A TECHNICAL REVIEW OF THE EMERGING TECHNOLOGIES FOR TREATING DEWATERING LIQUORS & PROCESS REJECT WATER

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Abstract

Over the last 20 years a number of biological treatment processes have emerged for treating high-strength ammonia liquors. In the water sector, the main four sources of high-strength ammonia liquors are leachate from landfill sites; and the dewatering liquor arising from municipal Anaerobic Digestion (AD) plants, Advanced Anaerobic Digestion (AAD) plants, and commercial Biowaste Anaerobic Digestion (BAD) plants.

As environmental standards have become more stringent, and the number of Advanced Anaerobic Digestion have increased; the requirement for side-stream treatment liquor treatment has concomitantly increased. The early liquor treatment plants were designed for complete nitrification; converting the high-strength ammonia liquor to nitrate. Over the last decade treatment processes have emerged for nitrification & denitrification, partial nitrification (nitritation) & partial denitrification (denitritation), and short-circuiting of the nitrogen cycle with partial nitrification and the conversion of ammonium directly into nitrogen (N_2) gas.

This paper discusses the variety of technologies that have emerged over the last 20 years such as specific leachate treatment plants, AMTREAT, Anammox, ANITA, DEMON, and the SHARON process; and details their suitability for treating different reject liquors; their requirements for flow and load balancing, process instrumentation, and process heating/cooling.

Key Words

AMTREAT, Anammox, ANITA, CANON, DEMON, Denitrification, Leachate, Nitritation, Nitratation, SHARON.

Introduction

Process reject liquors containing high concentrations of ammonia can be produced from a variety sources. In the water sector, the main four sources of high-strength ammonia liquors are leachate from landfill sites; the dewatering liquor arising from municipal Anaerobic Digestion (AD); dewatering liquors arising from Advanced Anaerobic Digestion (AAD) plants; and dewatering liquors arising from commercial Biowaste Anaerobic Digestion (BAD) plants.

During the last 30-years, more than 100 aerobic biological leachate treatment plants have been constructed on UK landfill sites which produce a leachate with an ammoniacal-N concentration often in excess of 2,000 mg/l NH_3 -N [1]. There are more than 500 municipal mesophilic anaerobic

digestion (MAD) plants processing over 700,000 tonnes of dry sludge per year ^[2]. Conventional MAD produces a digestate that typically contains aqueous ammoniacal-N concentrations of 500 to 1,000 mg/l. If the digestate is dewatered to produce a caked product, the aqueous ammonia will be present in the dewatering process reject water or liquor.

As the number of municipal Advanced Anaerobic Digestion (AAD) and commercial Biowaste Anaerobic Digestion (BAD) plants have increased, there has been an associated increase in the ammonia concentrations contained in the process dewatering liquors. At AAD plants, the anticipated concentration of ammonia is in the range 1,500 - 3,500 mg/l, whereas at BAD plants ammonia concentrations in excess of 5,000 mg/l have been encountered.

At municipal Sewage Treatment Works (STW), the traditional treatment strategy for these liquors has been to pass them back to the existing treatment works. However, with the increasing implementation of tighter and total nitrogen limits, and the increasing ammonia concentrations, this practice may not be feasible because such plants often have insufficient nitrifying capacity. Landfill sites and commercial BAD plants tend to be stand-alone plants, so there is not a STW to return the liquors to. Therefore, in all four applications there has been a move to treat reject liquors at a separate, dedicated plant.

There are a variety of processes for treating high-strength ammonia liquors including physicochemical and biological methods; stripping and scrubbing, biological nitrification and denitrification; and physical separation processes. This paper discusses the biological treatment processes that have emerged over the last 20 years such as specific leachate treatment plants, AMTREAT, SHARON, Anammox, ANITA, and DEMON; and details their suitability for treating different reject liquors; their requirements for flow and load balancing, process instrumentation, and process heating/cooling.

Nitrification and Denitrification Processes

Since the 1980s, significant experience has been built up regarding biological nitrogen removal at wastewater treatment plants ^[3]. The conventional N-removal processes, primarily consists of two sub-processes, nitrification and denitrification. The nitrification and denitrification processes are discussed below.

Nitrification

Nitrification is the term used to describe the two-step biological process in which ammonium (NH_4-N) is oxidised to nitrite (NO_2-N) and nitrite is oxidised to nitrate (NO_3-N) [4].

