ANAMMOX: A SUSTAINABLE PROCESS TO REMOVE NITROGEN FROM REJECT WATER GENERATED BY ANAEROBIC DIGESTION PROCESSES

K. RAMALINGAM¹, J.FILLOS¹, M.MEHRDAD¹, ISAIAH SHAPIRO¹, A.DEUR², AND K.BECKMANN²

1. The City College of New York, 160 Convent Avenue, NY, NY 10031
2. New York City Environmental Protection, 59-17, Junction Blvd., Flushing, NY11373
e-mail: KRamalingam@ccny.cuny.edu

EXTENDED ABSTRACT

The City College of New York (CCNY) in collaboration with New York City Environmental Protection (NYCEP) is currently engaged in operating a 1700 gallon pilot single stage partial nitritation/anaerobic ammonium oxidation (anammox) moving bed biofilm reactor (MBBR) at the 26th Ward waste water treatment plant (WWTP) in Brooklyn, NY. The MBBR is designed to remove nitrogen from the anaerobic digester reject water (centrate) emanating from the dewatering facility at the 26th Ward WWTP. This study was initiated as a result of earlier extensive bench-scale studies conducted by CCNY over a 2-year period, where the process proved effective in treating centrate generated at the Wards Island WWTP. The current pilot study of Anammox using a MBBR is the first of its kind in the United States.

The Anammox process is an anaerobic autotrophic biological process that can be used to remove nitrogen from centrate. The process has been used at several treatment plants in Europe where it demonstrated its effectiveness to remove nitrogen at a much lower cost than conventional nitrification/denitrification processes. The anammox process has the potential of being the most sustainable treatment process for centrate because of its reduced energy needs, elimination of any organic carbon source, and acting as a sink for carbon dioxide, one of the documented greenhouse gases.

The objective of the study was to provide further kinetic and operating data, test alternate loading rates, and provide guidance to the City and its consultants to eventually design a full-scale anammox process to treat centrate.

Startup of the pilot began in March 2011 with seeding from the activated sludge process only since an important objective was to develop “homegrown” anammox bacteria with real centrate and subject to all the variations in strength that the WWTP experiences. The startup challenges and the modes of operation implemented will be discussed in this paper that enabled enrichment of the biofilm with noticeable anammox activity observed by August 2011. Nitritation of the centrate is limited by the available alkalinity based on stoichiometry. An achievable target was then estimated to be in the range of 60 to 70% nitrogen removal at the operating temperature of 32-34°C without any chemical additions. With the addition of alkalinity, the performance of the pilot reactor reached between 80 and 85% further reinforcing the fact that sufficient alkalinity will enhance removal. The operational and maintenance challenges and the various phases of operation will be discussed.

Keywords: Anammox, nitritation, MBBR

1. INTRODUCTION

New York City Environmental Protection (NYCEP) owns and operates 14 wastewater treatment plants (WWTPs), some of which practice BNR or are in the process of being upgraded to achieve BNR. Although anaerobic digestion is practiced at all 14 WWTPs, dewatering is conducted at 8 centralized facilities. Reject water from centrifuges, or centrate, generated in these facilities can contribute up to 40% of a centralized facility’s
total nitrogen load. Assessment of BNR treatment alternatives has indicated that separate side stream treatment of centrate is a cost-effective alternative for several of the WWTPs.

To comply with the upcoming total maximum daily loads (TMDLs) for nitrogen imposed for the Jamaica Bay and Long Island Sound, NYCEP has been actively pursuing different nitrogen removal technologies under their nitrogen control action plan. Five of the fourteen plants are being upgraded to biological nitrogen removal (BNR) with the provision of treating centrate separately. In three of the plants traditional nitrification/denitrification is being practiced while one plant has the SHARON process installed. All these facilities require an external carbon source, methanol or glycerol, sodium hydroxide for alkalinity, and significant energy demand for aeration resulting in high operating costs.

The City College of New York (CCNY) in collaboration with NYCEP is currently engaged in operating a 1700 gallon, (6.4m\(^3\)), pilot single stage partial nitritation/an aerobic ammonium oxidation (anammox) moving bed biofilm reactor (MBBR) at the 26th Ward waste water treatment plant (WWTP) in Brooklyn, NY. The MBBR is designed to remove nitrogen from the anaerobic digester reject water, (centrate), emanating from the centralized dewatering facility at the 26\(^{th}\) Ward WWTP. This study was initiated as a result of earlier extensive bench-scale studies conducted by CCNY over a 2-year period, where the process proved effective in treating centrate generated at the Wards Island WWTP. The ongoing pilot study of a single stage MBBR nitrogen removal using anammox was the first of its kind in the United States.

