

KEY PARAMETERS FOR CONTROL OF DEMON DEAMMONIFICATION PROCESS

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ABSTRACT: A suspended growth deammonification process has been in full-scale operation for over two years in Austria. Three US utilities have embarked on piloting this process at two locations: New York City and Alexandria, Virginia. Deammonification is a two-part autotrophic reaction involving two distinct biomass populations. In the first step aerobic ammonia oxidizing bacteria (AOB) nitrify partially ammonia to produce nitrite. In the second step anaerobic ammonia oxidizing microorganisms (anammox) autotrophically denitrify these products to nitrogen gas. Alkalinity limitations and ammonia inhibition are used to control the production of near equimolar nitrite and ammonia, while limiting nitrite toxicity is key to facilitating autotrophic denitrification. The paper describes the parameters that are important to control single-sludge suspended growth deammonification and how the DEMON process uses pH to control the two key reactions, at the same time controlling residual nitrite levels to prevent nitrite toxicity.

KEYWORDS: Deammonification, reject water, sludge liquor, side-stream, nitrite toxicity, Demon, anammox

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INTRODUCTION

Deammonification of high strength ammonia streams is a cost efficient process alternative to conventional nitrification/denitrification. Deammonification involves two process steps – the partial nitritation of ammonia and the subsequent anaerobic oxidation of the residual ammonia by nitrite to nitrogen gas (Figure 1). Both process steps are catalysed by different consortia of organisms, i.e. a population of aerobic autotrophic ammonia oxidizers (AOBs) and a consortium of anaerobic autotrophic ammonia oxidizers (anammox). Partial nitritation requires a stoichiometric oxygen demand of only 40% compared to complete nitrification. No carbon dosage is required due to the autotrophic nature of the process; in fact the process removes a small amount of CO₂ from the atmosphere.

Nitrite as the intermediate product serves not only as a substrate for anammox organisms but also results in irreversible poisoning at increasing concentration levels. The objective of this research is to experimentally quantify the role of nitrite poisoning on the operation and control of the suspended growth deammonification process. Pilot-scale in-situ experiments were conducted to

define the impact of nitrite on deammonification and to develop a calibrated kinetic expression for nitrite poisoning. For the modeling approach, there are two options available:

1. Temporary inhibition: reduction in the growth rate of the anammox organisms
2. Permanent toxicity: increased decay rate.

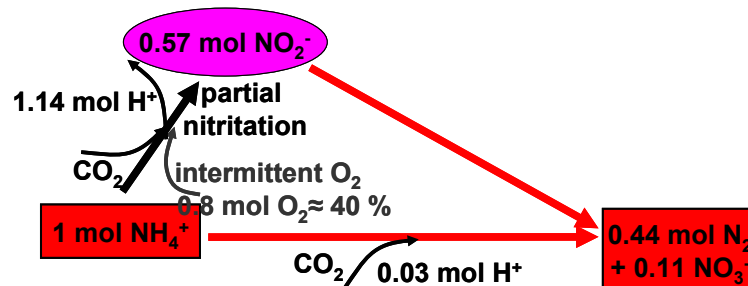


Figure 1 – Partial nitrification and anaerobic ammonia oxidation as the two steps of the deammonification process.

Nitrite toxicity in suspended growth deammonification process. There are several reports in literature giving threshold values of irreversible nitrite toxicity. Strous et al. (1999) allude to the negative influence of nitrite concentration and exposure time on anammox performance. Fux (2003) observed a loss of anammox activity of 87% in a two stage pilot plant at an average nitrite level of 42 mgNO₂-N/L within 11 days. For a single sludge system, Nielsen et al. (2005) point to “the continuous threat of reactor failure due to oxygen overloading and subsequent nitrite poisoning of the anammox biomass”.

The detrimental impact of nitrite on anammox activity was also demonstrated with the anammox enrichment reactor operated at the New York City 26th Ward facility (the enrichment reactor is to be used as a seed source for a pilot-scale DEMON reactor). The enrichment reactor was operated under anoxic conditions at 35°C and fed rejection water supplemented with sodium nitrite and ammonium chloride (NO₂-N : NH₄-N ratio = 1.15). Figure 2 presents nitrite concentration and nitrogen uptake data from this reactor (expressed as grams of NO₂-N or NH₄-N consumed per day). Due to a failure in pH adjustment for approximately 12 hours in early July 2006, the pH increased to 8.2 and the nitrite consumption rate declined, resulting in an increase in the reactor nitrite-N concentration from < 1 mg/L to 72 mg/L. pH control was re-established (7.3 – 7.5), but from this day through early August 2006, anammox activity declined precipitously as the biomass was exposed to nitrite-N concentrations up to 50 mg-N/L (the decrease in the nitrite-N concentration during this period correspond to the feed pump being shut off for several hours). During this period, the nitrite-N and ammonium-N loading rate was reduced gradually; in late August 2006, the nitrite-N concentration was consistently below 10 mg-N/L. As the concentration stabilized in the reactor below 2 mg/L, increased growth and activity of the anammox organisms occurred.

