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NH_4^+ ad-/desorption in sequencing batch reactors: simulation, laboratory and full-scale studies

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ABSTRACT

Significant NH_4-N balance deficits were found during the measurement campaigns for the data collection for dynamic simulation studies at five full-scale sequencing batch reactor (SBR) waste water treatment plants (WWTPs), as well as during subsequent calibrations at the investigated plants. Subsequent lab scale investigations showed high evidence for dynamic, cycle- specific NH_4^+ ad-/desorption to the activated flocs as one reason for this balance deficit. This specific dynamic was investigated at five full-scale SBR plants for the search of the general causing mechanisms. The general mechanism found was a NH_4^+ desorption from the activated flocs at the end of the nitrification phase with subsequent nitrification and a chemical NH_4^+ adsorption at the flocs in the course of the filling phases. This NH_4^+ ad-/desorption corresponds to an antiparallel K^+ ad/-desorption.

One reasonable full-scale application was investigated at three SBR plants, a controlled filling phase at the beginning of the sedimentation phase. The results indicate that this kind of filling event must be specifically hydraulic controlled and optimised in order to prevent too high waste water break through into the clear water phase, which will subsequently be discarded.

Key words | dynamic simulation, NH_4^+ adsorption, nitrogen removal, process control, SBR

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INTRODUCTION

During the last few decades numerous wastewater treatment plants (WWTPs) have been designed and built worldwide with facilities for nitrogen removal. In almost all full-scale applications the nitrogen removal process is a combined denitrification/nitrification process. This specific nitrogen removal pathway has been implemented into a series of models for the activated sludge process (Henze *et al.* 2000; Rieger *et al.* 2001). These models fit the real world quite well in the case of conventional plants with regard to nitrogen removal. Recently it has been shown that these models also can be used successfully for different approaches to the investigation of SBR plants (Keller & Yuan 2002; Rönner-Holm *et al.* 2006). However, according to Rönner-Holm *et al.* (2006) it was not achieved that the simulated NH_4-N data corresponded satisfyingly with the cross-checked online data concerning the internal processes in the full-scale reactors. In order to develop new control strategies by dynamic simulation a better adjustment of the simulated data is necessary. These findings were in accordance with earlier indications for NH_4-N balance deficits in full-scale SBRs (Holm *et al.* 2000).

New mechanisms for NH_4^+ elimination have been described recently, like the anammox process (Abma *et al.* 2007) and the SHARON process (Hellinga *et al.* 1998). Nielsen (1996) had found a purely chemical NH_4^+ ad-/desorption to activated sludge flocs at conventional

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activated sludge plants. Furthermore a specific N storage process analogous to the P and C storage process as included in the ASM3 + EAWAG-bio-P-model cannot be excluded.

Therefore, first of all, the objective of this study was to determine the nature of the NH_4-N balance deficits in order to adjust the used simulation models ASM1, ASM2 and ASM3 if necessary. Furthermore, the population structure of nitrifiers (ammonia and nitrite oxidizers) and of anammox bacteria was analysed in the activated sludge of the simulated SBR plants so far. Cycle-specific NH_4^+ adsorption and desorption tests were performed at those full-scale plants as well to prove the findings of Nielsen (1996) especially for SBR plants. In addition, the amounts of different cations were determined during the cycle-specific NH_4^+ ad- and desorption tests.

Another objective was to examine reasonable full-scale uses of the described phenomenon. Different tests were performed on full-scale SBR plants for the selective manipulation of full-scale cycle strategies to profit from this phenomenon at a large scale, and to improve the treatment performance by implementing an additional, controlled filling phase at the beginning of the sedimentation phase. In this context the three main goals were:

1. Transforming the mainly "unreactive" sedimentation phase into a partly "reactive" phase with denitrification and biological P-removal without significant NH_4^+ transfer into the clear water phase.
2. Using this specific filling phase for an improvement of the "chock loading" effect resulting in a decreasing sludge volume index.
3. Causing specific cycle circumstances which might favour the establishment of anammox bacteria.

