Combined partial nitritation and Anammox biofilm system as a sustainable solution for supernatant treatment

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Abstract Nowadays, as the effluent water regulations become more stringent, there is a need to treat wastewater in the most efficient manner and according to sustainability principles. One of the possibilities to meet this challenge is treatment of side streams, which are usually returned to the main influent of Wastewater Treatment Plants (WWTP) increasing the total load. Following processes occurring in natural ecosystems a new biological technology - combination of partial nitritation and Anammox processes - for treatment of nitrogen-rich supernatant coming from digested sludge dewatering has been developed. The first stage of the process is an oxidation of half of the ammonium to nitrite (partial nitritation process). The following stage - Anammox process - is an anaerobic oxidation of ammonium and nitrite nitrogen to dinitrogen gas. The process has been successfully tested in a technical-scale pilot plant with a continuous supply of supernatant at Himmerfjärden WWTP. Kaldnes rings were provided for biofilm growth. Almost two-year experiences in operation of the two-stage process have been presented in this paper. The results showed that a proper adjustment of dissolved oxygen (DO) concentration in the bulk liquid and a pH value drop in the partial nitritation reactor is essential to obtain the ammonium-to-nitrite ratio (NAR) in the effluent close to 1.3 as required for the Anammox process. It took four months to recover the Anammox bacteria activity after NO₂-N inhibition.

Keywords Anammox; deammonification; digester supernatant; partial nitritation

Introduction

In order to meet more stringent guidelines for wastewater treatment many existing plants apply the nitrification/denitrification process for nitrogen removal. Conventional biological methods require additional aeration tank volume, dosage of chemicals as external carbon source and consequently an additional investment cost. It has been shown that making an optimal use of the existing process units and applying complementary processes can lead to an increase of the nitrogen removal capacity.

One of promising complementary processes is treatment of a stream from the dewatering of digested sludge. During municipal sludge digestion, about 50% of bound in the sludge nitrogen is usually released to a wastewater stream in the form of ammonium, as a protein breakdown occurs (Siegrist, 1996). As a result, the ammonium concentration in such stream could be up to 2 kg m⁻³ (Strous et al., 1997). In Wastewater Treatment Plants (WWTP) with anaerobic sludge digestion supernatant is recirculated to the main stream and it significantly influences the volume of the biological steps. This internal stream called supernatant contains up to 15-20% of the total nitrogen load (Jansen et al., 1993), while it makes up to only 2% of the total influent flow. A proper management of supernatant would significantly reduce the nitrogen load to the activated sludge system and at the same it would decrease the investment costs and prevent critical nitrogen concentrations in the wastewater treatment plant effluent. Investigations performed at 66 WWTPs in Sweden, showed that 23% of plants used a separate supernatant treatment; most of them apply sequencing batch reactor (SBR) technology (personal communication). These numbers confirm that here is a need for separate treatment of supernatant.
Recently discovered Anammox bacteria allowed researchers to develop a new sustainable technology – the deammonification process – for a separate treatment of the ammonium-rich digester supernatant (van Loosdrecht and Jetten, 1998; Jetten et al., 1999; Hippen, 2001; Seyfried et al., 2001; van Dongen et al., 2001; Fux, 2003; Plaza et al., 2003; Gut, 2006). In this process the main reactions are: oxidation of half of the ammonium to nitrite (partial nitritation) followed by anaerobic oxidation of the remaining ammonium with the formed nitrite (Anammox) according to the reactions:

\[
\text{Nitritation: } 2\text{NH}_4^+ + 1.5\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{NH}_4^+ + \text{NO}_2^- + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad \text{(reaction 1)}
\]

\[
\text{Anammox: } \text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad \text{(reaction 2)}
\]

\[
\text{Total: } 2\text{NH}_4^+ + 1.5\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O} \quad \text{(reaction 3)}
\]

\(\text{NH}_4^+\) and \(\text{HCO}_3^-\) are the main ions existing at about the same concentration (in mM) in the digester supernatant. The whole process is based on conversions of these two ions.

To evaluate the sustainability of the technologies the following criteria are usually used: energy and chemical demand, process stability, sludge production, area requirements and production of greenhouse gases. Deammonification based on the partial nitritation/Anammox processes shows lower sludge production and energy consumption, if compared to the traditional nitrification/denitrification (Mulder, 2003). In addition, the deammonification process does not require any organic matter additions (chemicals) if compared to e.g. Sharon-Anammox process. Finally, the introduction of this new method for treatment of ammonium-rich side streams, such as supernatant from digested sludge dewatering, can reduce the costs of plant operation and make the management more sustainable. These benefits allow for concluding that the process can be evaluated as a sustainable process and it is worth more detailed investigations.

