Alternative processes of nitrogen removal
from wastewater —
startup of nitritation reactor

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Abstract: Efficient nitritation was tested in SBR with the aim to accumulate nitrites and to minimize nitrates production in reject wastewater with 500 mg L^{-1} $(NH_4^+ + NH_3)$-N and with different molar ratios of HCO_3^- : $(NH_4^+ + NH_3)$-N (1.1—2.1). More than 80 % efficiency of nitritation and permanent inhibition of NOB were achieved at the ratios of 1.7—1.9 and at the loading of 0.16—0.6 kg $(NH_4^+ + NH_3)$-N m^{-3} d^{-1}. Under these conditions, the outflow pH was in the range of 5.9—6.5, outflow c $(NO_2^- + HNO_2)$-N increased up to 400 mg L^{-1} and c (NO_3^-)-N dropped below 50 mg L^{-1}. Undissociated HNO_2 was confirmed as the main inhibitor of NOB.

Keywords: AOB, nitritation, NOB inhibition, sequencing batch reactor, sludge reject water

Introduction

Alternative processes to standard nitrification + denitrification are either "full" nitritation (NI) + denitritation (DI) or "partial ca. 50 %" NI + Anammox (AAO) (Pitter P., 2015). Exploitation of both processes for the purpose of wastewater treatment is in the last 15—20 years quite often reported but the number of "full-scale" applications is still limited (Lackner et al., 2014). These processes can be applied in particular for the sludge reject wastewater, anaerobically pre-treated industrial wastewater or digestate from biogas plants with high concentrations (c) of nitrogen (N) (hundreds to thousands of mg L^{-1}), low biodegradable COD and high temperatures (T) (30—40 °C). However, in recent years, the research attention is paid also to the applications for cold wastewater like landfill leachate or anaerobically pre-treated sewage wastewater with dozens of mg L^{-1} of N (Kouba et al., 2015). Crucial precondition for both processes is NI, i.e. oxidation of ammonia $(NH_4^+ + NH_3)$-N into nitrite $(NO_2^- + HNO_2)$-N by ammonium-oxidizing bacteria (AOB), while the nitrite-oxidizing bacteria (NOB) oxidizing $(NO_2^- + HNO_2)$-N into (NO_3^-)-N are in the reactor inhibited. This will give the savings mainly of oxygen (O_2) for NI and COD for denitrification (Drtil and Hutňan, 2013). NOB are more inhibited by low c(O_2) (below 1 mg L^{-1}), higher T (above 30—35 °C) in combination with short sludge retention time (θx) (units of days) and higher c of substrate and product (mainly by undissociated forms of NH_3 and HNO_2) than AOB (Drtil and Imreová, 2016). The inhibition with NH_3 and HNO_2 can be achieved mostly by using sequencing batch reactor (SBR) with the semi-continuous inflow and c gradient of the substrate and the product. Under these conditions, the impact of c(O_2), θx and T is not so important. The long-term (multiyear) "partial" NI in SBR with inhibition of NOB and without regulation of c(O_2), θx, pH and T has been described in e.g. (Svehla et al., 2014). The authors reached similar results even in a pilot wastewater treatment plant (WWTP) (Radechovský et al., 2015). It is necessary to point out that NI reactor with "partial" (50 %) NI produced wastewater for final treatment by AAO process, i.e. in the reactor at the end of the cycle were hundreds of mg L^{-1} $(NO_2^- + HNO_2)$-N and $(NH_4^+ + NH_3)$-N and less than dozens of mg L^{-1} (NO_3^-)-N. Unlike (Svehla et al., 2014; Radechovský et al., 2015), we focused on a more effective NI (at least 80 %) which should produce wastewater suitable for the final treatment by DI (not AAO), i.e. at the end of the cycle in the reactor there should be hundreds of mg L^{-1} $(NO_2^- + HNO_2)$-N and only dozens of mg L^{-1} $(NH_4^+ + NH_3)$-N and (NO_3^-)-N. We have been oxidizing 500 mg L^{-1} $(NH_4^+ + NH_3)$-N in NI SBR mostly with the same conditions as in (Svehla et al., 2014; Radechovský et al., 2015) (no regulation of c(O_2), θx or T). For a more than 50 % efficiency of NI, the pH must be controlled. A typical reject wastewater has molar ratio of HCO_3^- : $(NH_4^+ + NH_3)$-N equal to 1. Since NI of 1 mole of $(NH_4^+ + NH_3)$-N produces ca. 2 moles of H^+, we can not expect significantly higher efficiency than 50 % (Pitter, 2015; Drtil and Hutňan, 2013). The only way to increase it, is the addition of another moles of HCO_3^- (bicarbonate, lime or connection of NI with DI, where HCO_3^- are produced biologically). The detailed analysis (Pitter, 2015) of reject