METHODS

The simulations and calibrations were carried out according to Rönner-Holm *et al.* (2006), the ad-/desorption tests according to Nielsen (1996), Kiehn (2006) as well as the determinations of the cations. The fluorescence *in situ* hybridization (FISH) analyses were carried out according to Daims *et al.* (2005) with the oligonucleotide probes EUB338I-III (specific for the domain *Bacteria*), S-G- Ntspa-0662-a-A-18 (genus *Nitrospira*), S-∗-Ntspa-1431-a-A-18 (*Nitrospira* sublineage I), S-∗- Ntspa-1151-a-A-20 (*Nitrospira* sublineage II), NIT3 (*Nitrobacter* spp.), NEU (halophilic and halotolerant *Nitrosomonas* spp.), NmV (*Nitrosococcus mobilis*), Cluster6a192 (Nitrosomonas oligotropha lineage), Nsv443 (genus *Nitrosospira*), and Amx368 (anammox bacteria). For details of the probes please refer to probeBase (Loy *et al.* 2003). The full-scale SBR tests were executed on the basis of Schwitalla (2007). Figure 1 shows the nine probing events on the cycle strategy time-scale. Figure 2 shows the location of the samples taken.

RESULTS AND DISCUSSION

Indications for NH_4^+ balance deficits by dynamic simulation studies

Figure 3 presents the online measured NH_4-N concentrations of the SBR plant Hettstedt (30,000 PE) in the course of one 6-hour cycle during the measuring campaign for the ASM1 calibration of the plant. The interrupted line shows the NH_4-N curve calibrated with ASM1. It is obvious that the simulated NH_4-N values are above the measured online data, especially directly before the beginning of the aeration phase. This does not only apply to the cycle shown, but also for all 43 examined cycles of this plant as well as to 119 of 127 additionally examined cycles at four other simulated and calibrated SBR plants. All these plants (Bad Zwischenahn 41,000 PE, Deuz 12,500 PE, Spenge 22,500 PE and Weisstal 21,000 PE) treat mainly municipal waste water and exhibit complete nitrification, almost complete

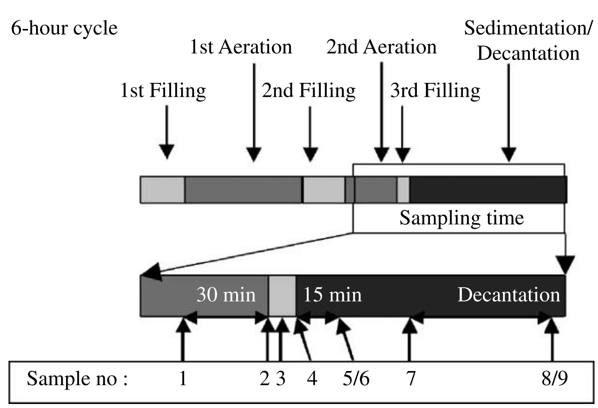

Figure 1 | Sampling events on the cycle strategy time-scale of the 6-hour cycle.

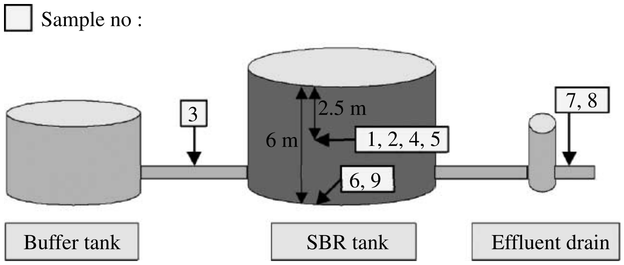

Figure 2 | Location of samples taken.

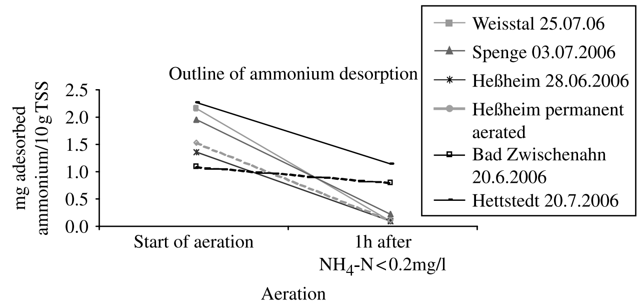

Figure 4 | Results of the NH_4^+ desorption tests with KCl-solution.

denitrification and biological phosphorus elimination. In all cases the online data were confirmed by laboratory cross-checks.