Nitrification Step 1 - Nitritation

The process of converting ammonium to nitrite:

$$2NH_4^{+} + 3O_2 \Rightarrow 2NO_2^{-} + 4H^{+} + 2H_2O$$
 (1)

Nitrification Step 2 - Nitratation

The process of converting nitrite to nitrate:

$$2NO_2^T + O_2 \Rightarrow 2NO_3^T \tag{2}$$

Total Nitrification Reaction

$$2NH_4^+ + 4O_2 \Rightarrow 2NO_3^- + 4H^+ + 2H_2O$$
 (3)

From equations 1 & 2, it can be seen that three molecules of oxygen per two molecules of ammonium are required during nitritation, and one molecule of oxygen per two molecules of nitrite is required during nitratation.

Denitrification

Denitrification is the term used to describe the biological reduction of nitrate to nitric oxide, nitrous oxide, and nitrogen gas. Biological denitrification is an integral part of biological nitrogen removal, which involves both nitrification and denitrification.

In biological nitrogen removal processes, the electron donor is typically one of three sources: (1) the biodegradable soluble COD in the influent wastewater, (2) the bsCOD produced endogenous decay, and (3) an exogenous source such as methanol (CH_3OH), acetate (CH_3COOH), or glycerol ($C_3H_5(OH)_3$).

Denitrification Step 1 - Denitratation

The process of converting nitrate to nitrite:

$$CH_3OH + 3NO_3 \Rightarrow 3NO_2 + CO_2 + 2H_2O \tag{4}$$

or

$$2CH_3OH + 6NO_3 \Rightarrow 6NO_2 + 2CO_2 + 4H_2O$$
 (5)

Denitrification Step 2 - Denitritation

The process of converting nitrite to nitrogen gas (N₂)

$$CH_3OH + 2NO_2 \Rightarrow N_2 + CO_2 + 2OH + H_2O$$
 (6)

or

$$3CH_3OH + 6NO_2 \Rightarrow 3N_2 + 3CO_2 + 6OH^2 + 3H^2O$$
 (7)

Overall Denitrification Reaction

The overall process of converting nitrate to nitrogen gas

$$5/6\text{CH}_3\text{OH} + \text{NO}_3^- \Rightarrow 1/2\text{N}_2 + 5/6\text{CO}_2 + \text{OH}^- + 7/6\text{H}_2\text{O}$$
 (8)

or

$$5CH_3OH + 6NO_3 \Rightarrow 3N_2 + 5CO_2 + 6OH^- + 7H_2O$$
 (9)

In comparing the denitrification steps, from equations 5 & 7, it can be seen that two molecules of methanol per six molecules of nitrate are required during denitratation, and three molecules of oxygen per six molecules of nitrite are required during denitritation. The overall denitrification process stoichiometrically requires five molecules of methanol per six molecules of nitrate. The nitrification-denitrification pathway is shown in figure 1 below.

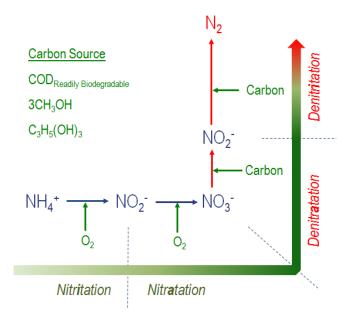


Figure 1: Nitrification – Denitrification Pathways

In the mid-1990s, a number of alternative high strength ammonia treatment processes have emerged which short-circuit nitrification & denitrification, and claim to be more efficient than conventional nitrification and denitrification processes ^[3]. However, as the characteristics of process reject water vary significantly. The selection of the appropriate liquor treatment technology also varies.

The reject liquors ammoniacal-N, COD, phosphorus, nitrite, and suspended solids concentration; the influent temperature; the volumetric flow; the required effluent standard; and the operational input will all affect the selection of the appropriate liquor treatment technology.

Where the influent flow and load is highly variable, the stoichiometric benefits of short-circuiting nitrification and denitrification can be limited in comparison with the requirement for a robust and flexible process. The following section describes the differences between the various processes.

Leachate Treatment Nitrification/Denitrification Processes

Historically Sequencing Batch Reactors (SBR) were at the heart of most of the successful leachate treatment systems [5]. The extended aeration nature of the process provided great stability of the biological process, which is important to minimise operator inputs to the treatment process, and allowed very high efficiencies of aeration to be achieved [1]. Although well-designed and operated treatment plants based on SBR process have demonstrated over many years that essentially complete removal of BOD and ammoniacal-N can be achieved consistently, treated leachates have generally contained high concentrations of nitrate-N, often in excess of 1,000mg/l. As environmental standards have tightened, increasingly, treated leachates are required to contain very low concentrations of nitrate. During the 1990s, leachate treatment systems evolved with the use of rooves, and venturi aeration systems allowed temperatures to be maintained at a minimum of 20°C throughout the year for optimum nitrification. The typical SBR process for treating leachate was replaced with a multi-stage activated sludge process utilising an aerobic zone, post-anoxic zone, post-anoxic aeration zone, with an internal recycle; and ultrafiltration membranes for solids separation [1]. Glycerol was adopted as the carbon source for denitrification. Phosphoric acid is added as a nutrient, and hydrochloric acid is dosed automatically to achieve optimum pH-values for the nitrification and denitrification processes.