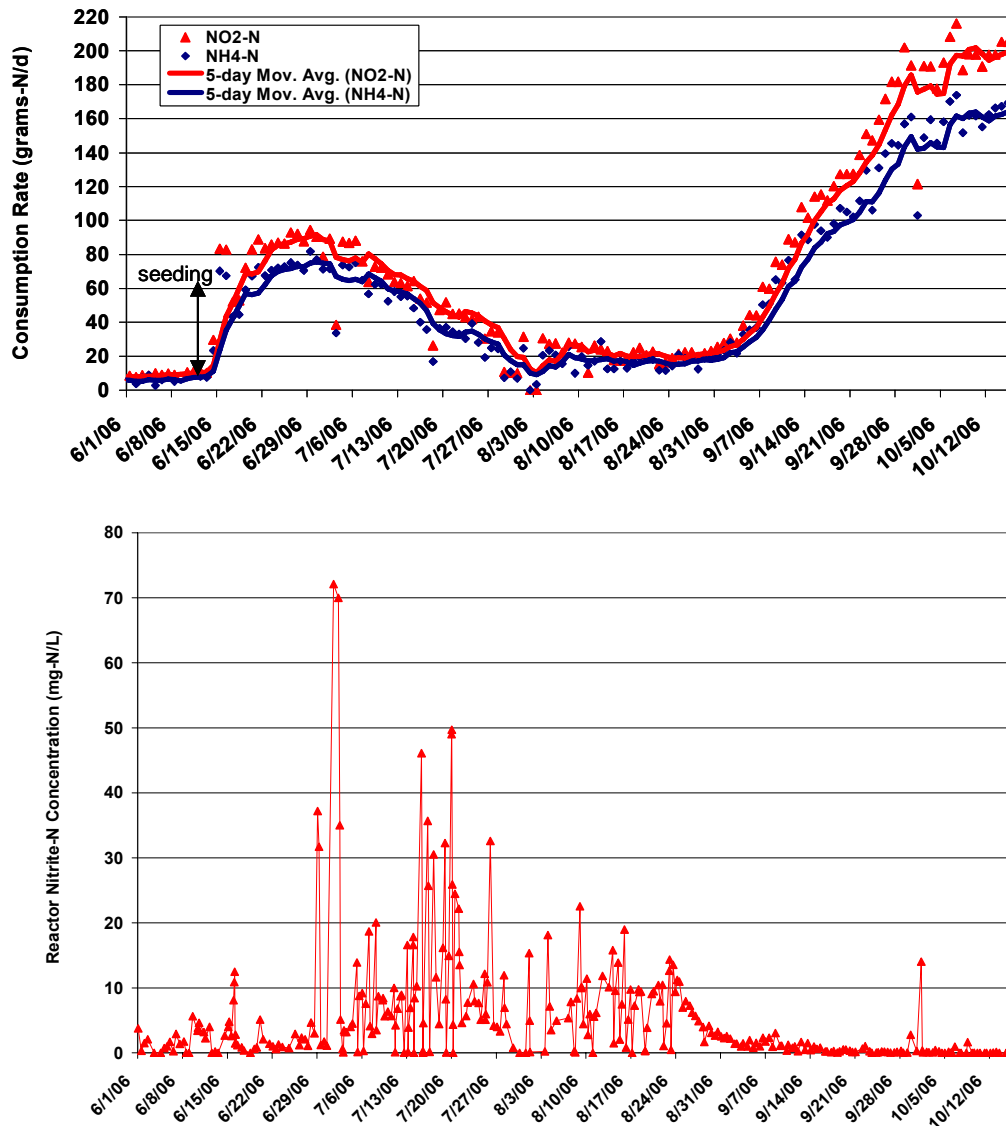


Figure 2 – Nitrite and ammonia uptake profiles corresponding to residual nitrite concentration in the anammox enrichment reactor in New York – nitrite toxicity even at low concentration level hinders enrichment of anammox biomass.

METHODS

pH-controlled intermittent aeration. A single-sludge suspended growth sequencing batch deammonification process has been implemented at a full-scale wastewater treatment plant in Strass, Austria (Wett, 2006). This process has successfully been operating for more than 2 years with an average ammonia removal rate of more than 90%, and a turnover rate of 300 kg N per day. The major benefits of implementing this process are significant reductions in aeration and carbon requirements for nitrogen removal. Other benefits include reduced sludge and greenhouse gas production. There are many reasons for the success of the process at Strass including vigilant

operations and maintenance and a finely-tuned efficient process control system. The DEMON® process is operated in a SBR system governed by 3 control mechanisms – time-, pH- and DO-control:

1. 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 (Figure 3) both deammonification processes – partial nitrification and anaerobic ammonia oxidation – are operated.
2. These two successive processes conversely impact pH. The partial nitrification 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).
3. 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.

In addition to these control steps, additional safeguards are instituted to prevent over-aeration and thus poisoning of the process.