Anaerobic ammonium oxidation (anammox) is a recently discovered microbiological process that converts ammonia (NH\(_3\)) and nitrite (NO\(_2^-\)) directly to nitrogen gas (N\(_2\)) (van de Graaf 1990). The responsible microorganisms, collectively referred to as “anammox bacteria”, belong to the genera *Brocadia*, *Kuenenia*, and *Scalindua* within the planctomycetes phylum (Jetten 2005). These bacteria possess a specialized intracellular compartment called the anammoxosome which is the site of anammox metabolism (van Niftrik 2004), and exhibited a stoichiometry described by Equation 1-1 when grown in synthetic media (Strous 1998).

\[
\begin{align*}
1 \text{NH}_4^+ + 1.32 \text{NO}_2^- + 0.66 \text{HCO}_3^- + 0.13 \text{H}^+ & \rightarrow \\
1.02 \text{N}_2 + 0.26 \text{NO}_3^- + 0.66 \text{CH}_2\text{O}_{0.5}\text{N}_{0.15} + 2.03 \text{H}_2\text{O} 
\end{align*}
\] (1-1)

Anammox bacteria tend to grow in biofilms either on abiotic surfaces or as compact suspended aggregates in the form of granules. Granule and biofilm formation allows for highly efficient biomass retention, which is necessary for the enrichment of slow growing microorganisms such as anammox bacteria. An additional phenomenon observed in anammox biomass is its tendency to grow deep within multispecies biofilms and granules that may include ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). The above stated characteristics, therefore, must be considered in the selection and design of an appropriate configuration of an anammox process. In the single-stage process, which is the subject of this paper, partial nitritation and anammox are performed in a single reactor. Nitritation activity and anammox activity are still separated spatially by their arrangement within biofilms as shown in Figure 1 and among the suspended solids. AOB thrive on the aerobic surface of the biofilm, a single-stage MBBR, consume oxygen, alkalinity, and nitrify ammonia to nitrite. The thickness of the surface aerobic layer depends on the penetration of oxygen through the biofilm which is limited by diffusion rate and the oxygen demand of the AOB. Below the aerobic layer, dissolved oxygen concentration reduces to zero and thus the deeper layers of the biofilm become anoxic. In the anoxic zone anammox bacteria convert the nitrite produced by the AOB and the ammonia still available to nitrogen gas with a portion of the nitrite oxidized to nitrate during synthesis.
This paper will detail the startup and optimization experiences at the pilot under different operating strategies such as removal with and without external alkalinity addition. Extensive molecular work was also carried out during this study. Two separate papers presented recently at the “9th International Conference on Biofilm Reactors”, May 28-31 2013, Paris, France, discussed the results of the speciation of the AOB and anammox bacteria in the biofilms grown on carriers in the MBBR and micro profiling of nitrite within granules suspended in a sequencing batch reactor.

2. PILOT FACILITY OF THE SINGLE STAGE NITRITATION/ANAMMox MBBR

The MBBR pilot facility was located at the 26th Ward WWTP in Brooklyn, NY. The 26th Ward WWTP has a designed capacity of 85 MGD (3.2x10^5 m^3/d) and is a centralized dewatering facility which accepts additional anaerobically digested sludge from the Coney Island, the Jamaica, and from other WWTPs as needed. Figure 2, shows a simplified flow diagram of sludge dewatering as practiced at the 26th Ward WWTP. The digested sludge is dewatered by centrifuges, producing a sludge “cake”, and a liquid stream, centrate, which is directed to a Centrate Wet Well where ferric chloride and dilution water are added to prevent the formation of struvite in downstream reactors. From the wet well the centrate is pumped to Aeration Tank 3 for nitrogen removal by conventional nitrification/denitrification. A small portion of this same centrate is diverted to the anammox MBBR pilot facility. The centrate pumped is characterized by high concentrations of SS, ammonia nitrogen, alkalinity, and a relatively low concentration of biodegradable COD. Operating experiences have shown periodic spikes in concentration of all parameters cited in response to changes in the quality of the digested sludge being dewatered and to the performance of the centrifuges.
Objectives of the study included startup of the pilot MBBR without anammox bacteria seeding, collect additional process kinetic and operating data, evaluate the potential savings of a single stage MBBR compared to the alternate methods, assess the effect of loading rates on process performance, and provide guidance for design and startup of a full scale facility.

