Development and implementation of a robust deammonification process

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Abstract
Deammonification represents a short-cut in the N-metabolism pathway and comprises 2 steps: About half the amount of ammonia is oxidised to nitrite and then residual ammonia and nitrite is anaerobically transformed to elementary nitrogen. Implementation of the pH-controlled DEMON® process for deammonification of reject water in a single-sludge SBR system at the WWTP Strass (A) contributed essentially to energy self-sufficiency of the plant. The specific energy demand of the side-stream process results 1.16 kWh per kg ammonia nitrogen removed comparing to about 6.5 kWh of mainstream treatment. Has this resource saving technology already approached state of the art? Deammonification has been operated in full-scale now for almost 3 years without interruption reaching annual ammonia removal rates beyond 90%. Biomass enrichment and DEMON-start-up in Strass took a period of 2.5 years whereas start-up period at the WWTP Glarnerland (CH) was reduced to 50 days due to transfer of substantial amounts of seed sludge.

Key words ammonia, anammox, demon, pH-control, rejection water, side-stream

INTRODUCTION
Considering the global nitrogen cycle one gets aware of the tremendous anthropogenic influence on large-scale N-mass fluxes. About 27% (Gijzen, 2001) of the fixation of the elementary nitrogen from the atmosphere happens by an industrial catalytic process mainly for fertiliser syntheses. Produced organic matter releases ammonia during degradation. Especially eutrophication shows evidence for excess nitrogen transferred to the hydrosphere. A sequence of oxidation and reduction processes yields elementary nitrogen which is recycled to the atmosphere. Wastewater industry requires enormous resources to install and operate nitrification/denitrification for a partly compensation of the global N-misbalance. Obviously nitrogen mass transfers have become a major concern of human activities on one hand to improve agricultural output and on the other hand to reduce harm on receiving water bodies. All the more surprising it is that deammonification for highly efficient N-removal has not been applied till now. The significance of this process has not even been recognised despite its massive occurrence in natural habitats – it contributes up to 50% to the removal of fixed N from the oceans (Arrigo, 2005). Under anaerobic conditions an autotrophic metabolism can directly oxidise ammonia by means of nitrite (Figure 1).

Figure 1. Nitrogen cycle presenting deammonification as a metabolic short-cut of N-conversion
Strous et al. (1999a) managed to identify the missing lithotroph as a new planctomycete which catalyses anaerobic ammonia oxidation according to following equation (1):

\[
\begin{align*}
\text{NH}_4^+ + 1.32 \text{NO}_2^- + 0.066 \text{HCO}_3^- + 0.13 \text{H}^+ & \rightarrow \\
& \rightarrow 0.26 \text{NO}_3^- + 1.02 \text{N}_2 + 0.066 \text{CH}_2\text{O}_{0.5}\text{N}_{0.15} + 2.03 \text{H}_2\text{O}
\end{align*}
\] ...

(1)

Stoichiometric coefficients of this reaction have been derived in closer detail on base of an elemental balancing approach (Takacs et al., 2007). The appropriate molar ratio of the two reactants has to be provided by partial nitritation of ammonia by ammonia oxidisers AOBs. Further oxidation of nitrite to nitrate has to be repressed by ammonia inhibition of nitrite oxidisers NOBs (Turk and Mavinic, 1987). While high ammonia influent concentration facilitates optimised metabolic routing, accumulation of nitrite concentrations endangers process stability due to toxic impact on anammox organisms (Strous et al., 1999b). Finally specifically AOBs are the autotrophic organisms showing highest sensitivity to inorganic carbon limitation (Wett and Rauch, 2002; Guisasola, 2007). Both consecutive process steps – partial nitritation and anaerobic ammonia oxidation – are referred to as deammonification.