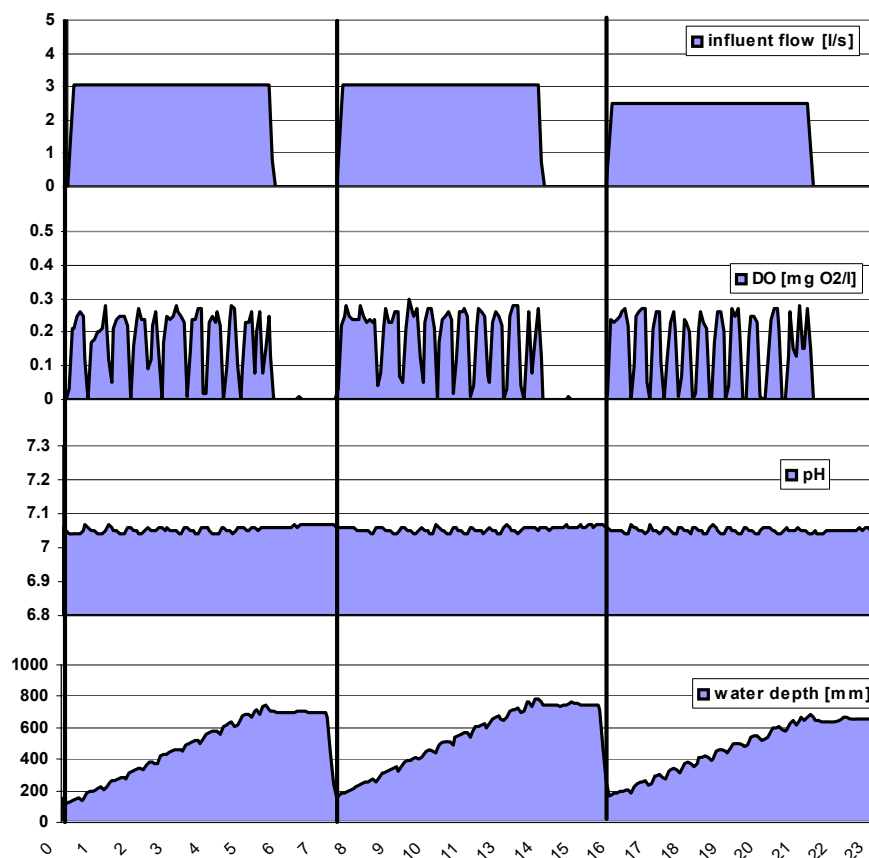


Figure 3 – Profiles of process variables (flowrate, DO, pH and water level) displaying the control of intermittent aeration by a tight interval of pH-setpoints during 1 day of operation.

The reject water is fed continuously during the react cycle. The aeration system is activated within a very tight pH-control interval of $\Delta 0.01$. Aeration is initiated at the upper pH set-point. The nitrification reaction leads to H^+ production and drives down the pH-value to the lower set-point where aeration stops. In the subsequent anaerobic step, all the accumulated nitrite is used for oxidizing ammonia. In the course of this biochemical process the recovered alkalinity, as well as the continuous feed of alkaline reject water leads to an increase in pH to the upper set-point where aeration is switched on again. The stripping effect of CO_2 due to aeration represents an additional driver of the key variable: pH (Figure 4).

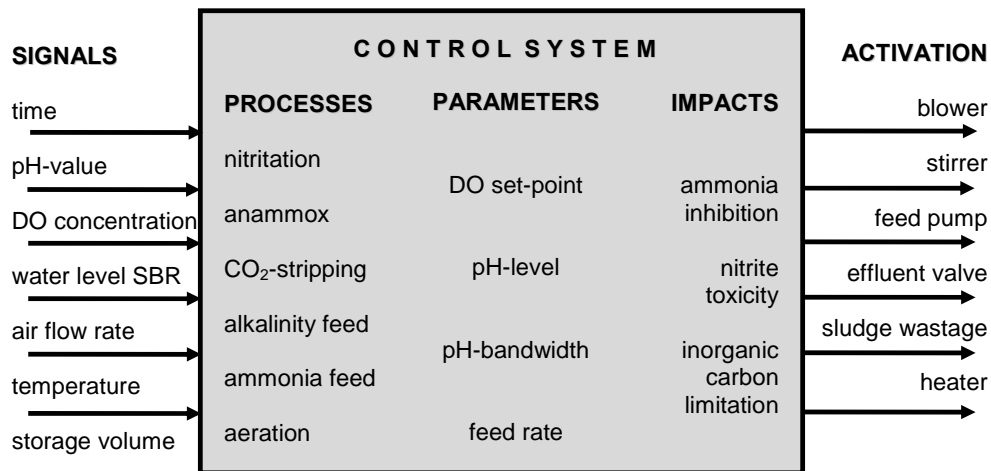


Figure 4 – Control scheme of the DEMON process – parameter selection aims to optimize process performance considering ammonia inhibition, nitrite toxicity and inorganic carbon limitation.

After seeding the full-scale reactor in Strass in 2004 the load was gradually increased (weekly average N-removal in Figure 5) and a continuous ammonia removal efficiency of 90% was achieved.

