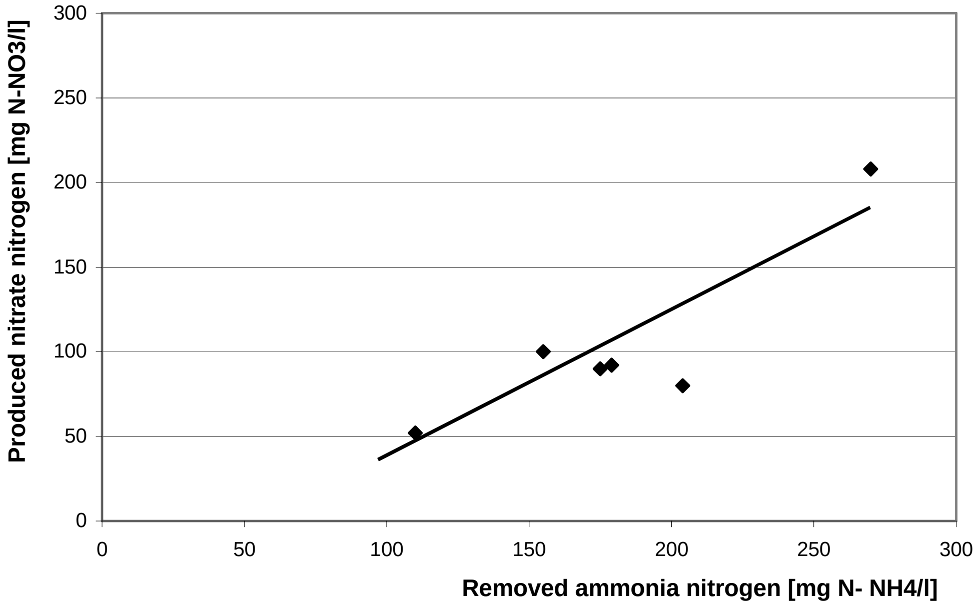

Figure 2. Correlation between removed ammonia and nitrates produced.

The difference between the amount of removed ammonia nitrogen and produced nitrates nitrogen constitutes the amount of the removed nitrogen in gaseous form. This confirms the mechanism of nitrates consumption increase in comparison to ammonia, resulting in the lower production of nitrates, rising reducing equivalents used in synthesis reactions and the growth of autotrophic organisms of the anammox type. It can also be assumed that a small amount of nitrates could be an effect of direct organic matter denitrification. In the course of the deliberations heterotrophic denitrification could also be considered. However, due to relatively low COD and the limited amount of organic carbon provided by recirculated activated sludge the significance of heterotrophic organisms could be excluded. As a result the obtained results can be presented as nitrogen removal (Fig. 3)

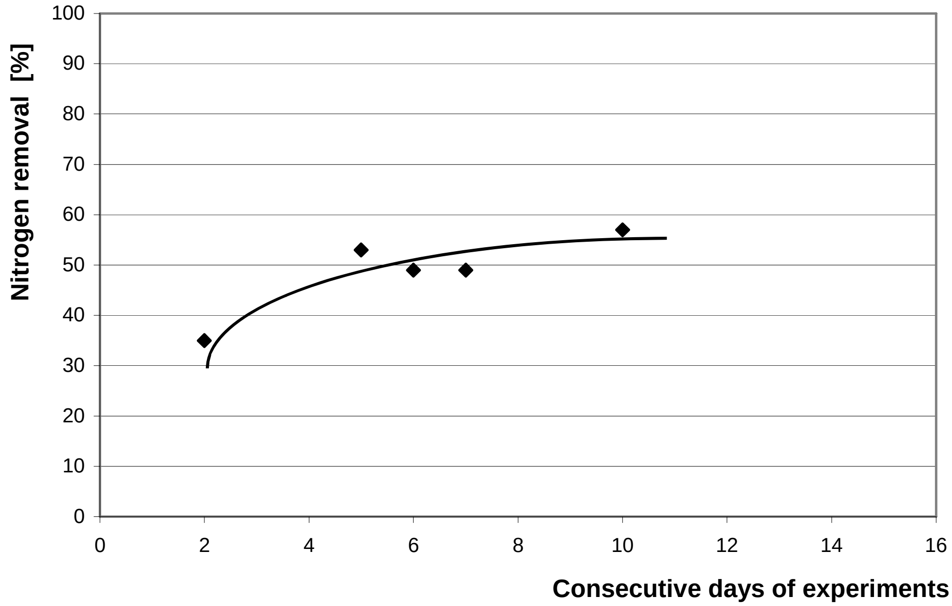

Figure 3. Effects of nitrogen removal.