These two reaction steps can be conducted in two individual units providing different sludge retention times and conditions where nitrite produced in the aerobic reactor and residual or by-passed ammonia are fed to the anaerobic reactor (van Dongen et al., 2001). In an alternative approach both process steps are operated in a single-sludge system (Sliekers et al., 2002). This process requires an aerated system and appropriate process control to prevent built-up of toxic nitrite concentrations due to oxygen excess. The concept has not been “purposefully tested on pilot or full scale, but is known to occur accidentally in sub-optimally functioning full-scale nitrification systems” (Schmidt et al., 2003). This paper will present long-term full-scale experiences with a pH-based control system which determines the length of aeration intervals depending on the current production of H+ ions or nitrite, respectively.

**METHODS**

**pH-controlled deammonification system (DEMON®)**

A control system for a single sludge SBR system has been developed in order to provide boundary conditions for sufficiently accurate adjustment of all 3 mentioned impacts, i.e. ammonia inhibition, nitrite toxicity and inorganic carbon limitation (Figure 2). The controller is established out of three main mechanisms – time-, pH- and DO-control – listed according to their order of hierarchy.

- **Time control** defines operation cycles of 8 hours each, involving a fill/react phase, a settling period and a decant period. During the react period of about 6 hours of the SBR cycle both deammonification processes – partial nitritation and anaerobic ammonia oxidation – are operated.
- **These two successive processes**versely impact pH. The partial nitritation reaction depresses the pH and the anaerobic ammonia oxidation reaction elevates the pH. The actual duration of aeration intervals are ruled by the pH-signal, which characterizes the current state of reactions (pH-control).
- **The set-point of dissolved oxygen** (DO control) control is specified at a low range, close to 0.3 mg/l in order to prevent rapid nitrite accumulation and to maintain a continuous repression of the second oxidation step of nitrite to nitrate.

Beside these control steps, additionally monitored states (redox potential and electrical conductivity) and programmed safeguards cover eventual failure scenarios, specifically over-aeration and thus poisoning of the process.
Figure 2. Control scheme of the DEMON process – parameter selection aims to optimize process performance considering ammonia inhibition, nitrite toxicity and inorganic carbon limitation (Wett et al., 2007)

Full-scale implementation at WWTP Strass

Described deammonification process has been implemented at the WWTP Strass, Austria, in an SBR tank (Figure 3) with a maximum volume of 500 m$^3$ and at loading rates up to 340 kg of ammonia nitrogen per day. The aeration system is activated only within a very tight pH-bandwidth of 0.01. Due to oxygen input nitritation runs at a higher rate than anaerobic ammonia oxidation and H$^+$ production drives the pH-value to the lower set-point and aeration stops. While dissolved oxygen is depleted all the nitrite that has been accumulated during the aeration interval is used for oxidizing ammonia. In the course of this biochemical process some alkalinity recovers and additionally alkaline rejection water is fed continuously to the reactor until the pH-value reaches the upper set-point and aeration is switched on again.
RESULTS AND DISCUSSION
Conversion from nitrification/denitrification to deammonification
Since 1997 a side-stream SBR has been operated in a nitrification/denitrification mode at WWTP Strass. Primary sludge was dosed to provide carbon for nitrite reduction. Then in July 2004 2.5 m³ of seed sludge were introduced to the tank volume of 500 m³. The inoculum contained anaerobically ammonia oxidising biomass after an enrichment period of 2 years (Wett, 2006). Since the same reactor environment was used but different operation strategies and control settings there was an ideal chance to monitor the transition period and compare differences in process performance.

In nitrification/denitrification mode the SBR was operated at mixed liquor suspended solids concentrations of about 10 g/L due to primary sludge dosage and the need for enhanced endogenous respiration. After switching to deammonification at initial low loading conditions heterotrophic biomass decayed and TSS concentration was driven down to about 3 g/L (Figure 4). Growing deammonification capacity and loading resulted in climbing TSS values up to about 5 g/L corresponding to a sludge retention time SRT of more than 30 days. The portion of volatile suspended solids VSS was in the range between 60 and 65% depending on the inorganic fraction contained in primary sludge. After this impact had been cut off the VSS content increased to an annual average value of 70% (Table 1).