2.1 Pilot Anammox MBBR Process Flow Diagram

Figure 3 depicts the flow schematic of the MBBR pilot facility. The facility includes a lamella clarifier, three storage tanks with volumes of 850 gal (3.2 m³), 2000 gal (7.6 m³), and 1000 gal (3.8 m³), respectively, a 1000 gal (3.8 m³) feed tank, and the main MBBR, which was operated at a capacity of 1100 gallons, (initially), and then at an increased capacity of 1700 gallons, (6.4 m³) at a later stage. Several centrifugal and submersible pumps are used to convey centrate from the lamella clarifier through the series of storage tanks and the heated feed tank to the MBBR. The pumps are operated either manually or with pre-set timers. The lamella clarifier captures suspended solids in the feed, especially during excursions from the average, and reduces their concentration by approximately 80 - 85%.

On-line instrumentation controls aeration and monitors the following process parameters: temperature within the centrate wet well, Lamella influent, feed tank, and MBBR; total suspended solids in the Lamella influent; and pH, concentrations of DO and nitrite–nitrogen, and airflow rate to the MBBR. A programmable logic controller enables different aeration schemes of the MBBR, based on a selected DO concentration, an intermittent aeration cycle, or a combination of both approaches.
Flow from the storage tanks is first pumped into the feed tank where electric heaters adjust the temperature of the centrate in order to maintain the optimum range of 32°C to 34°C in the downstream MBBR. From the feed tank, flow is pumped by means of a peristaltic pump to the 1700-gal MBBR, which holds the Kaldnes K1® carriers occupying approximately 33% of the reactor volume. The media provide a surface area of 500 m²/m³ for biofilm growth. The MBBR reactor is equipped with a variable-speed mixer specifically sized to move the media continuously within the reactor. An air compressor supplies air to the MBBR through a set of four fine-bubble membrane diffusers. Effluent from the MBBR flows into a plant drain and thus is returned to the head of the main treatment plant.

3. RESULTS and DISCUSSION

3.1 Startup of the Pilot MBBR

Startup of the pilot MBBR began in March 2011. One of the mandates imposed by NYCEP was to not seed the reactor with anammox bacteria. Hence, only activated sludge solids from the WWTP were added to the MBBR and thus the anammox bacteria that eventually grew on the carriers was termed “homegrown” and reflected the actual centrate with all the variability in strength and composition that would be experienced in a full scale side stream treatment facility. The focus on the discussion here will be on the following:

- Startup challenges and the modes of operation attempted that enabled enrichment of the biofilm with AOB and anammox bacteria by August 2011.
- The process optimization phase where the nitrogen removal target was 60 to 70% removal which was limited by the available alkalinity in the centrate and operating at the optimal temperature of 32-34°C.
- Improved nitrogen removal to 80-90% removal by supplementing the alkalinity available with addition of sodium hydroxide.

In March 2011, because the centrate fed to the MBBR was diluted inadvertently with washwater at the centrifuges, it had ammonia concentrations in the range of 200 mg/L, much lower than the average concentration of 400 mg/L which was advantageous since there was no need to further dilute the centrate to control nitrite buildup during startup. This initial phase of operation was targeted toward promoting the growth of AOB and biofilm thickness on the carriers. During this period, aeration was cycled between continuous and intermittent phases to maximize the nitrification of ammonia and achieve a nitrite concentration of 50 to 70 mg/L in the bulk phase. Sufficient growth of biofilm and the start of anammox activity became evident by August 2011. Figure 4 shows performance data during the startup period with fairly consistent concentration of nitrite within the period of mid-May to mid-July and negligible amount of nitrate being produced.

Once nitrification was established operating conditions remained essentially the same other than slight modifications to regulate the concentration of nitrite. A gradual reduction of nitrite is evident from a high of approximately 100 mg/L to 65 mg/L in July and then to less than 25 mg/L by the beginning of August, 2011. Figure 4 also shows that the concentration of nitrate in the MBBR effluent began to increase and plateau to a constant value suggesting possible anammox bacteria growth activity. This is further reinforced in Figure 5 where the influent and effluent TIN start diverging towards the end of July 2011 confirming nitrogen removal. Concurrent to these observations, visible red nodules appeared on the K1 Kaldnes® carriers also shown in Figure 6.
The nitrogen removal performance of the single stage MBBR pilot ideally depends on the growth of AOB on the surface of the film providing NO\textsubscript{2}-N to the anammox bacteria residing deep within the biofilm. The NO\textsubscript{2}-N and the remaining NH\textsubscript{3}-N penetrate the biofilm and provide the necessary substrate in an anoxic environment for the anammox bacteria. The strategy selected to stimulate growth of the anammox bacteria and improved nitrogen removal performance included:

- Maintain continuous operation of the pilot with emphasis on conditions that promote biofilm buildup, i.e., sustain low mixing/turbulence within the reactor
- Maintain the optimum temperature range of 32\textdegree to 34 \textdegree C
- Control nitritation activity by varying the DO concentration and/or the ratio of oxic/anoxic periods to maintain the NO\textsubscript{2}-N concentration below 50 mg/L; it has been reported that higher nitrite concentrations may be inhibitory

### 3.2 Optimization Phase Without Supplemental Alkalinity Addition

Once anammox activity became evident during startup, aeration was switched to a continuous mode in order to increase the nitritation rate to support the apparent higher anammox activity. However, though the enhanced nitritation increased ammonia removal, 70 to 75\%, TIN removal still averaged between 50 and 60\%, thus eluding the target objective of up to 70\%.
Figure 7, shows the DO concentration in the anammox MBBR pilot from October 2011 through December 2012. During this period the anammox MBBR pilot was operated under various conditions with respect to DO and HRT in order to target a maximum nitrogen removal efficiency of 70% while maintaining the percent of nitrate produced at or below the stoichiometric value of 11%. Eight different strategy periods with respect to DO were attempted as indicated on Figure 7 with letters A through H. These strategies, listed in Table 1, include assessing the process under complete oxic conditions or oscillating between oxic and anoxic conditions. The ratio of oxic to anoxic intervals was varied as well as the cycle length. Additionally, different maximum and minimum DO concentrations were investigated for each period. During these periods, the aeration control varied between the three control schemes cited, (DO, Time, and Time/DO), to achieve the desired DO concentration. For all periods the primary effort was to balance the activities of the AOB, NOB and anammox bacteria for maximum performance. For the period of October 2011 through March 2012, the target removal of 70% was met only sporadically as shown in Figure 8. The primary cause appeared to be the inability to control NOB activity while maximizing nitritation by the AOB. The increasing nitrate concentration above the theoretical 11% was an important factor that kept nitrogen removal below the target of 70%.

Available literature on the anammox process recommend lowering the DO concentration or introducing anoxic periods in the operation (Jardin and Hennerkes 2012, Yang 2011) to suppress the NOB growth. Hence, the operation was switched to the aerobic/anoxic mode in March 2012. The expectation was that the percent nitrate would decrease with diminished NOB activity and consequently improve total nitrogen removal. The target removal of 70% still proved to be elusive as AOB activity was impaired as shown in Figure 9 due to the long anoxic periods although the DO concentration was between 2-3 mg/L during the oxic period. In addition NOB activity persisted resulting in deterioration of process performance. Furthermore, ex-situ batch tests under anoxic conditions (data not shown here) conducted during this period with non-limiting nitrite indicated that the anammox activity in the main reactor was primarily limited due to the scavenging of the nitrite by the NOB as evidenced by the increase in nitrate concentration in the reactor shown in Figure 8 during this period.

Figure 9 shows that during the initial continuous aeration period when DO was maintained between 0.8 -1.0 mg/L, the nitrate production increased beyond the expected stoichiometric level of 11% indicating NOB activity. This process is essentially a balancing act wherein the dual populations of AOB and anammox have to be nurtured and the NOB have to be suppressed. This was one of the vexing operating challenges faced during this phase of operation through the beginning of March 2012. To overcome this stagnant level of operation, the operation was re-assessed. One of the observations was a very thin biofilm on the carrier media. It was thus decided to increase the volume of the reactor from 1100 to 1700 gallons (4.2 to 6.4 m$^3$) which resulted in an increase in water depth from 6 to 10 ft, (3m) but with the same volume of carriers, now at 30% of the volume. This modification led to reduced turbulence due to aeration and increased nitrogen load per unit area and consequently a thicker biofilm. The aeration regime during this next phase was continuous with the DO concentration set at approximately 2 mg/L. The nitritation rate increased but the overall nitrogen removal still stayed lower than expected due to the persistence of NOB activity.
Figure 7: DO concentration in the anammox MBBR pilot.