To show better the differences between produced nitrates and removed ammonia nitrogen a fragment of experiments was shown in Fig. 4. The lines in Fig 4 are indicating only the trends of changes.

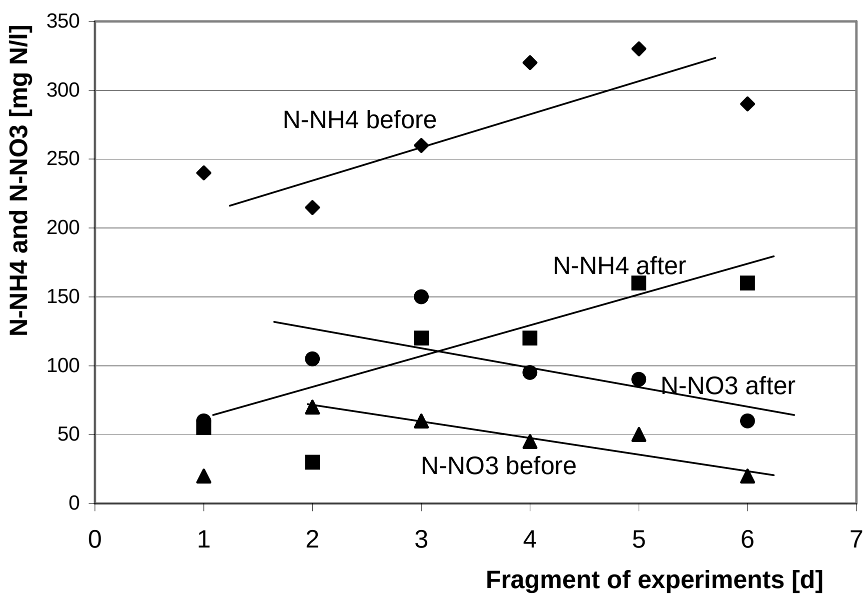

Figure 4. Changes of ammonia nitrogen and nitrates nitrogen in following days of experiments (an extract of results).

During the last few years it was found that certain bacteria, belonging to the Planctomecytales are capable of simultaneous ammonia and nitrite removal under anaerobic conditions. To that process an acronym ANAMMOX (ANaerobic AMMonia OXidation) was given – (Sliekers et al. 2002;

Van Loosdrecht and Jetten, 1998). Bacteria participating in the aforementioned process are usually described as Anammox-bacteria. The reaction of ammonia conversion with nitrite to dinitrogen gas by anaerobic ammonium oxidizers could be described by the below given equation.

$$NH_3 + 1{,}32\ NO_2 + H^+ = 0{,}26\ NO_3^- + 1{,}02\ N_2 + 2\ H_2O \qquad (1)$$

However, first a part of ammonia has to be converted partly to nitrite by oxygen limited aerobic ammonia oxidizers, according to equation;

$$NH_3 + 1.5\ O_2 \rightarrow NO_2^- + H_2O + H^+ \qquad (2)$$

Combining equation 1, and 2, a summary reaction can be given:

$$NH_3 + 0{,}85\ O_2 = 0{,}11\ NO_3^- + 0{,}44\ N_2 + 0{,}14\ H^+ + 1{,}43\ H_2O \qquad (3)$$

Very often the first reaction is denominated as the Annamox reaction, or described as the Anammox process. Partial ammonia oxidation to nitrite (Eq. 2) under oxygen limited conditions is describe under different names and different acronyms are given to that process. Most often the process of partial ammonia oxidation is also accompanied with partial nitrifcation. Combining the process of nitritation and ammonium anaenrobic oxidation (with nitrite) and simultaneous partial nitrification, the process can be described as Anammox/nitrification process.