Incorporation of an ultrafiltration membrane for solids separation has allowed the process to operate continuously, but adopting the extended aeration characteristics of the SBR process has ensures robust biological treatment process can be retained.

The AMTREAT Nitrification/Denitrification Process

The AMTREAT process was initially developed in 1992 with funding from a consortium of 3 Water Authorities looking for a solution to the problem of nitrifying high strength digested sludge liquors. There were initial pilot-plants located at Manor Farm and Wargrave STWs. In 1995 further research by a 4th Water Authority ratified the process as being a very stable and robust system for the reduction of ammonia in sludge liquors.

The initial development work optimised the ammoniacal-N loading rates and operational temperatures that could be employed to achieve ammoniacal-N removal ^[6, 7]. Therefore, the AMTREAT plant, whilst still providing robust biological treatment, it is a high-rate activated sludge plant for treating high-strength ammonia liquors. The compact, high-rate ammonia treatment system has a relatively small footprint compared to conventional activated sludge and leachate treatment processes, and full nitrification of high-strength ammonia effluent can be achieved, with typical ammonia removal rates in excess of 97% ^[8, 9, 10].

The first full-scale plant was installed at Cliff Quay STW in 1998 for Anglian Water. The plant was designed for complete ammonia removal, and comprised of a centrate sump, centrate buffer tank, heat exchanger, AMTREAT reactor, final settlement tank; and included sodium hydroxide dosing as a source of alkalinity; and process heating to maintain the Amtreat reactor at 25°C. The main sewage treatment works at Cliff Quay is a high-rate activated sludge plant, and the Amtreat plant was designed to return a fully nitrified effluent back to the activated sludge plant to reduce the amount of aeration required.

The second plant was installed at Ashford STW in 2008 for Southern Water. This plant was configured for complete ammonia removal and partial denitrification and alkalinity recovery, with a pre-anoxic tank for denitrification; the AMTREAT reactor for nitrification; and final settlement tanks for solids removal. The plant includes an internal nitrate recycle and RAS recycle to optimise denitrification and alkalinity recovery, which in turn minimises the sodium hydroxide dosing.

Like the leachate treatment plants described above, the AMTREAT process ensures robust biological treatment. The AMTREAT process can successfully treat a variety of high-strength process reject liquors; treating liquors arising from pre-digestion thickening, post-digestion dewatering, and condensate from a sludge drying plant. The liquors fed to the existing AMTREAT Plants are highly variable, with this variance including but not exclusively, the flow, the ammonia concentration, and the temperature. Irrespective of the quality and quantity of the liquor fed to the AMTREAT plants, the performance has been excellent, with a high-quality treated effluent being reliably produced.

Due to the robustness of the design, the process is not sensitive to the influent ammonia concentration, the influent COD concentration, the influent phosphorus concentration, or the influent temperature. At both plants the ammonia removal exceeds 99%; the BOD removal exceeds 75%, and the COD removal exceeds 80%.

ACWA are currently designing three new AMTREAT plants for Anglian Water at three AAD sites. The flexibility of the process has allowed two sites to re-use existing assets; including upgrading of the original plant at Cliff Quay. These third generation plants are designed to maximise nitrification, and are designed with glycerol and sodium hydroxide dosing to optimise denitrification and alkalinity recovery [11].

Partial Nitritation and Denitritation Processes

In the mid 1990s, two innovative processes for nitrogen-N removal were developed; the SHARON and the Anammox Process ^[3]. Both processes focused on the removal of nitrogen from digested sludge water. In the SHARON (Single reactor system for High Ammonium Removal Over Nitrate) process, ammonium is oxidized in one reactor under aerobic conditions to nitrite, which in turn is reduced to nitrogen gas under anoxic conditions by using an external carbon source.

In the Anammox process (Anaerobic Ammonium Oxidation) nitrite and ammonium are converted into nitrogen gas under anaerobic conditions without the need to add an external carbon source.