**Table 1**: Operating strategies during nitrogen removal at optimum temperature phase.

<table>
<thead>
<tr>
<th>Period</th>
<th>Aeration Strategy</th>
<th>Target Max DO</th>
<th>Target Min DO</th>
<th>Tested HRT(s)</th>
<th>Water Depth</th>
<th>Fill</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Oxic</td>
<td>1</td>
<td>0.5</td>
<td>0.8, 0.9, 1.2, 1.5</td>
<td>6.5</td>
<td>50</td>
</tr>
<tr>
<td>B</td>
<td>Oxic</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>6.5</td>
<td>50</td>
</tr>
<tr>
<td>C</td>
<td>Oxic/Anoxic</td>
<td>2 to 3</td>
<td>0</td>
<td>1, 1.3</td>
<td>6.5</td>
<td>50</td>
</tr>
<tr>
<td>D</td>
<td>Oxic/Anoxic</td>
<td>1 to 2</td>
<td>0</td>
<td>1.3, 1.5, 2</td>
<td>6.5</td>
<td>50</td>
</tr>
<tr>
<td>E</td>
<td>Oxic/Anoxic</td>
<td>1 to 2</td>
<td>0</td>
<td>1, 1.5</td>
<td>10.5</td>
<td>30</td>
</tr>
<tr>
<td>F</td>
<td>Oxic</td>
<td>4</td>
<td>3</td>
<td>0.5</td>
<td>10.5</td>
<td>30</td>
</tr>
<tr>
<td>G</td>
<td>Oxic</td>
<td>4</td>
<td>2</td>
<td>0.7</td>
<td>10.5</td>
<td>30</td>
</tr>
<tr>
<td>H</td>
<td>Oxic</td>
<td>3</td>
<td>1</td>
<td>0.5, 0.7, 1.0</td>
<td>10.5</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 8: Total Nitrogen Removal (TIN) efficiency and percent produced Nitrate in MBBR pilot. The dashed lines show the 70% objective TIN removal and 11% theoretical value of nitrate produced.
At this juncture, in July 2012, it was decided to switch to an aggressive mode of operation and the HRT was reduced from 1.5 to 0.5 days. The higher loading rate resulted in an almost exponential growth of the solids on the carriers as shown in Figure 10 and coincided with a step up in nitrogen removal and reduction in reactor nitrate concentration as shown in Figure 8. Once this level of operation was achieved, the HRT was re-adjusted to 1 day to optimize removal. The operating data starting September 2012 shows that the average removal improved to reach 60 and 70% more often.

However, the performance showed significant variability because of incoming centrate quality, excessive polymer dosages and process disruption due to super storm Sandy in October 2012. The process recovered and the removal since then has been consistently around 65-70% again limited by the available alkalinity in the centrate.

3.3 Optimization Phase with Alkalinity Addition

In order to overcome the limitation due to the available alkalinity, addition of sodium hydroxide, at 50% strength by weight was initiated on January 15, 2013. The additional alkalinity would allow for further nitritation of the ammonia and thus greater removal of nitrogen by the anammox bacteria. The rate of addition of the sodium hydroxide was controlled by the pH in the MBBR, namely, by maintaining the preselected upper and lower set points of 7.3 and 7.4. The additional controls instituted were the following two interlocks that were built into the PLC:

- For safety, shut-off the sodium hydroxide, caustic, pump after 30 minutes of continuous operation
• To limit excess aeration, shut-off the compressor when the ammonia concentration dropped below 20 mg/L.

Thus, the first interlock was to safeguard the process against inadvertent excess caustic addition and the second one was to prevent unnecessary aeration when ammonia is low that can lead to higher DO concentrations and possible stimulation of NOB activity.

Figure 11 shows a plot of the pH before and after alkalinity addition. Since alkalinity addition was initiated, the pH was held within the range of 7.3 and 7.4 and for the period shown the average caustic consumption was 0.69 gpd, (2.6 L / day). Aeration mode was continuous. The average nitrogen removal performance for the period with alkalinity addition was greater than 72% and once the feed quality improved, the removal average was above 80% as shown in Figure 12 for the period from January 15 thru March 15. During this period, there were process upsets such as high polymer in the incoming centrate or spikes of COD which were detrimental to the process as seen by the sharp drop in performance. The data also shows that the process bounces back to high performance levels without any lag time as soon as the disturbances ceased.

![Figure 11: pH values before and after alkalinity addition](image-url)
4. CONCLUSIONS
A single stage nitritation/anammox MBBR seeded with only activated sludge solids from a step feed BNR plant and fed centrate developed its own “homegrown” anammox bacteria in approximately 150 days. Process optimization efforts that involved both control of DO concentration, nitrogen loading rates, and biofilm thickness achieved a nitrogen removal within the range of 60 to 70% without any alkalinity addition. When alkalinity addition was introduced, the nitrogen removal rates increased to as high as 90% with an average value for that period being between 70 and 80%. This clearly demonstrated that nitrogen removal was limited initially to a large part by the limited alkalinity available in the centrate. Limiting NOB activity involves a balancing act of DO concentration, oxic/anoxic periods, and biofilm thickness, and the characteristics of the centrate being treated. Unfortunately no specific values of any of the above parameters were identified that would guarantee enrichment of AOB and anammox bacteria at the absolute exclusion of NOB activity.

REFERENCES