The obtained results are in conformity with results achieved in the partial Anammox process, or more precisely in the Anammox/nitrification process. . When the dissolved oxygen concentration was maintained at a level of 0,85 mg O_2/l, an increase in the effects of ammonia removal was noticed, with simultaneous small increase of the nitrates and nitrites concentration. At the same time an insignificant decrease of pH was measured. Samples where the dissolved oxygen concentration increased above 1,0 mg O_2/l the pH decreased significantly, in conjunction with nitrates increase. Therefore the concentration of dissolved oxygen is detrimental in the process of ammonia removal. Biological anaerobic oxidation of ammonia nitrogen, and denitrification performed by the so called nitritation bacteria can explain the losses of nitrogen in the treatment process. It can be assumed that ammonia was mainly transformed to gaseous dinitrogen.

Under limited amounts of dissolved oxygen, the bacteria are utilising nitrites produced in the process of aerobic oxidation of ammonia, and are not involved in aerobic oxidation of NO_2^-. Most probably nitrites oxidising bacteria are only present if dissolved oxygen is in abundance. In dissolved oxygen limited conditions (< 1,0 mg O_2/l) a competition for oxygen between aerobic and anaerobic oxidation of ammonia could take place. Another possibility is inhibition of nitrites oxidation at high ammonia concentration.
Because no external source of organic carbon was available and observed removal of ammonia the presented process can be considered as a totally autotrophic process.

CONCLUSIONS

An original biological process of ammonia nitrogen removal was presented. A process of limited nitrification and denitrification was applied, which permitted in a single reactor a 55 % removal of ammonia nitrogen from digested sludge supernantant. In the case of the sewage treatment plant, which was the source of the liquor, a decrease of up to 25 % of the total load of nitrogen to be removed in the sewage main stream is feasible. A distinct improvement of the overall effect of nitrogen removal can be achieved.

No similar to the SLIND process of ammonia nitrogen removal is known so far. The developed limited nitrification and denitrification process requires no external organic carbon source and can be performed at relatively low temperature – does not require heating. The carried out experiments leading to removal of up to 55 % of ammonia nitrogen removal are promising, but should be confirmed and optimised in forthcoming investigations.

REFERENCES

Helmer C., C. Tromm, A. Hippen, K.H. Rosenwinkel, C.F. Seyfried and S. Kunsti. (2001).Single stage biological nitrogen removal by nitritation and anaerobic ammonium oxidation in biofilm systems. Water Sci. Technol. 43, 311-320

Jetten M.S.M., M. Strous, K.T. Van de Pas-Schoonen, J. Schalk, G.J.M. Van Dongen, A.A. Van de Graaf, S. Logemann, G. Muyzer, M.C.M. Van Loosdrecht and J.G. Kurnen. (1999). The anaerobic oxidation of ammonium. FEMS Microb. Reviews.; 22, 421 – 437.

Kester R.A., W. De Boer and H.J. Laanbroek. (1997). Production of NO and N_2O by pure cultures of nitrifying and denitrifying bacteria during changes aeration. Appl. Environ. Miceobiol.; 63, 3872- 3877.

Kuai L.P. and W. Verstraete. (1998). Ammonium removal by the oxygen-limited autotrophic nitrification-denitrification system. Appl. Environ. Miceobiol.; 64, 4500 - 4506.

Mulder J.W., A.A. Van Graaf, L.A. Robertson and J.G. Kuenen. (1995). Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. FEMS Microb. Ecology. 16, 177 – 184.

Siegrist H., S. Reithaar, G. Koch and P. Lais. (1998).Nitrogen loss in a nitrifying rotating contactor treating ammonium-rich wastewater without organic carbon. Water Sci. Technol.; 38, 241 – 248.

Sliekers A. O., N. Derwort, J.L.C. Gomez, M. Strous, J.G. Kuenen and M.S.M. Jetten. (2002). Completely autotrophic nitrogen removal over nitrite in one single reactor. Wat. Res.; 36, 2475 – 2482.

Van Loosdrecht M.C.M and M.S.M. Jetten. (1998). Mircobiological Conversions in nitrogen removal. Water Sci. Technol., 38, 1-7.