Pilot plant-scale experiments have been carried out for four years at Himmerfjärden WWTP, south of Stockholm, Sweden, with the goal to study the partial nitritation/Anammox process for nitrogen removal from digester supernatant (Szatkowska et al., 2004; Szatkowska et al., 2005; Trela et al., 2004).

**Methods**

The pilot plant was operated as a two-step process continuously fed with supernatant from dewatering of the digested sludge. Half of the ammonium (320-910 g m\(^{-3}\) at the influent) was oxidised to nitrite in the first reactor (R1); the reactor consisted of three zones. The nitritation step was followed by the Anammox process (R2) in which half of ammonium reacted with nitrite to produce nitrogen gas. Both reactors, each of volume of 2 m\(^3\), were filled with Kaldnes rings (50% of volume) as biofilm carriers. The heaters placed in the first zone of each reactor kept the temperature level stable at around 30-35°C, while mixers assured adequate mixing conditions in each zone. The effluent from the first reactor was diluted with tap water. Following the clarifier in the nitritation step, the effluent from the first step was deoxidised while flowing through a column in an upward direction. The scheme of the pilot plant is shown in Figure 1.

The processes were monitored by on-line measurements of pH, temperature, and conductivity. The samples were collected from both inlet and outlet of each reactor. Nitrogen fractions, chemical oxygen demand (COD), organic acids, alkalinity and PO\(_4\)-P total have been analysed in the samples. Additionally other parameters like flow, dissolved oxygen (DO), temperature, pH, and conductivity (with a manual probe) in all zones have also been measured.
Results and discussion

Supernatant

The process of sludge digestion results in release of nitrogen to a wastewater stream, as protein breakdown occurs (see reaction 4). At the same time, the hydrogen carbonate counter ion is produced. The supernatant contains approximately equal amounts of hydrogen carbonate and ammonium ions on a molar basis.

\[
\text{C}_5\text{H}_7\text{O}_2\text{N} + 4\text{H}_2\text{O} \rightarrow 2.5\text{CH}_4 + 1.5\text{CO}_2 + \text{HCO}_3^- + \text{NH}_4^+ \quad \text{(reaction 4)}
\]

As it can be seen from reaction 4 the theoretical \(\text{HCO}_3^-/\text{NH}_4^+\) molar ratio should be equal to 1. The average value of this ratio in supernatant fed to the pilot plant during the described period was \(1.45\pm0.63\). The values higher than the theoretical one were registered due to higher values of \(\text{HCO}_3^-\) ions, observed in the supernatant when problems with the digestion process occurred. The second main ion, that is ammonium, also showed high variations. Supernatant is recognized as a stream with a low content of easily biodegradable organic matter. However, the average value of COD was equal to \(369\pm153 \text{ g m}^{-3}\) and the highest noted value was as much as \(704 \text{ g m}^{-3}\). The supernatant characteristic was found as very unstable. The composition of supernatant and its pH and conductivity, measured over almost two years time period, are shown in Table 1.

One of the aspects that should be taken into account when the partial nitritation/Anammox process sustainability is considered for supernatant treatment is temperature. Despite the fact that optimum temperature for high partial nitritation/Anammox process efficiency is 30-35 °C, it was proved that it is possible to run process in supernatant temperature of 20-25 °C (Szatkowska and Plaza, 2006).

### Table 1. Supernatant composition

<table>
<thead>
<tr>
<th></th>
<th>NH(_4)-N [mM l(^{-1})]</th>
<th>HCO(_3)- [mM l(^{-1})]</th>
<th>HCO(_3)-/NH(_4)-N [mM l(^{-1}) / mM l(^{-1})]</th>
<th>COD [g m(^{-3})]</th>
<th>PO(_4)-P tot [g m(^{-3})]</th>
<th>pH</th>
<th>Conductivity [mS cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>average</td>
<td>45.8</td>
<td>73</td>
<td>1.45</td>
<td>369</td>
<td>19</td>
<td>7.8</td>
<td>4.8</td>
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<tr>
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<td>40</td>
<td>0.63</td>
<td>153</td>
<td>13</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>min</td>
<td>23.0</td>
<td>15.8</td>
<td>0.37</td>
<td>168</td>
<td>2</td>
<td>7.4</td>
<td>2.9</td>
</tr>
<tr>
<td>max</td>
<td>65.5</td>
<td>189</td>
<td>3.20</td>
<td>704</td>
<td>46</td>
<td>8.1</td>
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<tr>
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<td>65</td>
<td>40</td>
<td>36</td>
<td>347</td>
<td>346</td>
</tr>
</tbody>
</table>

