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DEVELOPMENT OF A NOVEL DEAMMONIFICATION PROCESS FOR COST EFFECTIVE SEPARATE CENTRATE AND MAIN PLANT NITROGEN REMOVAL

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ABSTRACT

With an increasing need to reduce nitrogen loads from wastewater discharges, the wastewater industry is developing treatment processes that can effectively remove nitrogen with reduced chemical and energy costs. Technologies for standard deammonification are available for removing nitrogen from ammonia-rich streams produced during sludge dewatering. These processes use partial nitritation coupled with anaerobic ammonia oxidation (Anammox) to simultaneously remove ammonia and nitrite. These technologies use 34% of the air and no supplemental carbon as compared to conventional nitrogen removal processes. However, standard deammonification processes require effective suppression of Nitrite Oxidizing Bacteria (NOB) to be effective, which can require sophisticated operations. The discovery of a Glycerol Acclimated Biomass (GAB) that carries out accelerated denitratation led to the development of a novel deammonification process that produces the required nitrite via partial denitratation. The nitrite and residual ammonia is converted to nitrogen gas via anammox activity. This novel process removes up to 80% of the total nitrogen from centrate without the need for NOB suppression. The process uses 50% less energy and 75% less carbon than conventional BNR processes.

Keywords: anammox, deammonification, denitratation, nitrogen removal.

1 INTRODUCTION

Increasingly stringent nutrient discharge limits requires utilities to employ energy and chemical intensive biological nutrient removal (BNR) processes. Treatment of sidestream process flows generated from digested sludge handling processes (e.g. dewatering filtrate or centrate), has emerged as an economical complement to mainstream BNR due to the relatively low volume and high concentration of nutrients present in these flows. Dewatering sidestreams can make up 30% of nitrogen loads at some plants [1]. Sidestream treatment focuses on nutrient removal and can provide a higher factor of safety in the mainstream BNR process, as well as reduces the total nutrient loads to be treated in the mainstream process.

The work described here details the development of a novel deammonification process that may be applied for separate sidestream BNR or mainstream BNR. This process decreases theoretical oxygen and alkalinity demand requirements by up to 50%, as well as reduces supplemental carbon costs between 60%–80% versus conventional BNR processes, resulting in significantly reduced energy costs and carbon footprint of plant operations.

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1.1 Sidestream treatment

Separate centrate treatment (SCT) allows plants to treat a large portion of the nitrogen load in a separate, more easily controlled process while providing nitrifier biomass seeding and flexibility to main plant BNR operations. Conventional and emerging methods to carryout BNR in SCT systems include conventional treatment, standard deammonification, and partial denitratation/deammonification.

1.1.1 Conventional sidestream treatment

Sidestream treatment of nitrogen can be accomplished using the conventional approach of nitrification followed by denitrification. In this strategy, ammonia is oxidized to nitrite and then nitrate by aerobic ammonia oxidizing bacteria (AOB) and aerobic nitrite oxidizing bacteria (NOB) respectively. The nitrate is then denitrified to nitrogen gas via heterotrophic bacteria. This process requires 4.57 pounds of oxygen per pound of ammonia processed, 7.14 pounds of alkalinity per pound of ammonia processed and 6 pounds of supplemental carbon (COD) per pound of nitrate removed [2].

1.1.2 Standard deammonification/anammox

An alternative approach for sidestream treatment is the use of the de-ammonification process (Fig. 1). This process requires conversion of ~50% of the influent ammonia to nitrite by AOB, followed by the simultaneous removal of ammonia and nitrite by anammox bacteria. Standard deammonification requires a stable production of nitrite via suppression of NOB. Also, since anammox bacteria have very low growth rates, deammonification processes must provide sufficiently long solids retention times (SRT) for anammox bacteria growth [1].

1.1.3 Partial denitratation anammox

The development of a novel deammonification process aims to exploit existing infrastructure to reduce capital costs and operational complexity. The proposed partial denitratation/

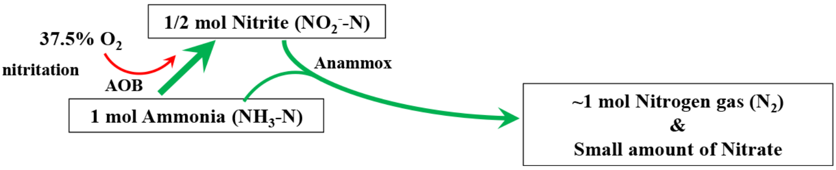

Figure 1: Overview of a standard deammonification process.