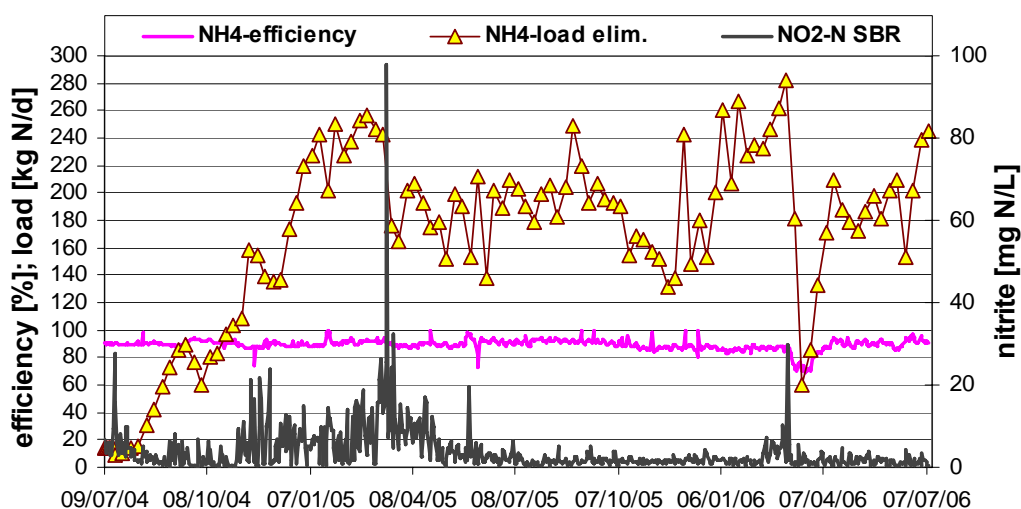


Figure 5 – Controlled nitrite level versus ammonia removal efficiency at the full-scale DEMON system in Strass during 2 years of continuous operation.

After the load increase the SBR was operated close to the process capacity as indicated by build-up of nitrite. In the subsequent period (after July 2005), optimum control adjustment brought the nitrite consistently down to around 2 mgN/l with only one major disturbance during a 2-year operation period: a broken effluent valve caused a severe loss of biomass followed by nitrite accumulation due to over-aeration. After a sharp reduction in loading the system recovered. A time-base aeration safeguard (to limit aeration) was implemented thereafter to prevent over-aeration in case of future disturbances.

Deammonification parameter estimation – full-scale system and kinetic reactor. Figure 6 shows a photograph of a pilot reactor installed for conducting kinetic experiments in Strass, Austria. The pipe-shaped plexi-glass SBR with a diameter of 0.25 m and minimum volume of 135 L is operated at a minimum water level of 2.75 m. Tall reactor geometry was selected in order to achieve a realistic representation of aeration performance and gas-stripping effects. Moreover, oxygen intrusion is prevented by such a low surface/volume ratio. Sludge settling characteristics are not significantly influenced by side-wall effects at diameters of at least 0.25 meter. The bottom of the reactor is covered with fine bubble membrane diffuser and the flow of pressurized air is continuously metered. On-line probes for pH (WTW: SensoLyt SEA) and DO (WTW: TO700IQ) measurements are installed and connected to the programmable logic control (Siemens Logo). Additionally water temperature is kept stable between 29 and 30 °C by controlling a heating element. For monitoring purpose (outside the control loops) ammonia and nitrate (WTW: VARiON 700Plus IO) is measured on-line and a pressure meter detects water level. All the collected data is transmitted to allow remote operation monitoring.