Partial nitritation

The effluent from digested sludge dewatering meets perfectly the conditions required for supernatant treatment during the first step – the partial nitritation process. Equal amounts of ammonium and hydrogen carbonate ions are necessary to convert half of ammonium to nitrite. From Figure 2a it can be seen that the \(\text{HCO}_3^-/\text{N}\) ratio responds to the NO\(_2\)-N production. Most
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points representing the NO$_2$-N production are concentrated within the range of 40-60% and the HCO$_3$/N ratio close to 1.1. During a partial nitritation almost complete consumption of alkalinity was noticed. At the same time, a proper nitrite-to-ammonium ratio (NAR) in the effluent was obtained. Such a ratio was noted when about half of ammonium was oxidised to nitrite. From Figure 2b it can be seen that during a two-year period a stable operation was maintained. It resulted in an almost complete utilisation of hydrogen carbonate ions while about 50% of NH$_4$-N was converted to NO$_2$-N.

![Figure 2](https://iwaponline.com/wpt/article-pdf/2/1/wpt2007005/91270/5.pdf)

**Figure 2.** a. NO$_2$-N production versus HCO$_3$/N ratio; b. alkalinity utilisation and nitrite nitrogen production (partial nitritation, R1)

In the course of alkalinity utilisation the pH value dropped. The average pH drop amounted to 1.3, over the whole period. Such a pH drop and a lower effluent pH value combined with a hydraulic retention time (HRT) equal to 1.9 days (ranging from 0.9 to 2.3) and high temperature prevented further oxidation of NO$_2$-N to NO$_3$-N. Therefore, during the operational period partial nitritation with only minor formation of nitrate nitrogen was obtained (Figure 3).

![Figure 3](https://iwaponline.com/wpt/article-pdf/2/1/wpt2007005/91270/5.pdf)

**Figure 3.** Nitrogen conversions (partial nitritation, R1)

Moreover, the pH value turned out to be the proper parameter for monitoring the nitritation process performance. In order to keep the effluent NAR close to the theoretical value of 1.3 a drop of pH by about 1.6 is required (Figure 4a). For the partial nitritation process and oxidation of half of ammonium dissolved oxygen must be provided. A proper adjustment of the DO concentration in the bulk liquid resulted in a sufficient pH drop. The relationship between the pH value and the DO (Figure 4b) indicated that DO values higher than about 1.2 g O$_2$ m$^{-3}$ did not result in a higher pH value drop.
A required NAR in the effluent has been maintained for almost two-year period and it enabled further efficient supernatant treatment within the Anammox process. The average NAR value was equal to 1.13 while varying from 0.2 to 2.2; the fluctuations were caused by unstable characteristics of the influent supernatant and process conditions.

**Anammox**

The nitritation step was followed by the Anammox process in which ammonium and nitrite nitrogen reacted to the nitrogen gas under anaerobic conditions. The process was performed at the average DO concentration in the bulk liquid equal to 0.20±0.12 g O₂ m⁻³. Such values are in agreement with studies on the influence of the dissolved oxygen on the Anammox process (Szatkowska et al., 2004; 2003). The average HRT was 2.9 days and it ranged from 1.8 to 3.8 days. Until the end of May 2004, the HCO₃⁻/CO₃²⁻ mixture was dosed to the process to keep pH at the optimal level; later on the dosing was ceased and Anammox worked excellently without any chemicals addition. During the process an increase of the pH value was observed; it rose from 7.2 in the influent up to 8.2 in the effluent, on average. The average temperature in R2 was equal to 32.7±3.0 °C. The influent to the reactor 2 was diluted to slowly build up the process. Dilution was then step-by-step withhold to slowly increase the influent nitrogen load; the highest influent inorganic nitrogen concentration was obtained on 13th August 2003. After that, a decrease in the nitrogen removal was noticed while the break down of the process occurred. During the whole described period the influent inorganic nitrogen concentration varied between 94 g N m⁻³ and 840 g N m⁻³ (Figure 5).

![Figure 5. Inorganic nitrogen in the influent and the effluent (Anammox, R2)](https://iwaponline.com/wpt/article-pdf/2/1/wpt2007005/91270/5.pdf)
When the first period of successful nitrogen utilization was recorded (May-Sep 2003), nitrates remained stable or were insignificantly reduced. It means that probably other than Anammox processes were also present in the reactor. During the second successful period (Feb-Dec 2004), an increase in nitrate was observed (5.1% of total influent nitrogen, on average). It could prove that mainly the Anammox process was taking place. However, according to the stoichiometry of the Anammox reaction about 11.2% of nitrate is produced. The remaining difference of 6.1% (11.2-5.1%) can be attributed to the presence of simultaneous denitrification process.