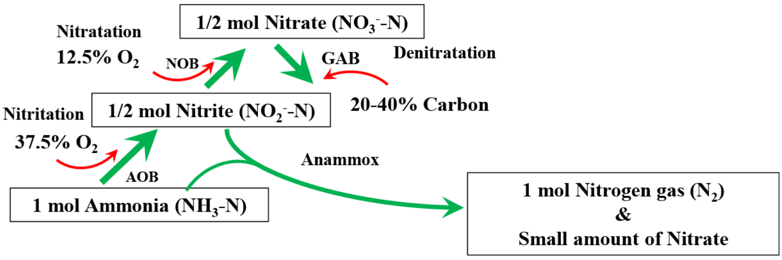

Figure 2: Overview of novel partial denitratation anammox pathway.

anammox process required that 50% of the influent ammonia in the centrate be converted to nitrite and then nitrate by AOB and NOB. This nitrate is then be subjected to denitratation ($NO_3 \rightarrow NO_2$) using glycerol Acclimated Biomass (GAB). Partial denitratation is followed by the simultaneous removal of ammonia and nitrite via anammox (Fig. 2) [3].

In this proposed deammonification process, a savings of 50% in oxygen demand and 60%–80% reduction in supplemental carbon can be achieved in comparison to existing conventional nitrification/denitrification processes. Further, this process is novel in that it does not require repression of NOB activity, which can be challenging, but instead uses glycerol to stimulate nitrite production and thereby exploits the inherent activity of the GAB to rapidly produce nitrite during the denitrification process [4]. Previous work performed by Hazen and Sawyer at the 26th Ward SCT process in New York City demonstrated that use of glycerol to drive denitrification can successfully select for and support anammox biomass by providing both nitrite and ammonia in an oxygen-free environment [5]. Research presented here demonstrates the effectiveness of this new deammonification process and identifies the important variables and parameters needed to optimize the process.

2 LABORATORY STUDIES

Sequencing batch reactor (SBR) studies were used to demonstrate the ability of this novel process to achieve high levels of TIN removal, and significant carbon and aeration savings, while avoiding the challenges associated with NOB suppression required in standard deammonification technologies.

2.1 SBR systems

The bench-scale studies used two parallel SBR systems. Each system included: (1) a 10-liter SBR glass spinner flask (Bellco Inc.); (2) a heated magnetic stir plate to mix the reactors and maintain a reactor temperature of 27°C; and (3) timers (Chrontol™) and automated pumps and valves to control the sequences shown in Fig. 3. Aerobic conditions were maintained via diffused air, and anoxic/anaerobic conditions were maintained using a CO_2/N_2 gas purge to attain a D.O. < 0.01 mg/l. Glycerol dosing was controlled by a self-timed syringe pump (New Era Pump Systems™). Control of pH in each reactor was automated via the addition of 0.2 N NaOH to maintain a pH of 7.5. Wasting of biomass was done periodically to maintain a 30-day SRT and to retain the Anammox biomass.

The SBRs were operated continuously for a period of approximately 10 months. The first three months were used to acclimate all of the different biomass populations, including AOB and NOB populations (nitrification), GAB (denitratation), and anammox biomass. A total of

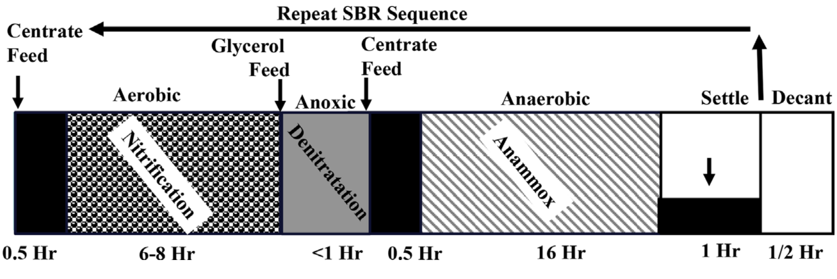

Figure 3: Denitratation-anammox SBR cycle.