Figure 4. Development of mixed liquor suspended solids concentration and volatile suspended solids before and after switching to deammonification mode without carbon dosage at WWTP Strass

Figure 5 shows how shifts in sludge composition and population dynamics affect sludge settling properties. Primary sludge dosing kept the sludge volume index SVI within the range between 50 and 100 mL/g. Then during the start-up period of deammonification settling characteristics started to deteriorate towards SVI values beyond 170 mL/g. Substantial solids wash-out contributed to the low TSS level during that period. When the system approached steady state conditions settling properties improved. Another peak in SVI values in March 2006 highlighted the correlation of increased operational level in nitrite concentrations and deteriorating settling properties. Nitrite concentrations typically have been controlled to values well below 5 mg/L and only during these two periods of aggressive load increase nitrite accumulated to more than 10 mg/L. The annual mean value of SVI amounts to 74 mL/g. Temperature profile in Figure 5 reflects the seasonal course of ambient temperature showing a distinct summer peak up to 36 °C and a low point at late fall when cold season coincidences with low load at the bottom of regional tourism. An accurate heat balance is difficult to calculate since no heater has been in use and mainstream wastewater in the neighbouring tank cools down the side-wall.
Operational performance at WWTP Strass
After the SBR system had been seeded in 2004 initial feed rates were kept low (Figure 3) in order to minimise nitrite and nitrate effluent values. Low nitrogen turnover and concentration level caused difficulties in evaluating heterotrophic and autotrophic nitrite reduction. Load rates had been continuously increased until the required mean weekly ammonia removal capacity of 250 kg N per day was achieved. During that period blower capacity and discharge equipment had to be adjusted to a 25-fold feed rate. The same start-up period revealed an amazing improvement in specific energy demand for aeration, stirring and pumping. In terms of stoichiometry the oxygen demand for nitritation/denitritation is 25% less than for conventional nitrification/denitrification and is reduced to 40% in case of deammonification. Additionally less heterotrophic respiration and higher α-value at lower TSS concentration contributed to energy savings. Therefore the specific energy demand decreased from a mean value of 2.9 kWh per kg of eliminated ammonia nitrogen down to below 1.0 kWh and levelled off at an annual average value of 1.16 kWh per kg N. At the same plant the measured specific energy demand for biological nitrogen removal in the mainstream treatment reaches 6.5 kWh/kg N – a comparison that underlines energy saving potential of side-stream treatment in general and of deammonification specifically although differences in COD-characteristics are neglected in this figures.

Table 1. Sludge properties, influent/effluent characteristics and treatment efficiency of DEMON rejection water treatment system at WWTP Strass (2005 annual average values and standard deviation)