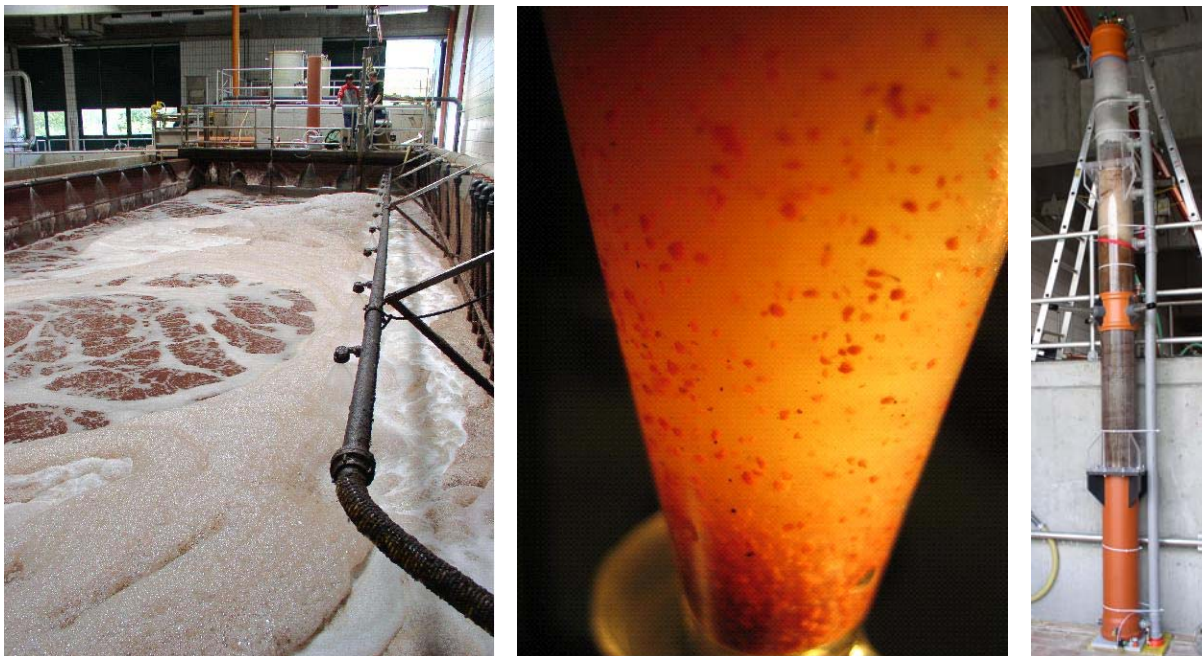


Figure 6 – Photograph of the full-scale DEMON-system (left; 500 m³ volume), extracted biomass (middle); and the experimental kinetic reactor system (right; 200 L volume).

This reactor is being used to evaluate performance characteristics of the DEMON® process. From the full-scale reactor in Strass excess sludge was used as seed in the kinetic reactor. The kinetic reactor is continuously operated (in parallel with the full-scale system) and stressed with increasing residual nitrite concentrations until failure is observed. The goal is to use the data obtained from the reactors to define the nitrite poisoning effect. Subsequent to experimentation, these results will be converted into a mathematical model using a process simulator.

Anammox activity measurement. The mass of active anammox organisms is quantified indirectly by ex-situ tests determining degradation rates of spiked nitrite loads. Activity measurements are conducted every second day in combination with periodical sludge wastage of 7 liters according to the following protocol:

- 1) Sampling of 5 L of sludge and spiking with 1250 mg of NaNO₂ (results NO₂-N > 50 mg/L)
- 2) Cover vessel, start mixing and wait 5 minutes for complete dissolution of salt
- 3) Measurement from filtered samples every 15 minutes: 5 data points for NH₄-N, NO₂-N, NO₃-N, temperature, DO, time
- 4) Determine TSS concentration and calculate N-turnover per g TSS and hour:
 $(d\text{NH}_4\text{-N} + d\text{NO}_2\text{-N}) * \text{TSS}^{-1} = \text{activity} [\text{g N} * \text{g TSS}^{-1} * \text{h}^{-1}]$

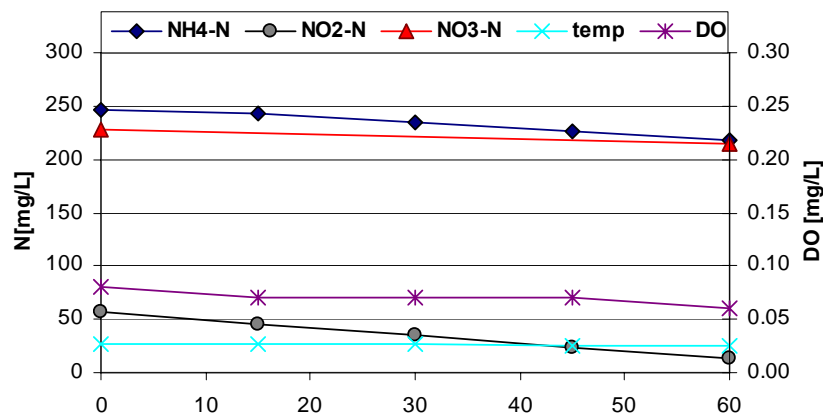


Figure 7 – concentration profiles of nitrogen compounds and survey variables temperature and DO during anammox activity measurement (sample test representing data point of 2nd of January in Figure 12).

From data in Figure 7, specific activity is calculated at 7.83 g NO₂-N and 13.05 g N_{total} per g TSS and hour, based on measured decrease in nitrite of 42.8 g per liter and 28.5 g of ammonia, respectively. The measured nitrite degradation profiles show a linear slope, i.e. no measurable acute impact of nitrite on anammox activity. Obviously neither the initial high nitrite level nor continued nitrite exposure period of one hour causes any significant change in degradation rates.

RESULTS AND DISCUSSION

Importance of controlling residual nitrite levels. The following section presents two experimental periods: The first one investigates impacts of an acute shock load of nitrite formed due to increasing DO values up to 1.0 mg/L. The second one investigates the impact of an

incremental nitrite accumulation during extended aeration periods at a wider pH band. Table 1 gives further details on operational conditions.