3-liters of centrate was added during each cycle. For step-feed operation, the centrate was added at the beginning and middle of the SBR sequence; for plug-flow operation all centrate ammonia was added at the beginning of the sequence. Nitrogen speciation was determined at the beginning and end of each step in the sequenced process. In addition, early proof of principle testing indicated that the effective removal (>70%) of nitrogen from ammonia-rich sidestreams could be achieved within a 30-hour SBR cycle.

3 RESULTS

Once the SBR systems were fully acclimated and initial proof of concept was successful, the studies focused on evaluating four primary optimization parameters for the denitratation/anammox process, including: (1) optimization of denitratation; (2) characterization of anammox activity; (3) establishment of initial SBR cycle; and (4) optimization of SBR sequence to maximize anammox performance.

3.1 Optimizing denitratation with GAB

Simple denitrification batch tests were carried out using enriched GAB to demonstrate the nitrite lock (denitratation) and to determine the timing of the anoxic cycle prior to the second addition of centrate ammonia to drive the anammox process. Figure 4a and b show typical

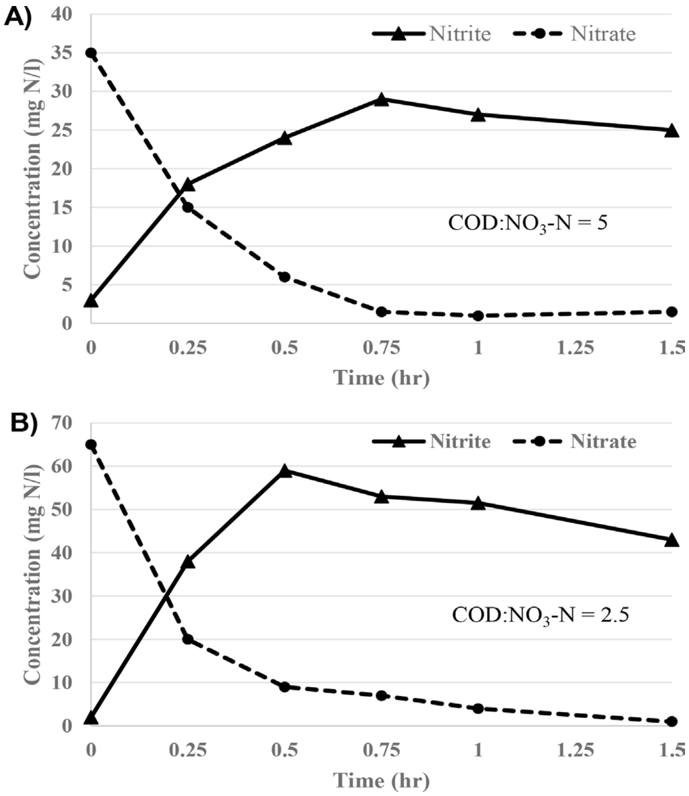

Figure 4: GAB denitratation at different COD doses.

denitrification batch test results. The results show that ~ 90% of the nitrate is converted to nitrite within the first 60 minutes of glycerol addition. The results also indicate that effective denitratation can be achieved by applying COD to a nitrogen dose that is significantly lower than the typical 6.0 mg COD to 1.0 mg NO_3-N required for full denitrification. The results in Fig. 4b show effective denitratation at a COD: N ratio of 2.5:1. Results indicated that the anoxic cycle should not exceed 60 minutes and that the glycerol dosing could be reduced by more than 50%.

3.2 Anammox characterization

The SBRs were seeded with anammox biomass that was harvested from a full-scale SCT process conducted in New York. This Anammox species was identified by researchers at Columbia University as *C. Brocadia caroliniensis* [5]. The activity of the acclimated anammox biomass was monitored by measuring ammonia and nitrite removal within the reactors during anaerobic conditions. Figure 5 shows the results from a typical anammox activity test. The results show that the anammox harvested from the SCT process had high anammox activity with simultaneous removal of ammonia and nitrite, and little to no change in background nitrate concentrations. In a pure culture of anammox biomass, a small increase in nitrate would be expected since 10%–15% of the nitrogen is converted to nitrate during the traditional anammox process [1]. However, this was not observed in these studies, likely because the biomass was not pure anammox and there was significant background denitrification taking place resulting in the uptake of residual nitrite, as well as some nitrate. The removal ratio (mg NH_3-N removed/mg NO_2-N removed) observed during the anammox testing averaged approximately 0.7, indicating that nitrite is preferentially used indicating background denitrification [6]. Figure 6 shows specific ammonia oxidation and nitrite removal rates as a function of applied ammonia dose. The anammox rates were comparable to the rates found in other anammox systems, ranging between 0.08–0.1 mg N/mg VSS-day [1].

