Use of Anammox in urban wastewater treatment

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Abstract  Nitrogen removal is the most complicating factor in urban wastewater treatment. Nitrification accounts for more than 50% of the oxygen need and requires long sludge ages. Denitrification is often hampered by a lack of COD. In fact it would be better to use this COD to generate methane. Recent research has shown that it is possible to remove ammonium by anaerobic ammonium oxidation leading to a much reduced need for aeration energy, no need for COD in the N-removal, and a considerable lower sludge production. The state of the art and the potential role in urban wastewater treatment are discussed.

Keywords  Anammox; nitrification; nitrite; wastewater

Introduction

Wastewater treatment is aimed at improving the general health conditions of the human population and minimising the impact of, or better integrating, the human society on the natural environment. In view of the last point removal of nutrients in the form of nitrogen and phosphorus is becoming more and more standard practice world-wide. Especially for Nitrogen removal many different methods exist and despite several decades of academic research still strong improvements are being made. These improvements focus on process engineering or microbiological aspects. At the process engineering side the development is towards more compact reactors based on biofilms, granular sludge or membrane separation. At the microbiological side it is based on minimising energy and chemicals need by applying ecophysiological approaches or discovery of new micro-organisms. One of the recently discovered conversion processes is the anaerobic ammonium oxidation (Anammox) process (Mulder 1992). This paper gives an overview of the state of art of this microbial conversion process and discusses the potential role in the treatment of urban wastewater.

Nitrogen conversion processes

Conventional N-conversions

For almost a century the nitrogen cycle was indeed seen as a cyclic process (Figure 1a). Since the discovery by Winogradski of ammonium and nitrite oxidising bacteria the nitrogen cycle was described in three phases: nitrification (oxidation of ammonium to nitrite or nitrate), denitrification (reduction of oxidised nitrogen species to nitrogen gas) and ammonium fixation (conversion of nitrogen gas by specialised bacteria into ammonium or organic nitrogen compounds). Especially the first two processes are used in sewage treatment plants.

Nitrification is performed by a small group of bacteria. These aerobic bacteria grow normally autotrophic. From a process engineering point, it is important that oxygen is supplied, and the aeration need for nitrification is over 50% of the total aeration costs.
nitrifying bacteria grow autotrophically and have therefore a low growth yield and as a result also a low growth rate. This implies that activated sludge usually consists of only a few percent of nitrifying bacteria, while the process has to be designed on the volumetric activity of the nitrifying bacteria. This results in extended processes requiring high amounts of energy and space. Improvements are found in better biomass separation techniques (e.g. in biofilm reactors, granular sludge processes or application of membranes) in order to obtain smaller reactor volumes. Also separation of heterotrophic and nitrifying sludge (two sludge or hybrid reactors) can contribute in decreasing reactor volumes (van Benthum et al., 1998, Muller, 1998). A second improvement is sought in preventing full oxidation to nitrate, and using nitrite as the intermediate for full nitrogen removal. This saves energy and needs less COD for full N-removal.

Partial oxidation to nitrite is feasible, certainly because two bacteria are involved in the ammonium oxidation process (ammonium–nitrite and nitrite–nitrate conversion). The only precaution one has to take is to ensure that the ammonium-oxidising bacteria get preference over nitrite oxidising bacteria. At elevated temperatures (> approx. 20°C) the second organism grows slower than the first, making it possible to design a process with a solids retention time in between the minimal retention time of the two organisms (Hellinga et al., 1999). At lower temperatures it is however impossible to prevent the presence of nitrite oxidisers with this method since they have a higher growth rate than ammonium oxidisers.