wastewater at T 20−30 °C and neutral pH shows that a part of $(NH_4^+ + NH_3)$-N as an undissociated NH_3-N is still present. NI of this form produces only 1 mole of H^+, therefore, the actual ratio of HCO_3^- : $(NH_4^+ + NH_3)$-N for effective NI should be slightly less than 2. Also a small fraction of $(NH_4^+ + NH_3)$-N is not oxidized (assimilation, stripping of NH_3). Those are the reasons why the optimal pH should be measured experimentally. In this paper we tested ratios of HCO_3^- : $(NH_4^+ + NH_3)$-N in the range of 1.1 to 2.1. The aim was to determine how these ratios affect the pH in the reactor and at which value the high activity of AOB will be maintained while NOB will be inhibited. pH by itself is not a decisive inhibitor. In wastewater with hundreds of mg L^{-1} $(NH_4^+ + NH_3)$-N and $(NO_2^- + HNO_2)$-N, pH affects mostly the percentage of undissociated forms, which should be more responsible for inhibition (Anthonisen et al., 1976). According to (Drtil and Imreová, 2016; Svehla et al., 2014; Jenicek et al., 2004) NOB should be more sensitive to changes but also AOB should not be completely resistant. For example in (Imreová and Drtil, 2014) it was measured that in the SBR with synthetic reject wastewater with 500 mg L^{-1} $(NH_4^+ + NH_3)$-N and with the ratio of HCO_3^- : $NH_4^+ + NH_3$-N $= 2$−2.1, the pH rose up at the end of the aeration cycle to 8.5−9.0. This value allowed more than 95 % NI but the absence of HNO_2 was so significant that NOB were not inhibited anymore. As soon as the ratio was decreased and the outflow pH dropped below 6.5, the NOB inhibition and accumulation of $(NO_2^- + HNO_2)$-N notably increased. However, at low pH the NI rate is lower. pH below 6.5 with high content of HNO_2 inhibited not only NOB but also AOB. It turned out that in a concrete system there should be a certain range of pH and $c(NO_2^- + HNO_2)$-N, when NOB are inhibited and AOB remain active. In (Imreová and Drtil, 2014) the optimum pH was 6.5−7 with 200−300 mg L^{-1} $(NO_2^- + HNO_2)$-N.

Material and methodology

The long-term experiment has been carried out in the same SBR as in (Imreová and Drtil, 2014; Imreová and Drtil, 2015) volume (V) = 1 L, feeding the reactor with synthetic reject wastewater 2 and 4 times per day, $c(NH_4^+ + NH_3)$-N = 500 mg L^{-1}, T = 22−28 °C, no draw of excess sludge and no aeration control). The aim of the experiment was to find the ratio of HCO_3^- : $(NH_4^+ + NH_3)$-N, when NI efficiency is more than 80 %, AOB are active and NOB inhibited at the same time, i.e. to find the conditions for substrate and product inhibition, without low O_2 and low θx inhibition. Each SBR cycle consisted of aeration, 0.5 h sedimentation, draw

of treated wastewater and fill of raw wastewater. Substrate was added 2 respectively 4 times per day (either at 8am/pm or at 8 and 2 am/pm). The first 0.5 hour after the fill, mixing without aeration took place in order to remove inflow acetate by DI. Since the excess sludge has not been discharged, the equilibrium Xc has built up spontaneously. The composition of the synthetic reject wastewater: 500 mg L^{-1} $(NH_4^+ + NH_3)$-N; 40 mg L^{-1} PO_4-P; $COD_{acetate}$ = 250 mg L^{-1}; pH = 7.8−8.1. The ratio of HCO_3^- : $(NH_4^+ + NH_3)$-N varied from 1.1 to 2.1 by addition of $NaHCO_3$. Real reject wastewater was used as a source of micronutrients (30 mL L^{-1}). Considering that the inoculum from municipal WWTP has not been previously exposed to such a high $c(NH_4^+ + NH_3)$-N, the reactor was loaded cautiously with diluted substrate for the first days (300 mg L^{-1} $(NH_4^+ + NH_3)$-N).