3.3 Establishing initial SBR cycle

Once both the GAB and Anammox biomass were adequately enriched and characterized, an initial SBR cycle was established. This included timing for nitrification, denitratation, and

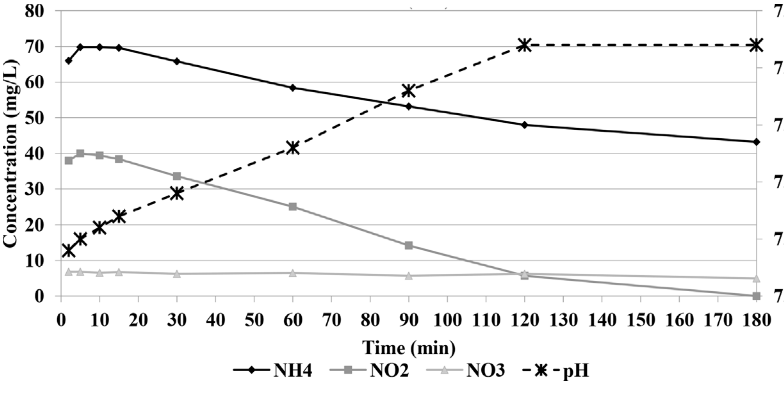

Figure 5: Anammox activity vs. applied ammonia concentration.

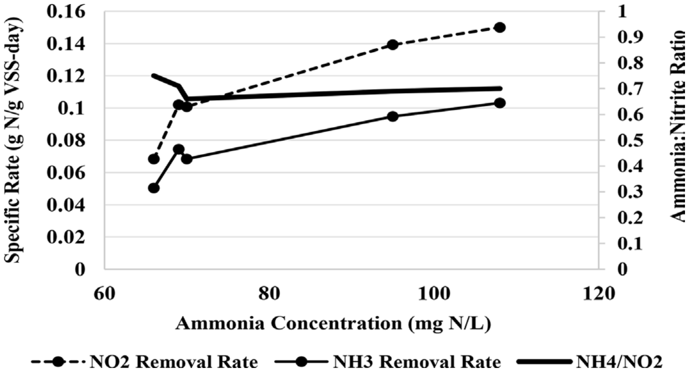

Figure 6: Specific ammonia and nitrite removal rates.

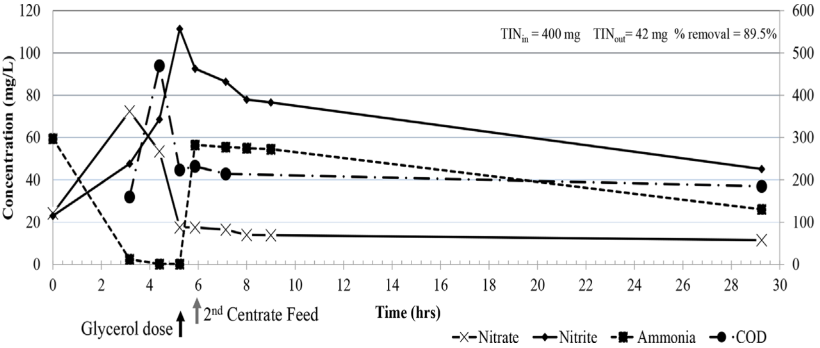

Figure 7: Nitrogen profile for denitratation/anammox step-feed SBR.

anammox sequences as well as carbon dosing to control the degree of denitratation. Initial sequence evaluation indicated that to achieve effective TN removal in the anammox sequence, ammonia levels had to be less than 200 mg/l and nitrate levels had to be less than 30 mg/l. However, higher levels of ammonia were effectively treated as the anammox biomass adapted to higher concentrations. The impact of high nitrate levels was controlled by ensuring a high degree of nitrate conversion during denitratation (proper glycerol dose) and consistent anoxic/anaerobic conditions to reduce nitrate levels. After testing numerous sequences, the initial step-feed SBR cycle shown in Figure 3 was established and served as the base cycle for process optimization. The initial cycle included an aerobic nitrification sequence of 6–8 hours, which was sufficient to fully nitrify up to 250 mg/l of centrate ammonia. The anoxic sequence was kept to less than one hour prior to the second centrate addition to minimize full denitrification, and ensure high conversion of nitrate to nitrite and maximum anammox removal. Figure 7 shows typical results obtained from the base step-feed SBR cycle. Once the initial SBR cycle was established, process optimization was carried out to evaluate the glycerol dose required to effectively carry out the partial denitratation and the impact of increased centrate ammonia loadings.