Table 1 – operational conditions during 2 experimental periods exhibiting parameter variations of DO and pH-band.

operational setting	Q_{flow} $\text{L}\cdot\text{h}^{-1}$	$\text{NH}_4\text{-N}_{\text{in}}$ $\text{mg N}\cdot\text{L}^{-1}$	Q_{air} $\text{L}\cdot\text{h}^{-1}$	DO $\text{mg O}_2\cdot\text{L}^{-1}$	pH bandwidth	Temp. $^{\circ}\text{C}$	$\text{NO}_{2,\text{conc.}}$ $\text{mg N}\cdot\text{L}^{-1}$	$\text{NO}_{2,\text{activity}}$ $\text{mg N}\cdot(\text{g SS})^{-1}\cdot\text{h}^{-1}$
increasing DO	2.25	1670	1380	0.5	0.02	29	4	2.56
	2.25	1670	1380	1.0	0.02	29	79	0.96
increasing pH-bandwidth	2.25	1675	960	0.28	0.02	29	1.7	8.24
	2.75	1680	1240	0.38	0.04	29	4.8	6.23

Elevated accumulation of nitrite. The characteristic pH saw-tooth profile in Figure 8 corresponds to the alternating aeration pattern in the reactor. Despite constant air flow rate, aeration intervals increase in duration and DO concentration increases, both effects indicating reduced respiration rates. The measured nitrite accumulation up to 79 mg $\text{NO}_2\text{-N}$ per liter impacts not only anammox organisms but also aerobic organisms.

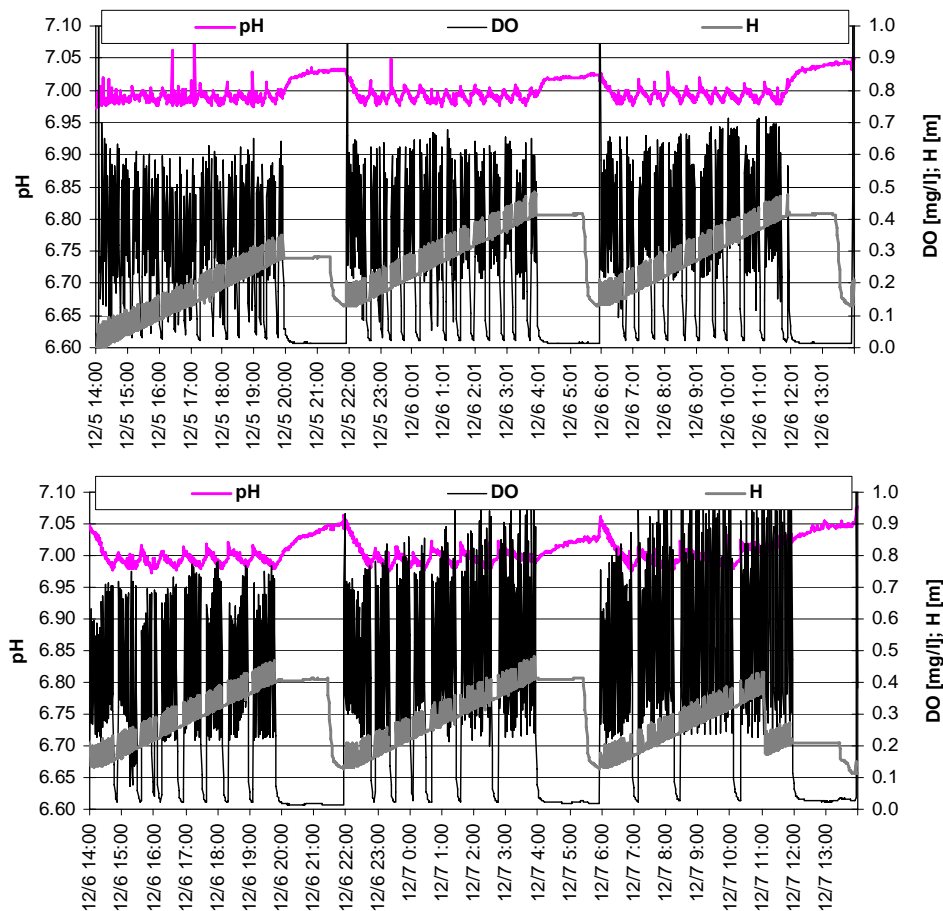


Figure 8 – Operational data (pH, DO and water level variation H) of the kinetic reactor during 2 days of excessive air supply causing a DO build-up from 0.5 to 1.0 mg/l.

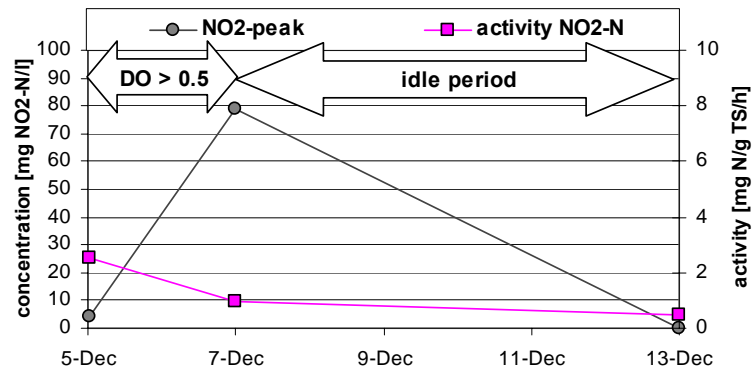


Figure 9 – High DO level causes nitrite accumulation up to 79 mg/l and as a further consequence a significant drop in anammox activity.