In total, three plants were investigated with ASM1, one plant with ASM2d and two plants were analysed with ASM3 + EAWAG-BioP. The differences between the simulated and monitored NH_4-N data occurred for all three models at a similar extent. An example for the balance deficits with the ASM3 + EAWAG-BioP model is shown in Figure 4 for the SBR plant Spenge. The simulated NH_4-N curves were generated according to the online calibration procedure in order to correspond them with the online data.

Detection of nitrifiers and anammox bacteria

Cultivation-independent FISH analyses confirmed that chemolithoautotrophic, aerobic ammonia- and nitrite-oxidizing bacteria occurred in all analyzed plants (Table 1). The observed community structures of these organisms are similar to those found in other nitrifying wastewater treatment systems (Juretschko et al. 1998; Daims et al. 2001) and are consistent with the measured nitrification activities. Theoretically, the detected NH_4-N balance deficits could result from the activity of anammox bacteria. These organisms oxidize ammonium anaerobically

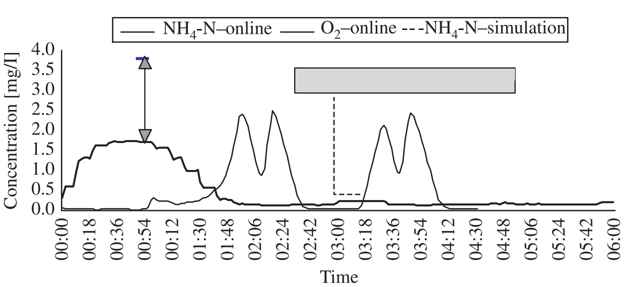

Figure 3 | Comparison of the online and simulated NH_4-N data for one 6-hour cycle on the 2nd of May 2003, WWTP Hettstedt, calibrated with ASM1.

and concomitantly reduce nitrite. The products of this metabolism are dinitrogen gas and small amounts of nitrate (Strous et al. 1999). At the beginning of all filling phases, the conditions were basically suitable for anammox bacteria as the reactors contained high amounts of NH_4^+ and NH_3^-/NH_2^-, but no O_2. Therefore, all plants were also screened by FISH with anammox-specific probes, but no anammox organisms were detected by this technique in any sample. The absence of anammox bacteria was probably caused by the aeration during the nitrification phase. Past research has shown that anammox bacteria living in wastewater treatment plants are sensitive to oxygen (Schmid et al. 2001).

Laboratory-scale NH_4^+ adsorption and desorption studies

Figure 4 shows the results of NH_4^+ desorption tests using one normal KCl solution of SBR activated sludge samples during one cycle. The amounts of NH_4^+ desorption vary slightly among the five analysed full-scale SBR plants, but the tendency is consistent: the desorption minima occur at the end of nitrification as well as up to one hour afterwards.

Figure 5 presents the results of NH_4^+ adsorption tests adding NH_4Cl to a final concentration of approximately 10 mg/l. Here too, the adsorption capacities vary among the five SBR plants. The tendency is again consistent: the activated sludge samples have the highest adsorption capacities after the nitrification phase.

The results of the desorption tests with one molar KCl indicate a competition of adsorption to negatively loaded activated sludge floc surface structures between NH_4^+ and K^+. Therefore, the three cations Ca^{2+}, Mg^{2+} and K^+ were investigated for their antagonistic adsorption/desorption

Table 1 | Abundances of nitrifying and anammox bacteria in the analyzed wastewater treatment plants. (+)—(++++) organisms were detected by FISH; abundances range from rare (+) to frequently observed (++++); n.d. = organisms were not detected by FISH

WWTP	Weisstal	Deuz	Spenge	Hettstedt	Bad Zwischenahn
Nitrite-oxidizing bacteria					
Genus *Nitrospira**	+	++	+	+	+
Nitrospira sublineage I†	++++	+++	++++	++++	+
Nitrospira sublineage II†	+	++	n.d.	+	n.d.
Nitrobacter spp.*	n.d.	n.d.	n.d.	n.d.	n.d.
Ammonia-oxidizing bacteria					
Halophilic or halotolerant *Nitrosomonas* spp. (e.g. *N. europaea*, *N. eutropha*)*	n.d.	n.d.	n.d.	+	n.d.
*Nitrosococcus mobilis**	n.d.	n.d.	n.d.	n.d.	n.d.
Nitrosomonas oligotroph lineage (lineage 6a)*	+++	++	+++	+++	+++
Genus *Nitrosospira**	n.d.	n.d.	n.d.	n.d.	n.d.
Anammox bacteria*	n.d.	n.d.	n.d.	n.d.	n.d.