3.4 Process optimization

For the partial denitratation/deammonification optimization testing the SBRs were run with a 24- to 30-hour total cycle length consisting of six sequences shown in Figure 3. The SBR cycle was run twice prior to decant. Dilution of centrate to achieve desired ammonia levels was achieved by using un-chlorinated plant effluent. The evaluation focused on optimizing the COD:N ratio to maximize denitratation at the lowest glycerol dose and determining the best ammonia load distribution to ensure a nitrite to ammonia ratio resulting in maximum anammox removal. The testes were carried out in step-feed mode (i.e. two centrate additions) and Plug-flow mode (single initial centrate feed) to mimic those two process configurations. The plug-flow operation required controlled partial nitrification of the influent centrate load, with the residual ammonia being used in the anammox sequence after the nitrate is denitratated. The plug-flow cycle was the same as that shown in Figure 3, but without the second centrate addition.

3.4.1 Step-feed SBR optimization

Figure 8 shows typical results from a double step-feed SBR Cycle. The COD:TIN ratio is the COD added to total inorganic nitrogen (TIN) added to each cycle. In this example, Cycle 1 achieved a 73% TIN removal, while Cycle 2 achieved 79% TIN removal. In the first cycle, nitrite production limited TIN removal since there was not enough nitrite available for the

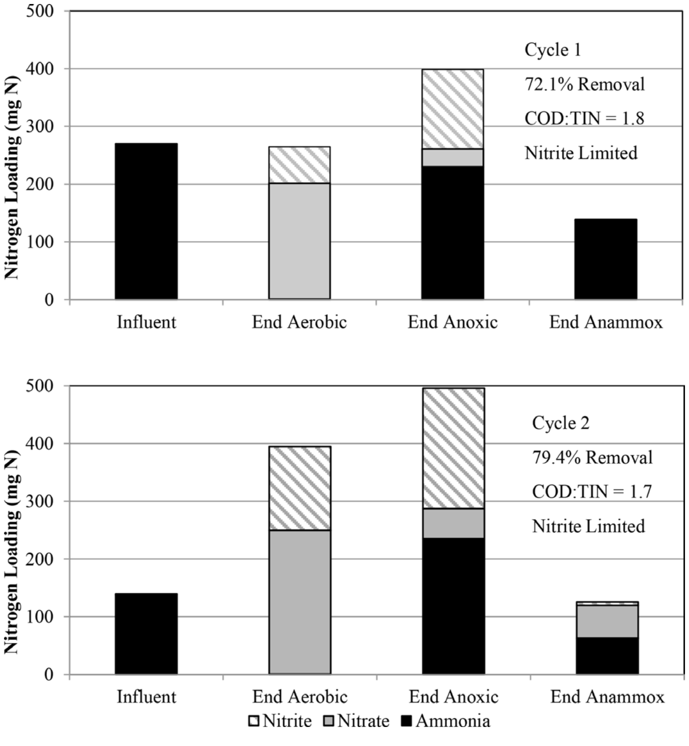

Figure 8: Results from SBR double cycle testing.

Table 1: Select double cycle SBR testing results.

NH_4 Loading	Moderate load		moderate load		High load
	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Avg. Cycle 1/2
TIN Load (mg)	470	650	499	608	950
COD:TIN	3.8	2.7	1.8	1.5	1.9
%Removal	59	80	72	79	77
%Removal	59	80	72	79	77
Limitation	Nitrite	Nitrite	Nitrite	Nitrite	Ammonia

NH_4 Loading	High load		High load		High load	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 1	Cycle 2
TIN Load (mg)	685	931	742	865	1,036	1,400
COD:TIN	1.3	1.0	1.6	2.3	1.2	1.4
%Removal	47	46	68	65	54	46
Limitation	Carbon	Carbon	Nitrite	Time	Carbon/Time	

anammox process to remove more ammonia; thus, a large amount of residual ammonia was present at the end of the anammox phase. In the second cycle, nitrite was less limiting, but there was still excess ammonia indicating that some additional removal was available. Table 1 shows results from a number of double cycle tests indicating the of percent TN removal and the process that limited greater levels of removal (i.e. nitrite production due to inadequate nitrification, excess ammonia, or inadequate COD addition).