Due to the Anammox reactor overloading and an inhibitory effect of too high NO$_2$-N concentrations, a decrease in the nitrogen removal efficiency was observed. From 20th August to 22nd October 2003, NO$_2$-N effluent concentration exceeded 70 g m$^{-3}$ and varied within the range of 104-162 g m$^{-3}$. Taking into account nitrite concentrations below 100 g m$^{-3}$, it was possible to find a relationship between NO$_2$-N in the reactor effluent and the removal efficiency (Figure 6a). It can be seen that nitrite concentration between 20-30 g m$^{-3}$ decreased the nitrogen efficiency by about 40%. It took four months to rebuild the Anammox capacity and to regain a stable and efficient process.

The main goal of the pilot-plant experiment was to obtain a stable operation of the Anammox process. The results obtained during almost two years operation indicated that it was possible to maintain both long-term stable process conditions and a high efficiency. The average nitrogen removal was equal to 63.7 % and varied between 6-97%. The system was not highly loaded with nitrogen but as it can be seen from Figure 6b the nitrogen removal increased linearly to the nitrogen load. The maximum removal of 0.9 g N m$^{-2}$d$^{-1}$ was obtained for the maximum load of 1.3 g N m$^{-2}$d$^{-1}$.

Figure 6. Correlation between: a Nitrite nitrogen in the effluent and nitrogen removal; b load and nitrogen removal; c ammonium and nitrite reduction; d NO$_2$red/NH$_4$red and nitrogen removal

As it was mentioned above, a proper NAR in the influent is essential to run the Anammox
process with a high efficiency since the Anammox process stoichiometry implies the consumption rate of NO$_2$-N and NH$_4$-N. From Figure 6c it can be seen that the ratio of reduced nitrite to utilized ammonium in moles is close to the theoretical value of 1.3. The slope of the curve developed from the experimental data was 1.19.

The relationship between a reduced nitrite/reduced ammonium ratio and nitrogen removal have been found taking into account points where minimum 60% of nitrogen reduction was obtained (Figure 6d). Due to the Anammox process, the maximum nitrogen removal efficiency of 88.8% can be achieved. 100% of process efficiency is not possible to obtain due to nitrate production during the process. From the Figure 6d it can be seen that to reach such reduction (88.8%) the NO$_2$-Nred/NH$_4$-Nred ratio should be around 1.0; it would mean that 100% of both nitrite and ammonium was utilized (100%/100%=1). Higher ratios were associated with a lower process efficiency e.g. nitrogen reduction was lower than 80% when the NO$_2$-Nred/NH$_4$-Nred ratio was above 1.23. It means that the whole accessible nitrite was used while some of ammonium remained and the process could not progress due to the lack of nitrite. Moreover, reductions higher than 88.8% again confirms a possibility that other process (or processes) took place in the Anammox reactor as well.

From the data obtained during almost a two-year process operation it can be concluded that it is possible to carry out the partial nitritation/Anammox process for a long time with a high efficiency. The process turned out to be a good solution for handling ammonium-rich streams, such as supernatant. The application of this technology can significantly contribute to the decrease of nitrogen load in the WWTP influent. Separate treatment of supernatant instead of its direct recirculation to the head of WWTP can reduce the total load to WWTP. In recirculated and then treated in partial nitritation/Anammox process supernatant the ammonium content is reduced and its contribution to the overall load is decreased from 15-20% to 3%. It can result in lower requirements for efficiency of the biological treatment at the WWTP. Nitrogen removal in a biological step could be reduced from 70-75 to 50-60% (Figure 7).

![Figure 7. WWTP flow scheme with application of partial nitritation /Anammox](https://iwaponline.com/wpt/article-pdf/2/1/wpt2007005/91270/5.pdf)

**Conclusions**

The experiments on application of partial nitritation/Anammox process for separate treatment of supernatant coming from dewatering of digester sludge showed that it is possible to obtain a long-term stable operation of both partial nitritation and Anammox process in a moving bed biofilm reactor.

Sufficient adjustment of HRT and DO in partial nitritation resulted in a pH value that next assured a proper NAR in the effluent. Such NAR (1.13) was close to the theoretical value (1.3) and was suitable for Anammox reaction. Composition of supernatant is an important factor in maintaining a long-term stable nitritation process. Especially, a hydrogen carbonate to ammonium ions ratio was found as very essential. Almost complete consumption of alkalinity was observed
during the process.

High average nitrogen removal efficiency of 64% was obtained in the Anammox reactor for two years experimental period. It was proved that the process could work without chemicals addition. Concentration of nitrite turned out to be the important factor in the Anammox process performance. To perform process successfully it is essential to assure the proper ratio of nitrite to ammonium concentrations in the influent. At the same time, the nitrite concentration must be controlled inside the reactor; to keep nitrogen removal efficiency above 60% it cannot exceed 20 g m\(^{-3}\). The four-month period was necessary to rebuild the process efficiency.

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References