Activity measurements comparing initial and final state (see dropping water level in Figure 8 due to sampling) provide clear evidence of nitrite poisoning. High DO concentration promotes aerobic nitrite formation against anaerobic nitrite reduction. Increasing the nitrite level further retards nitrite reduction resulting in an imbalance that drives the system to failure. Nitrite toxicity appears irreversible during an idle period of 6 days (Figure 9). From activity data the nitrite peak concentration is expected to be depleted within 1 day. Afterwards during remaining 5 days at assumed zero nitrite concentration the activity does not recover to the level prior to the nitrite shock. The irreversible nature of nitrite toxicity is also confirmed by draw-backs in anammox enrichment in New York corresponding to temporary nitrite peaks (Figure 5). Irreversible damage to anammox activity means that nitrite or its byproduct inactivates anammox cells (i.e. decay rates are substantially increased) and not just temporarily inhibit growth.

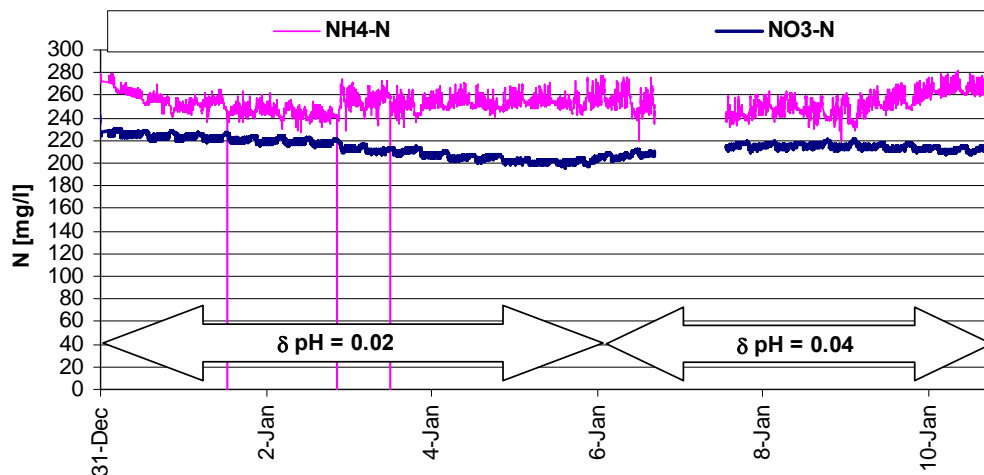


Figure 10 – On-line operational data of the Kinetic Reactor during 2 weeks at increasing pH-band of the aeration control system.

Incremental accumulation of nitrite. Investigation of incremental nitrite accumulation requires a longer observation period. Constant ammonia and nitrite levels in Figure 10 demonstrate stable deammonification performance during the initial two weeks of operation. In Figure 11, two sample diagrams are shown before and after a shift in pH-band from $\Delta 0.02$ to $\Delta 0.04$. The

overshoot in pH is caused by the alkaline feed and insufficient mixing during anoxic periods. The increase in pH band results in a longer aeration interval, thus leading to a periodical accumulation of a small amount of nitrite, climbing from a mean value of 1.7 to 4.8 mg NO₂-N per liter.