*Abundance relative to all bacteria detected by probes EUB338I-III.
†Abundance relative to all *Nitrospira*-like bacteria detected by probe S-G-Ntspa-0662-a-A-18.

behaviour. At the beginning and the end of the aeration phases during the ammonium adsorption tests no significant ad-/desorption of Ca^{2+} and Mg^{2+} could be detected. In contrast, the K^+ concentrations decreased significantly during the course of the aeration. This decrease is attributed to a K^+ adsorption to the activated flocs, while ammonium desorbs and gets nitrified. The highest K^+ adsorption rates were detected in Hessheim (1.51 mmol/10 g TSS), followed by Weisstal (0.38 mmol/10 g TSS), Bad Zwischenahn (0.24 mmol/10 g TSS), Spenge (0.16 mmol/10 g TSS), Deuz (0.08 mmol/10 g TSS) and no K^+ adsorption at all in Hettstedt.

At four plants (Bad Zwischenahn, Hettstedt, Spenge and Weisstal) ammonium adsorption tests were also performed with inflow waste water mixed 1:1 with activated

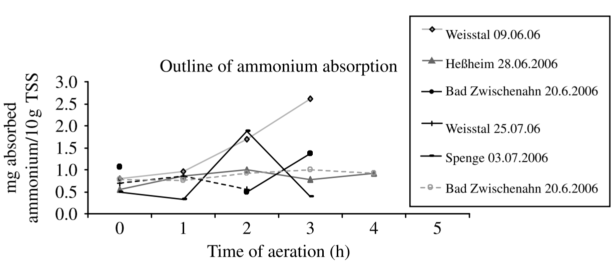

Figure 5 | Results of the NH_4^+ adsorption with feeding of NH Cl until 1 hour after NH_4-N < 0.2 mg/l.

sludge. While the NH_4^+ adsorption rates of waste water in Hettstedt and Bad Zwischenahn were slightly lower than with the NH_4Cl solution, at Spenge and Weisstal they were significantly higher. In total it is not clear whether these differences must be attributed to statistical noise.

Additional filling phases at the beginning of the sedimentation phase

At three SBR plants (Weisstal, Spenge, Bad Zwischenahn) full-scale experiments were performed with special controlled additional filling phases at the beginning of the sedimentation phase. At all three plants the SBR tanks were

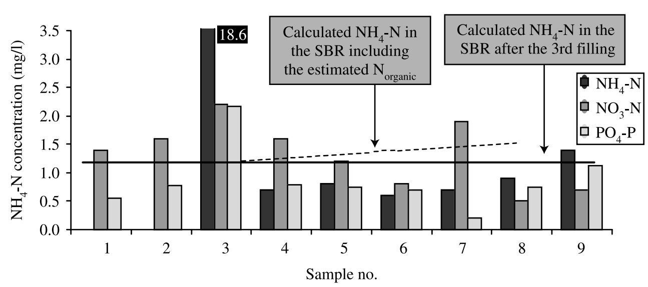

Figure 6 | Results of an experiment with a 3rd filling phase of the variant 4 with waste water, (1) 30 min prior 3rd filling, (2) directly prior 3rd filling, (3) filling sample, (4) directly after 3rd filling, (5) 15 min after 3rd filling, (6) sludge sample after 3rd filling, (7) start of decantation, (8) end of decantation, (9) sludge sample after decantation.