Attempts to prevent nitrite oxidation by imposing inhibiting conditions (e.g. pH, or NO₂⁻ level) are often successful on a short term basis, however in long term experiments adaptation often occur leading to formation of nitrate as intermediate (Alleman and Irvine, 1984, Verstraete et al., 1977). Nitrite oxidisers generally have a lower affinity for oxygen than ammonium oxidisers (Wiesmann, 1994). This lower affinity is not sufficient to fully eliminate the nitrite oxidation at low oxygen concentrations. However it has been shown that if denitrification is directly coupled to nitrification at low DO, an efficient out-competing of nitrite oxidation can be obtained (van Benthum et al., 1998). This either needs a high recirculation of the wastewater between aerobic and anoxic reactor zones or aerobic and anoxic zones in biofilms or granular sludge. The problem of the last option is that organic substrate needs to be present in the anoxic part of the biofilm, while it is preferentially oxidised over ammonium.

**Innovative N-conversions**

In the past decade the picture of the conventional N-cycle has significantly changed (Figure 1b). Two processes have been described that are more or less short cuts in this cycle. This is the denitrification by autotrophic nitrifiers and the anaerobic ammonium oxidation process. In the first process the regular ammonium oxidising bacteria are involved. Under
severe oxygen limitation, bacteria are able to oxidise ammonium to hydroxyl-amine. The
formed hydroxyl-amine is combined with ammonium to yield dinitrogen-oxide which is
released to the environment (Bock et al., 1995, Siegrist et al., 1998). Although ammonium
is removed without the use of an organic carbon source and with a low oxygen requirement,
this conversion is from an environmental point of view not desirable because of the release
of the dinitrogen oxide as a strong greenhouse gas.

Anaerobic ammonium oxidation (Anammox) is a process in which ammonium and nitrite
are combined to yield nitrogen gas (Jetten et al., 2001). This process could superficially be
seen as regular denitrification with ammonium as electron donor, however there is a large
biochemical difference. In normal heterotrophic denitrification the catabolism is rather sim-
ilar to aerobic respiration with oxygen. Substrate is oxidised in the cell, with NADH or
FADH as electron donors. These electron carries are subsequently converted at the cell
membrane to NAD+ or FAD+ while the electrons are transferred to oxygen or oxidised nitrogen
groups. The biochemistry of Anammox is clearly different (Jetten et al., 2001).

Microbiology of Anammox

Broda (1977) first postulated the Anammox process as one of a range of microbial conver-
sions ‘missing’ in nature. He postulated that such a microbial conversion process could
exist based on the fact that the conversion of ammonium and nitrite is a reaction with a large
negative free energy. Mulder (1992) made the first experimental observation while he was
studying an autotrophic denitrification process with sulphide as electron donor. Initially it
was assumed that nitrate was the preferred electron acceptor (Mulder, 1992). Only when it
was realised that nitrite is the actual electron acceptor it became possible to culture
Anammox cultures reproducible in lab-scale reactors (van de Graaf et al., 1996). Presently
the micro-organism involved is reasonably well characterised and also the catabolic route
has been established (Jetten et al., 2001).

Process design aspects for Anammox based processes

Two reactor systems

The Anammox process requires a feed containing ammonium and nitrite in roughly
equal amounts. This means that in a first aerobic nitrification process full oxidation to
nitrate needs to be prevented while also only a 50% oxidation efficiency of the ammonium
oxidation needs to be ensured. The Anammox process has already very low growth rates at
temperatures of 30–40°C, making the process not directly suitable for lower temperatures
where even lower growth rates might occur. If the process is applied at elevated tem-
perature the lower growth rate of nitrite oxidisers relative to ammonium oxidisers can be
efficiently used for selective enrichment of ammonium oxidising bacteria (as applied in the
Sharon process, Hellinga et al., 1999). In the context of municipal wastewater this process
is generally applied to sludge digester effluents (e.g. Mulder et al., 2001). In these effluents
the counter-ion for ammonium is under normal circumstances bicarbonate. The bicar-
bonate can function as a buffer for the acid production due to ammonium oxidation. When
50% of the ammonium is oxidised all the bicarbonate is used. At that point the pH will drop
leading to a strong inhibition of ammonium oxidation. This gives a ‘natural’ control for the
process. Indeed it has been shown (van Dongen et al., 2001) that it is possible to run
a Sharon reactor with continuous aeration giving a stable effluent consisting of an ammo-
nium–nitrite mixture in a ratio required for the Anammox process without any process
control needed, except for the aerobic solids retention time.