As seen in Table 1, typically the higher the total ammonia load the lower the removal rate. For step-feed tests where nitrite was limiting, there was not enough ammonia added in the initial centrate feed to produce an adequate amount of nitrite to remove the ammonia added in the second centrate feed. For tests where carbon was limiting, there was excess nitrate after the denitratation step indicating that there was not enough carbon added to completely convert all nitrate to nitrite via denitratation. Finally, for cycles where time was limiting, the ammonia loads in the second centrate feed exceeded the time allowed for anammox to remove the ammonia, and excess nitrite and ammonia were present at the end of the anammox sequence. Assuming complete nitrification of the initial centrate ammonia load, the degree of anammox removal is strongly dependent upon the distribution of ammonia load in the step-feed cycle and the degree of denitratation (i.e. COD:N ration). If the ammonia is distributed adequately, a COD:N dose less than 2.5 can consistently achieve TN removals greater than 80%.

3.4.2 Plug-flow SBR cycle optimization

To overcome the need for a second centrate addition (i.e. step-feed) and avoid inadequate nitrite production. A series of ‘Plug-flow’ SBR tests were carried out with the full centrate ammonia load added at the begining of the cycle, which relied upon partial nitrification to produce nitrate for the denitratation process. The residual ammonia (un-nitrified centrate ammonia) was allowed to enter the anammox phase where it was oxidized along with the produced nitrite. The sequence for these tests was similar to Figure 3, but with all centrate ammonia load added in the initial feed only. Figure 9 shows results from two plug-flow SBR cycles run in series.

As the application of glycerol continued, the biomass in the system acclimated to high levels of nitrite and ammonia resulting in the selection of AOBs over NOBs resulting in nitrite production over nitrate during the nitrification process. This explains the high levels of nitrite produced at the end of the aerobic sequence. This allowed for even lower doses of glycerol to be added to convert lower levels of nitrate to nitrite in the anoxic sequence. With significant nitrite produced in the nitrification step, approximately 30% of the TIN removal was attributed to short-circuit denitrification ($NO_2 \rightarrow N_2$) while the other 70% was attributed to anammox activity. The results from the double cycle partial nitrification SBR tests indicate that for optimal efficiency of anammox removal, the glycerol (COD) dose needs to be a function of the NOx concentration attained at the end of the nitrification sequence. This would be a key operational parameter. If COD is overdosed, then there is a waste of chemical and poor removal of ammonia by anammox since much of the nitrite produced by the AOBs and GAB would be denitrified by the excess carbon instead of being used in the anammox process. Both underdosing and overdosing of COD leaves excess ammonia at the end of the cycle. If the glycerol is underdosed there is not enough nitrite produced by the GAB biomass to effectively remove ammonia in the anammox process. These results indicate that the ideal $COD{:}NO_x$ dose is approximately 2.5 and will depend upon temperature, solids inventory, and

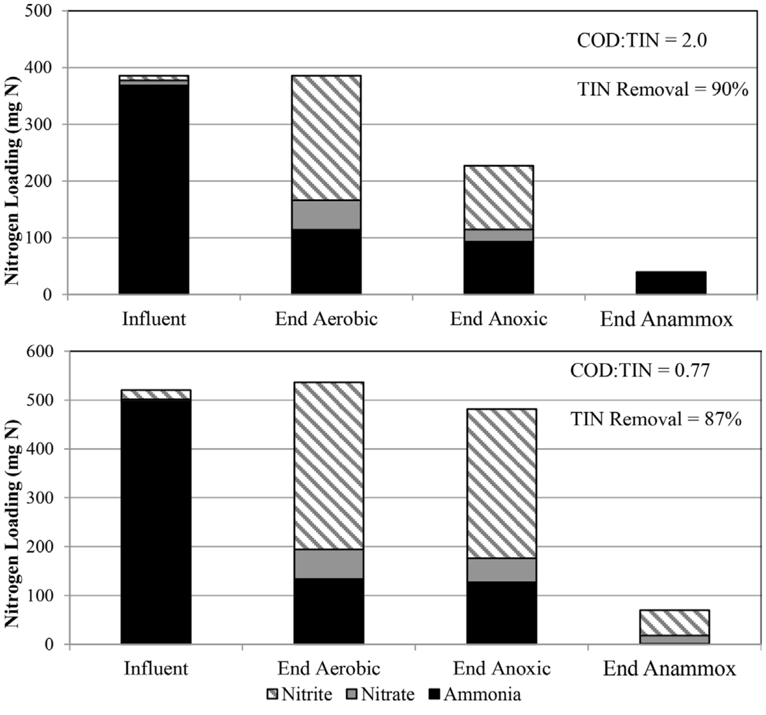

Figure 9: Partial nitrification SBR cycler performance.