Results and discussion

Adaptation of AOB has proven to be surprisingly fast. At the starting loads 0.1−0.16 kg $(NH_4^+ + NH_3)$-N $m^{-3}d^{-1}$ the inoculum has adapted to a more than 80 % NI within 10 days. Once the ratio of HCO_3^- : $(NH_4^+ + NH_3)$-N increased to 2−2.1, the outflow pH increased to 8.3−9 and accumulation of $(NO_2^- + HNO_2)$-N associated with inhibition of NOB started significantly decreasing. Outflow $c(NO_2^- + HNO_2)$-N was less than 100 mg L^{-1} and $c(NO_3^-)$-N was above 300 mg L^{-1}. Coming to the ratio of 1.7−1.9, the outflow pH dropped below 6.5 and NOB inhibition immediately started. $c(NO_2^- + HNO_2)$-N increased to 350−400 mg L^{-1} and $c(NO_3^-)$-N dropped below 50 mg L^{-1}. NI efficiency was still at 80−90 %. At lower ratios pH dropped below 6.0 and the inhibition of NOB as well as AOB started (NI less than 80 %). As an optimum ratio for more than 80 % NI and NOB inhibition we can recommend a value of 1.7. We could also give the value of 1.9 as an optimum but most of the reject wastewater has the ratio at approx. 1 and to achieve higher values the addition of alkali is required.

The results have also shown that inhibition of NOB in the SBR with more than 80 % NI (not partial 50 %) was caused mainly by an HNO_2, although according to (Svehla et al., 2014; Radechovský et al., 2015; Anthonisen et al., 1976; Jenicek et al., 2004) also NH_3 should contribute to the inhibition. NH_3 occurs in the reactor mainly at the beginning of each cycle after the addition of the substrate and HNO_2 mainly at the end. The actual effect of HNO_2 and NH_3 is represented by the comparison of pH and c ranges in the SBR during aeration cycles at various ratios of HCO_3^- : $(NH_4^+ + NH_3)$-N

Tab. 1. The comparison of pH and c range of undissociated forms of NH_3 and HNO_2 in stages with higher and lower ratio of $HCO_3^- : (NH_4^+ + NH_3)$-N.

Ratio	pH outflow average	pH range during the cycle[*]	$c(HNO_2)$-N range during the cycle[*] mg L^{-1}	$c(NH_3)$-N range during the cycle[*] mg L^{-1}	NOB	AOB
2.1	8.5	8.1—9.1	0.001—0.006	15.0—110	active	active
		→8.1—8.8	→0.002—0.010	→0.50—20.0		
1.7	6.2	7.5—8.2	0.003—0.020	10.0—15.0	inhibited	active
		→6.1—6.6	→1.000—3.000	→0.01—0.10		

[*]pH and $c(HNO_2)$-N and (NH_3)-N in the SBR were changing during the aeration cycle; pH reached the highest point cca 2 hours after the fill of substrate (pH increased due to the addition of the substrate, DI of acetate and CO_2 stripping) and the lowest during the last hours of the aeration cycle which was at the level of the outflow pH (decreased due to NI).
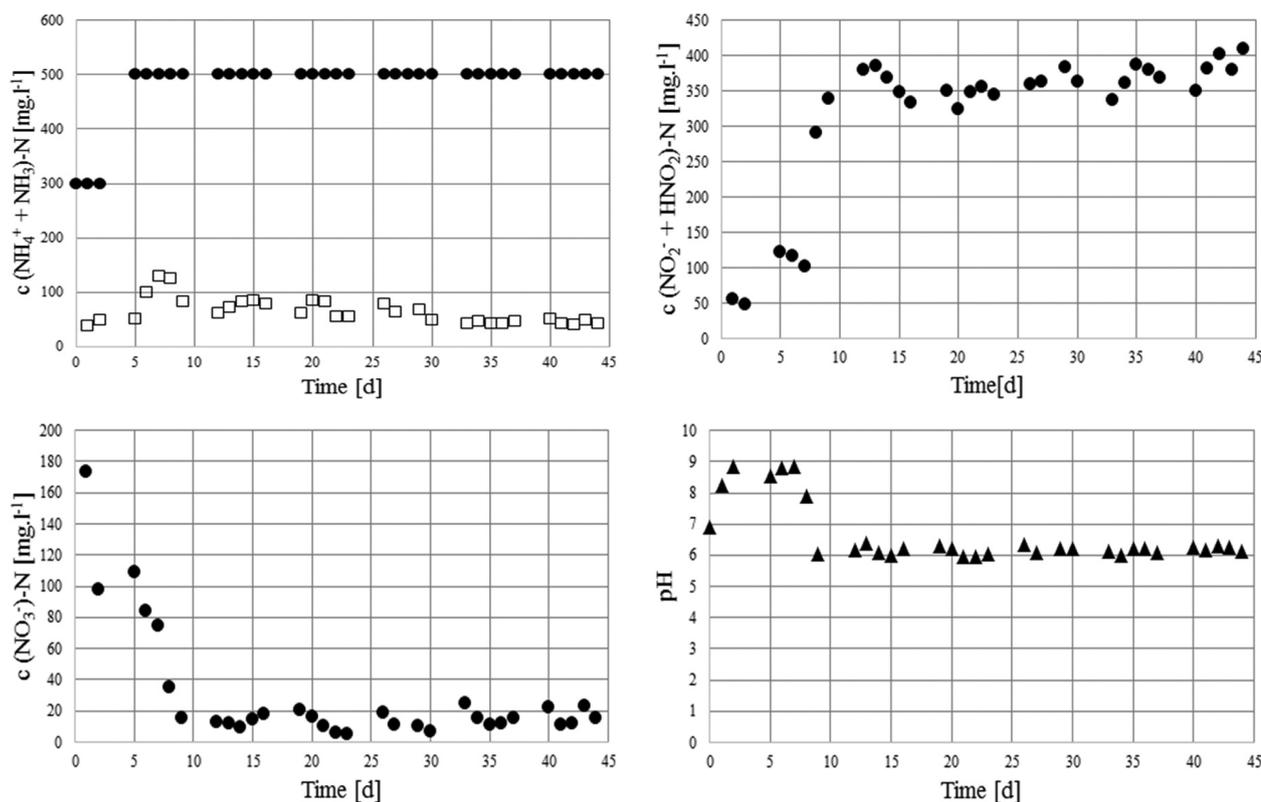