The production of ammonium can also be achieved in systems with sludge retention
provided that the SRT is chosen such that it is in between the minimal SRT required by
ammonium and nitrite oxidising bacteria. Such a process would have potentially a smaller
reactor volume, however due to the high oxygen demand this retention time is considerable in order to supply enough oxygen to the system. The disadvantage of such a process is the larger complexity due to biomass retention facilities and the extra control needed for the SRT management independent of the HRT. The choice for a retention system or chemostat system therefore largely depends on the concentration of ammonium in the influent and specific investment costs.

Once a mixture of ammonium/nitrite is obtained this can be fed to a reactor with biomass retention (preferential biofilms or granular sludge). Such an influent is highly selective for Anammox bacteria, making the second stage process design rather stable. The aerobic pre-treatment removes all potential remaining BOD so no heterotrophic organisms can grow in the system. This makes that in such a system the sludge will get highly enriched in Anammox bacteria, leading to high specific sludge activities. Many different biofilm or granular sludge reactor systems will give a good result. So the choice of reactor is mainly based on controllability and economic considerations. For the Anammox process a special reactor has been designed by Paques bv Balk (see Figure 2), based on the principles of internal circulation reactions. Due to internal gas collectors connected to a draft tube the produced dinitrogen gas is used to mix the reactor contents. The well-mixed character of this reactor combined with an easy formation of granular sludge makes it a very stable configuration for the Anammox process.

One reactor systems

A combination of ammonium oxidation and denitrification can easily be achieved in biofilm system under a limiting oxygen concentration regime. The inner part of the biofilm is then anoxic and ammonium oxidised in the outer region of the biofilm can be denitrified in the inner part. For conventional nitrification/denitrification process the problem is that the electron donor for denitrification is more rapidly oxidised then the ammonium. If ammonium is the electron donor this problem doesn’t occur (see Figure 3). The CANON
(Completely Autotrophic Nitrification over Nitrite) process (Strous 2000) exploits this possibility. In a few cases this process was more or less by incident found, when aerobic ammonium oxidising biofilm systems were overloaded (Hippen et al., 1997, Siegrist et al., 1998). Also the OLAND process described by Kual and Verstraete (1998) is likely based on the same principle. Initially the observed nitrogen losses in these biofilm reactors were attributed to denitrification by normal nitrifiers, however more recent investigations showed that the Anammox bacteria were involved in the conversions.

The CANON process was theoretically evaluated by Hao et al. (2002a) This study revealed that the most relevant criterion for the process is an adequate oxygen level in the reactor. It was found that most coefficients describing the process are insensitive towards the conversion in the process. This is because the process is dominated by diffusion (and luckily the diffusion constant is well known) and the thickness of the biofilm. The oxygen concentration should be such that the diffusion of oxygen to the biofilm should be stoichiometrically coupled to the ammonium load, roughly 1.7 gram oxygen per gram ammonium. This implies that a higher ammonium load should be associated to a higher oxygen concentration in the bulk liquid. There appears to be a rather small optimal DO range (Figure 4), below which ammonium removal is not full, while above that value nitrate accumulates in the effluent. This makes application of such a process depending on a proper process control. It was also revealed that with decreasing temperature (Figure 5), or increasing load, the required minimal biofilm thickness increases. This results from the decreasing activity of the bacteria with decrease in temperature or the larger biofilm space per surface area needed at increased loading or decreased temperature. At lower temperatures the use of granular sludge might therefore be limited because to large granules would be needed, or the DO under working conditions will get to small to be controllable in practise. At the other hand for applications at lower temperatures this option of a combined nitrifying/Anammox biofilm is the only practically feasible option because of the insurance of a stable conversion to nitrite.