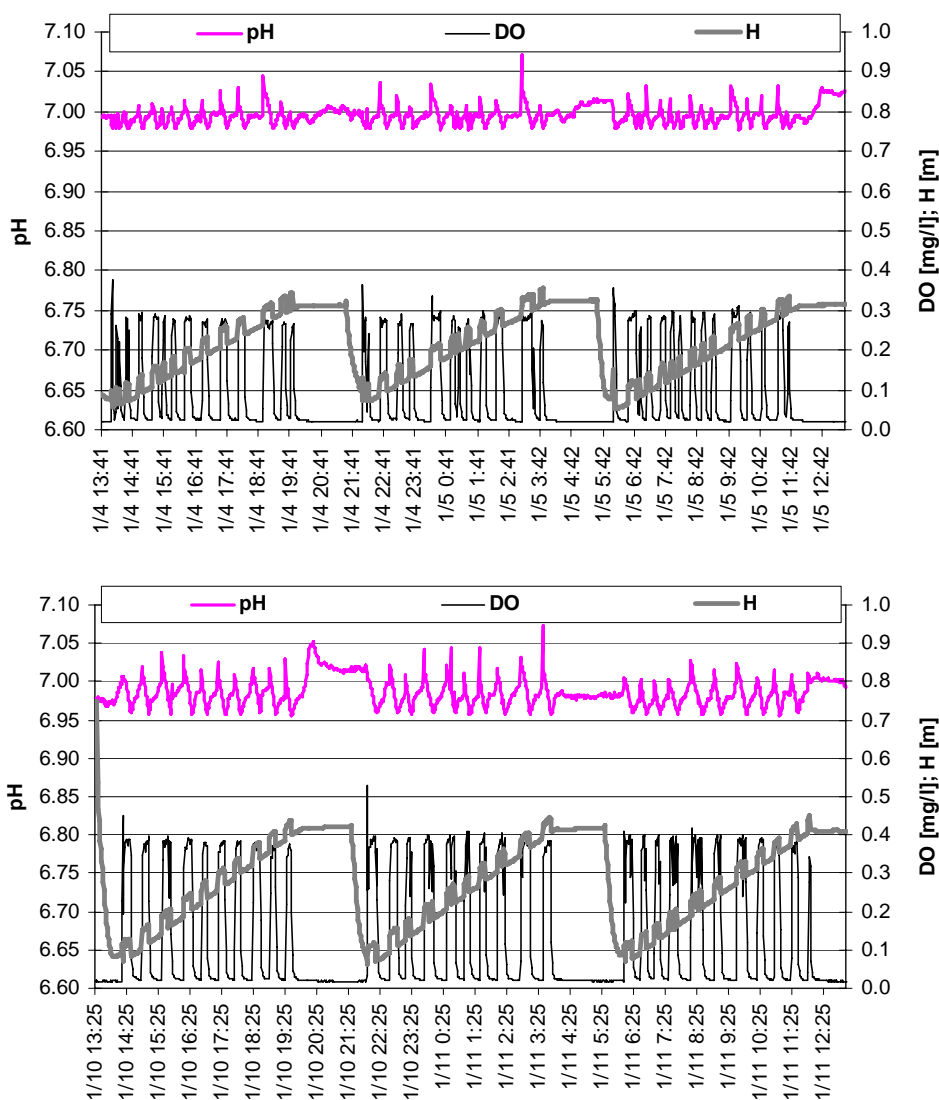


Figure 11 – Extended aeration intervals after adjustment of pH-band from 0.02 (above) to 0.04 (bottom).

This increment in nitrite level (of only 4.8 mg NO₂-N per liter) results in a continuous decrease in anammox activity (Figure 12). Despite the loss of almost one third of anammox activity no system failure is indicated – suggesting a resilience of a system operated with excess anammox inventory. This observation points to a solid biological reserve capacity that increases confidence in the operational safety of the system. Whether this decrease in activity for a small increase in nitrite concentration represents inhibition or irreversible poisoning is subject to current testing.

Furthermore, the long-term exposure to higher concentrations of nitrite is not clearly understood and will be subject to future testing.

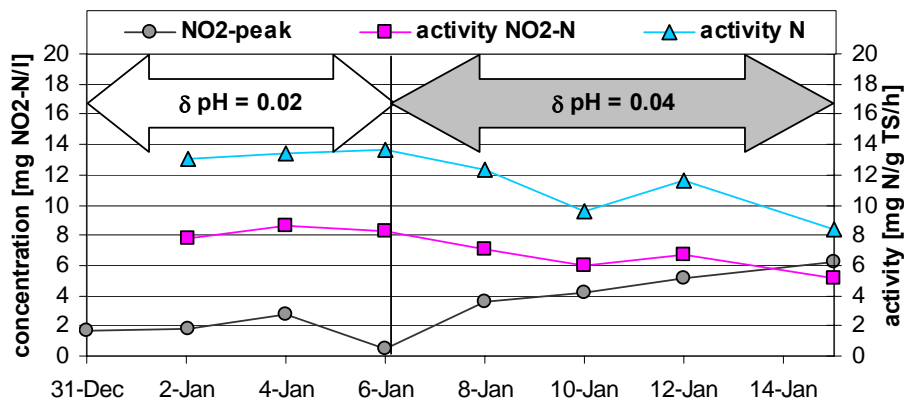


Figure 12 – Extended aeration intervals cause a slight nitrite accumulation and as a further consequence a drop in anammox activity.

CONCLUSIONS

Understanding the role of nitrite is paramount for the control of the deammonification process and for its wide-scale implementation for treating high strength ammonia water such as in digester recycle streams. Three important conclusions can be extracted from this work:

- A high concentration of accumulated nitrite results in an irreversible toxic impact on anammox organisms in the suspended growth deammonification process. Therefore this impact should be addressed as toxicity and not inhibition. In terms of modeling increased nitrite levels accelerates decay rates and does not slow growth rates.
- A low concentration of accumulated nitrite, as low as 4.8 mg NO₂-N per liter, also results in a decrease in anammox activity over a longer period. Whether this low concentration effect is irreversible or temporary is currently being studied.
- The presented protocol for measuring the state of anammox activity reflects the current process capacity. Setting suboptimal pH set points (process controls) can substantially reduce activity without significantly influencing the removal efficiency. Conversely, optimal setting of control parameters contributes to higher activity, but also provides an operational safety factor.

ACKNOWLEDGEMENT

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