<table>
<thead>
<tr>
<th></th>
<th>TSS</th>
<th>VSS</th>
<th>SVI</th>
<th>temp.</th>
<th>flowrate</th>
<th>NH4-removal</th>
<th>N-removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactor</td>
<td>4.3 ± 0.8</td>
<td>3.0 ± 0.8</td>
<td>73.6 ± 12.4</td>
<td>27.8 ± 1.7</td>
<td>117 ± 39</td>
<td>90.3 ± 2.95</td>
<td>85.8 ± 4.93</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>NH4</th>
<th>NO2</th>
<th>NO3</th>
<th>CODsoluble</th>
<th>CODparticulate</th>
<th>specif.energy</th>
</tr>
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<tbody>
<tr>
<td>influent</td>
<td>1844 ± 92</td>
<td>0</td>
<td>0</td>
<td>614 ± 27</td>
<td>241 ± 140</td>
<td>1.16 ± 0.21</td>
</tr>
<tr>
<td>effluent</td>
<td>179.4 ± 51.7</td>
<td>4.4 ± 6.9</td>
<td>76.8 ± 48.1</td>
<td>344 ± 4</td>
<td>305 ± 61</td>
<td>1.16 ± 0.21</td>
</tr>
</tbody>
</table>
The mean annual ammonia elimination efficiency calculated from daily measurement values amounted to 90.3% ± 2.95% (Table 1). The total nitrogen removal rate was only slightly less (85.8% ± 4.93 %) because the nitrate produced in the process was denitrified by the heterotrophic biomass grown on the organic carbon content of the rejection water. From process stoichiometry a nitrate production of 11 % of ammonia turn-over is expected. Comparison of ammonia removal and nitrate effluent load (Table 1) yields a final nitrate production rate of 4.6% which indicates subsequent reduction of more than half of generated nitrate. Due to alkalinity recovery nitrate reduction is beneficial also to the ammonia removal rate as shown by the correspondence of both elimination profiles in Figure 7. Furthermore should be noted that periods of lower ammonia removal rates correspond with low loading. This phenomenon can be explained with increasing SRT and decreasing temperature in low load periods leading to enhanced growth of nitrite oxidisers NOBs. Additional nitrate production drives down overall removal efficiency and can be defeated by additional excess sludge withdrawal. The only significant failure event occurred in March 2006 in high-load season when the effluent valve broke and about a quarter of the biomass was washed out overnight. Over-aeration and climbing nitrite concentration up to 30 mg/L caused a severe draw-back in process performance and required a couple of weeks for full recovery (Figures 6 and 7).
Rapid start-up at WWTP Glarnerland
As mentioned above the biomass enrichment period took 2 years and the actual start-up of the full-scale reactor in Strass another half a year until the end of 2004. By then of course a huge amount of seed sludge was available to accelerate the start-up of the next DEMON system. At the WWTP Glarnerland, Switzerland, a nitritation/denitritation system for side-stream treatment had been operated for several years (Nyhuis et al., 2006). Boundary conditions and design figures (ammonia loads up to 250 kg N to the reactor volume of 400 m³) are comparably with the situation in Strass with the only exception of higher dilution of rejection water (about 1000 mg NH₄-N/L instead of 1800 mg/L).

Figure 8. Improvement of nitrogen effluent concentrations at climbing load rates during start-up period at WWTP Glarnerland (Nyhuis et al., 2006)

After solving some bureaucratic constraints the transport of seed sludge crossing EU-outer border could be organised. A single truck load of 20 tons of liquid sludge was transferred. This amount equals about 500 kg of TSS with the deammonification capability for about 60 kg NH₄-N per day (Figure 8). Therefore immediately after introduction of the seed sludge regular plant operation could be started at loads of about one third of the final capacity. During the next 55 days the feed-rate was increased and controller settings were adjusted until target effluent concentrations of 50 mg/L for ammonia- and nitrate nitrogen were met.

CONCLUSIONS
Deammonification appears as an attractive option for treatment of high-strength ammonia streams and provides a high resource saving potential. In terms of the nitrogen cycle – the starting point of this presentation – deammonification has reduced the specific energy requirement for nitrogen conversion towards the range of the highly developed industrial N-fixation process. Long start-up periods and lack of operational reliability have frequently been reported as major short-comings of deammonification technology. Presented full-scale case-studies could demonstrate the importance of a robust control strategy in order to integrate a side-stream deammonification system into everyday’s routine operation operators are confident with. Applied volumetric loading rates up to 0.7 kg ammonia N per m³ showed even higher removal efficiency than low-load situations. Moreover transfer of sufficient amount of seed sludge has proven to accelerate the start-up period down to about 50 days.
ACKNOWLEDGEMENT
Successful implementation of the DEMON process happened within an informal cooperation (without funding) between the Association for Wastewater Purification Achental/Inntal/Zillertal AIZ and the Institute of Infrastructure/Environmental Engineering IUT of the Innsbruck University. We acknowledge this confiding and enduring collaboration with the competent plant operators and owe special thanks to M. Hell for intense supervision of the pilot plant.

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