**Place of Anammox in urban waste management**

In urban water management systems the first application is likely for the treatment of sludge digester effluents or other concentrated nitrogen flows. These can comprise up to 20% of the N-load of a treatment plant. Although this is a relative small fraction of the total treatment of these flows can prevent extension or upgrading of the actual treatment plant. If
the aeration capacity is limiting extension of the aerated volume is not needed (Mulder et al., 2001). If the denitrification capacity is limiting a reduced aeration need might open the potential to increase the anoxic space, while the use of Anammox prevents the need for adding extra COD to the system. Implementation of the process in the main line of the treatment process can lead to a significant minimisation of the environmental impact of the treatment plant (Jetten et al., 1997). The aeration requirement for COD and N-removal is reduced by 60%. Because the COD removal can be done in a high loaded system, the sludge can be easily digested and approximately 50% of the incoming COD can be converted in methane gas. The net sludge production in such a system is reduced by 25%. In principle this process can be combined with phosphate recovery (Hao and van Loosdrecht, 2003). A biological P-removal process is then needed in order to concentrate the phosphate to a level that makes it feasible to produce a precipitate with a high enough P-content to allow proper reuse. In that case approx. 50% of phosphate can be recovered. However the methane production will be reduced also by 50%, and the aeration demand is somewhat increased. Table 1 shows calculations of what implementation of Anammox technology could mean for wastewater treatment in The Netherlands (25 million p.e.).

Another interesting potential for application of Anammox based processes occurs when urine is separately collected. Urine contains approximately 80% of the N-load and 60% of the P-load to a treatment plant (Larsen and Gujer, 1996). Separate collection leads to an extremely simplified treatment process. The process can be designed such that all remaining nutrients are removed by sludge growth. The produced sludge can be digested to produce methane and regain as much as possible the chemical energy in the wastewater. Phosphate in the urine can be simply recovered as struvite. The ammonium in the urine could also be recovered easily because of the high ammonium concentration. However it is questionable whether this always the best choice, ammonium production in industry is highly efficient and one easily invests more energy in ammonium recovery then needed for ammonium production and removal. Application of Anammox makes the latter route even less energy consuming.

If urine is separately collected an alternative transport system needs to be developed. During this transport the emission of ammonium needs to be prevented. This can be done by acidifying the urine, which also solves potential problems with precipitation of minerals from urine. Acidification can most effectively be achieved by nitrifying roughly 50% of the ammonium to nitrite. At that point the pH drops below seven and the solution can safely be transported. This solution forms the perfect influent for an Anammox process (Udert, 2003). A treatment process based on separate urine collection has been proposed and evaluated (Wilsenach and van Loosdrecht, 2003). A conventional treatment process with nutrient removal needs around 6.25 W per person. If from the total urine production 50% is collected separately an energy production of 1.6 W per person could be achieved giving a net energy saving of 7 W per person and an associated reduction in CO₂ emissions.

Table 1 Comparison between conventional and Anammox based process for The Netherlands (25 million p.e.) including sludge treatment by burning

<table>
<thead>
<tr>
<th></th>
<th>Conventional low loaded activated sludge process</th>
<th>Pretreatment + Anaerobic Digestion + Anammox</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy production from methane production</td>
<td>0</td>
<td>40 MW</td>
<td>+ 40 MW</td>
</tr>
<tr>
<td>CO₂ emission due to external energy generation</td>
<td>400 kton/year</td>
<td>6 kton/year</td>
<td>– 394 kton/year</td>
</tr>
<tr>
<td>Power consumption</td>
<td>80 MW</td>
<td>41.1 MW</td>
<td>– 39 MW</td>
</tr>
<tr>
<td>Sludge production</td>
<td>370 kton VSS/year</td>
<td>270 kton VSS/year</td>
<td>– 100 kton VSS/year</td>
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</table>
Conclusion

ANAerobic AMMonium OXydation can greatly contribute to a strong reduction of the environmental impact of wastewater treatment processes. Anammox combined with partial nitrification has reached a stage where it is applied at full scale for wastewater with high ammonium content and elevated temperatures. Using Anammox at lower temperatures and ammonium concentrations is still a big challenge for direct application to urban wastewater treatment.

References