degree of GAB acclimation. This represented a 75%–80% reduction in glycerol requirement compared to the traditional BNR process. After long-term acclimation to glycerol and high nitrite levels, the ratio of total COD added to total TIN added to the system could be as low 1.5 to 2.0. In addition, due to other losses (i.e. biological uptake and background denitrification and SND) it is ideal to nitrify excess ammonia in the nitrification cycle to ensure that excess nitrite is produced and that the effluent nitrogen is primarily nitrite, which can be removed later via denitrification.

4 SUMMARY AND ADDITIONAL STUDIES

The results obtained from the anammox proof-of-principle bench-scale studies demonstrate that the new denitratation/deammonification process using newly discovered anammox biomass can achieve consistent TN removals of up to 80% with proper carbon dosing and effective pH and dissolved oxygen control. The process proved to be quite robust and completely independent of NOB suppression, which is a major benefit of the process. The process requires approximately 50% of the air and 25% of the supplemental carbon required for traditional BNR processes. As the process acclimated to higher nitrite levels due to partial nitritation and denitratation, the amount of glycerol needed was significantly reduced and a larger portion of the TIN was removed via shortcut denitrification.

Based on the proof of principle results presented here, a pilot test of the partial denitratation/anammox process was carried out at 26th Ward WWTP in New York [3]. Results from the lab study and the pilot suggest that this process has great promise under certain applications and warrants further piloting and full-scale demonstration. Additional studies using primary effluent in lieu of centrate demonstrated that this process may have applications for main stream deammonification, relying on about 50%–60% TIN removal from anammox and 40%–50% removal through short-cut and traditional denitrification [7].

A proposed schematic of a full-scale installation of this new process at a typical aeration tank (SCT OR main plant) is shown in Figure 10**.** For a full-scale application, enhanced retention of the anammox bacteria would be achieved through use of hydrocyclones, inclined plate settlers, or fixed film media. The retained anammox bacteria would be recycled within the

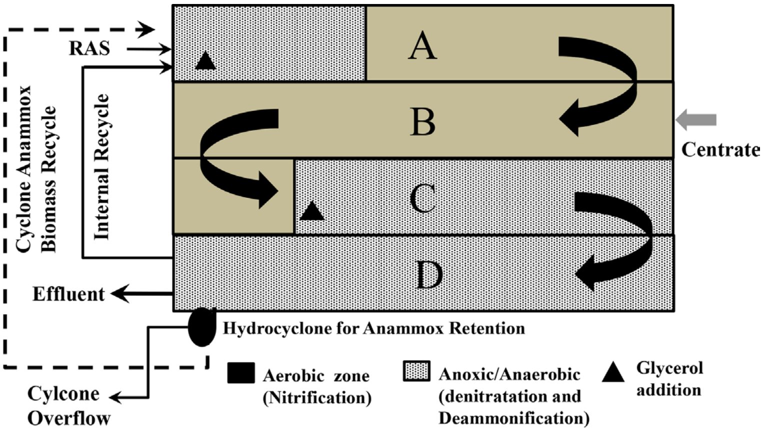

Figure 10: Proposed application of novel denitratation/deammonification process in SCT or main plant BNR.

process, while the discharged solids, containing mostly AOB and NOB, would be used to bioaugment the mainstream process nitrification performance. Attempts could be made to bioagument the mainstream process with the anammox bacteria to stimulate mainstream deammonification, which would yield further energy and cost savings. This system would not be limited by NOB suppression or high centrate solids and would likely be able to handle variable centrate flows and quality in much the same way as conventional SCT BNR processes currently operate. Additional large-scale pilot testing and full-scale demonstration are needed to gain a better understanding of the process controls, operational conditions and limitations, and potential for implementation as a main-stream BNR process are needed.

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