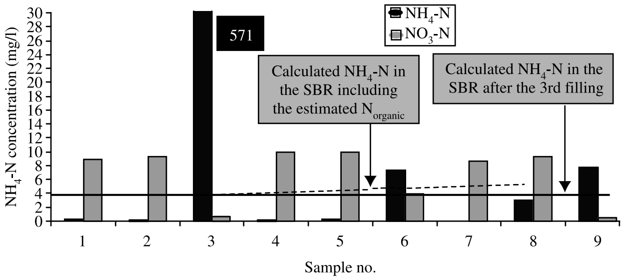

Figure 7 | Results of an experiment with a 3rd filling phase of the variant 3 with process water, (1) 30 min prior 3rd filling, (2) directly prior 3rd filling, (3) filling sample, (4) directly after 3rd filling, (5) 15 min after 3rd filling, (6) sludge sample after 3rd filling, (7) start of decantation, (8) end of decantation, (9) sludge sample after decantation.

filled punctually with high velocities of 500 m^3/h in Weisstal (reactor volume of 2 × 1,560 m^3), 600 m^3/h in Spenge (reactor volume 3 × 2,920 m^3) and 400 m^3/h in Bad Zwischenahn (reactor volume 3 × 2,488 m^3).

Five slightly different filling regimes were investigated. As a control the first variant was without an additional filling event. In the second variant the additional filling event took place 5 min before the beginning of the sedimentation phase. The third variant started exactly with the beginning of the sedimentation phase, the fourth variant 5 min later and the fifth variant 10 min later. The filling amounts varied between 27 up to 190 m^3, that is 0.9–7.6% of the total reactor volume. In all cases a partly NH_4-N break-through into the clear water supernatant was observed, varying between 40–90 % of the theoretic value at full mixing. The four filling variants showed no significant difference in the NH_4-N break-through.

Figure 6 presents the results of one variant 4 experiment in Weisstal. The calculated NH_4-N concentration at complete intermixing based upon NH_4-N filling load is approximately 80% higher as the measured values during decantation (sample 7 and 8). This filling was done with 85 m3 raw municipal waste water after the primary clarifier.

Figure 7 shows the results of a different variant 3 experiment in Weisstal. The calculated NH_4-N concentration at complete intermixing based upon NH_4-N filling load is 3.9 mg/l. At the beginning of the decantation the NH_4-N concentration was <0.2 mg/l, and only at the end of decantation did it increase to 3.0 mg/l. This filling was done with 10 m^3 sludge liquor with a much lower filling velocity of 50 m^3/h. Another important difference to the above experiment is a higher denitrification rate in the sludge fraction indicated by sample 9.

CONCLUSIONS

FISH analyses confirmed that aerobic nitrifiers were present in all plants, but also showed that known anammox bacteria were absent and did not cause the observed ammonia deficits. Cycle-specific NH_4^+ ad- and desorption processes in SBR activated sludge samples could be proven within a range of 1.0–2.5 mg NH_4^+ per 10 g MLLS. The possibility of desorption by a high quantity of K^+ and the increase of K^+ in the water phase by addition of NH_4^+ is a strong sign for the purely chemical adsorption of positively charged NH_4^+ ions to negative surface charges of the activated sludge flocs. Further planned model simulations will show if the implementation of this ad- and desorption chemism into the ASM group will resolve the previous NH_4-N balance deficit.

The full-scale practical applications have already been introduced at various SBR plants. Under additional use of the NH_4^+ adsorption capacity of the activated sludge, a significant proportion of the almost non-reactive sedimentation phase can be transferred into a reactive phase for denitrification and biological phosphorus release purposes, without leading to the estimated NH_4^+- transfer into the supernatant. This is currently performed by means of controlled loads at the beginning of the sedimentation phase in a horizontal/tangential direction near the bottom in the rotation direction of the reactor content. However, even in the case of strongly reduced filling velocity there is still a part break-through of NH_4-N into the supernatant, which is considered to be caused by the punctual fillings. Therefore, using only punctual fillings, the full-scale applications are regulated. These special filling events never exceed a freely chosen waste water amount and they only take place if the NH_4-N concentration in the reactor is <0.4 mg/l at the beginning of the loading phase. They will be automatically stopped when 2 mg/l NH_4-N is exceeded. Therefore an NH_4-N online measurement for controlling this specific load is recommended.

The full-scale applications have shown that during the sedimentation phase a significant denitrification rate and a part P-release takes place at a higher rate than without additional filling.

So far, the sludge volume indexes have not changed. Only long term monitoring will show any influences.

At present there are tests in preparation to minimise the NH_4-N break-through into the clear supernatant and to increase the filling load by means of hydraulic simulations of reduced filling velocities in combination with distributed filling systems.

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