Fig. 1. Profile of $(NH_4^+ + NH_3)$-N (inflow ●, outflow □), $c(NO_2^- + HNO_2)$-N (outflow), $c(NO_3^-)$-N (outflow) and pH (outflow) during the verification NI experiment.

(Tab. 1). Basically, it is a range of $c(NH_3)$-N and (HNO_2)-N in the reactor that biomass had to deal with. The c of undissociated forms were calculated according to (Pitter, 2015; Anthonisen et al., 1976) from the measured values of $c(NH_4^+ + NH_3)$-N, $c(NO_2^- + HNO_2)$-N, pH and T. Tab. 1 shows that during the phase with the ratio of 2.1, NOB were not inhibited neither by the $c(NH_3)$-N = 110 mg L^{-1}, but in the phase with ratio of 1.7 they were inhibited already with the $c(NH_3)$-N = 15 mg L^{-1}. Therefore, the critical inhibitor can not be NH_3 but HNO_2. Inhibiting $c(HNO_2)$-N are in the range of hundredths to units of mg L^{-1}.

The successful startup of NI with NOB inhibition in SBR fed by synthetic reject wastewater ($c(NH_4^+ + NH_3)$-N = 500 mg L^{-1}; first 3 days 300 mg L^{-1}; $HCO_3^- : (NH_4^+ + NH_3)$-N = 1.7; Bv = 0.16 kg $(NH_4^+ + NH_3)$-N m^{-3} d^{-1}; 4 × 80 mL = 320 mL d^{-1} of substrate per day; V = 1 L; retention time = 3 d) was confirmed in a verification experiment Fig. 1. Substrate feeding was interrupted during the weekends (no production of reject wastewater at WWTP). As an inoculum, nitrifying activated sludge from municipal WWTP was used. Adaptation to high $c(NH_4^+ + NH_3)$-N and more than 80 % NI occurred within 9 days. After 1 month the

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efficiency of NI was already at the level of 90 %. The inhibition of NOB and the accumulation of $(NO_2^- + HNO_2)$-N occurred also within 9 days, as a consequence of NI startup connected with pH decrease to 5.9—6.2. NOB inhibition was permanent also during the weekends without inflow. During 1.5 month of startup Xc decreased from the starting value of 1.6 to 0.9 g L^{-1} and stabilized on this value in a while later.

Conclusions

The main conclusions from laboratory modelling of NI of synthetic reject wastewater with $c(NH_4^+ + NH_3)$-N = 500 mg L^{-1} at different ratios of $HCO_3^- : (NH_4^+ + NH_3)$-N in SBR are:
— undissociated HNO_2 has been confirmed as the main inhibitor of NOB
— more than 80 % NI and permanent inhibition of NOB (even during weekends without influent) were achieved at ratios of 1.7 and 1.9 and at Bv = 0.16—0.6 kg $(NH_4^+ + NH_3)$-N $m^{-3}d^{-1}$. Under these conditions outflow pH was in the range of 5.9—6.5, outflow $c(NO_2^- + HNO_2)$-N increased to 350—400 mg L^{-1} and $c(NO_3^-)$-N dropped below 50 mg L^{-1}
— adaptation of AOB from municipal WWTP to the high c N was very fast (till 10 days).

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