The SHARON Process

The SHARON process is a high-rate process for the removal of total nitrogen operating with minimal sludge retention time $^{[12]}$. Due to differences in growth rates of the bacterial species at the process design temperature (30 to 40° C) a selection can be made wherein the nitrite oxidising bacteria can be washed out of the system while ammonia oxidising bacteria are retained along with denitrifying bacteria. Use of this metabolic mode of operation allows for a 25% reduction in aeration energy required for nitrification and a 40% reduction in the amount of carbon addition needed for denitrification.

Nitritation
$$2NH_4^+ + 3O_2 \Rightarrow 2NO_2^- + 4H^+ + 2H_2O$$
 (1)

Nitration
$$2NO_2^- + O_2 \Rightarrow 2NO_3^-$$
 (2)

Denitratation $2CH_3OH + 6NO_3^- \Rightarrow 6NO_2^- + 2CO_2 + 4H_2O$ (5)

Denitritation
$$3CH_3OH + 6NO_2^- \Rightarrow 3N_2 + 3CO_2 + 6OH^- + 3H^2O$$
 (7)

During conventional biological nitrogen removal; ammonium is oxidised to nitrite, nitrite oxidised to nitrate, nitrate is then reduced back to nitrite, and finally nitrite reduced to nitrogen. Therefore, theoretically, from the above equations, the SHARON process, which short-circuits nitrification-denitrification, the oxygen requirement can be theoretically reduced by 25% and the carbon requirement can be theoretically reduced by 40%.

As the sludge retention time is equal to the hydraulic retention time no control of mixed liquor suspended solids is required. This makes the SHARON process very stable in situations where large fluctuations in influent suspended solids occur. The core concept on which the process is based is that at liquor temperatures above 15°C, and especially between 30-40°C, the growth rates of the ammonia oxidising bacteria are greater than those of the nitrite oxidizing bacteria. This allows for the design of a selective reactor where in nitroso-genera bacteria (nitritation) predominate over the nitro-genera bacteria (nitratation). The nitrite produced is converted to nitrogen gas by denitrifying bacteria under anoxic conditions.

The SHARON plant is configured with a pre-anoxic tank, and an aerobic tank, with an internal recycle between the two tanks. The pre-anoxic tank is dosed with glycerol as a carbon source, sodium hydroxide as a source of alkalinity, phosphoric acid, micro-nutrients, and anti-foam. Nitrification and denitrification are exothermic processes. Therefore, they produce heat. With a design influent ammoniacal-N concentration in the region of 3,000 mg/l, the bulk liquid is recirculated through a cooling heat exchanger to maintain the reactor temperature between 30 and 40°C. Although the influent ammonia-N concentrations can be typically in the region of

3,000 mg/l, the reject water fed to a SHARON process is typically controlled so the influent is fed at a constant flow rate and the ammoniacal-N concentration does not exceed 1,600 mg/l NH₄-N.

The equations above show that by short-circuiting nitrification-denitrification, the oxygen and carbon requirement are reduced. Howver in practice, to take advantage of this it is essential to control the Solids Retention Time (SRT); the Hydraulic Retention Time (HRT); the influent ammonia concentration; the dissolved oxygen concentration; and reactor temperature. Where the environment is regularly switching between anoxic and oxic conditions, there is an oxygen removal requirement that is not covered in the above equations, as described below.

Oxygen Removal

$$CH_3OH + 1.5O_2 \Rightarrow CO_2 + 2H_2O$$
 (10)

In an anoxic zone, the available oxygen must first be consumed to a dissolved oxygen concentration of <0.3mg/l so that the bacteria are forced to substitute the nitrite as the electron acceptor and reduce the nitrite to nitrogen gas (Equation 6). Therefore, in order to minimise the external carbon dosing, the initial treatment step should be in the absence of free oxygen.

The AMTREAT process includes a de-oxygenation zone, or stilling tube, which is designed to reduce the dissolved oxygen concentration prior to the flow entering its pre-anoxic zone, whereas, the SHARON process transfers flows direct from an oxic zone to an anoxic zone, therefore, although the oxygen and carbon requirement is reduced by short-circuiting nitrification and denitrification, there is a carbon requirement for the oxygen depletion as the liquor is re-circulated from the oxic zone.

Nitrous Oxide

It has been reported that short-circuiting nitrification-denitrification by nitritation-denitritation gives rise to elevated emissions of nitrous oxide $(N_2O)^{[13]}$. During denitrification, autotrophic ammonia oxidizing bacteria (AOB) oxidise ammonia to nitrite (NO_2^-) , followed by the reduction of NO_2^- to nitric oxide (NO), nitrous oxide (N_2O) and molecular nitrogen (N_2) . Conditions that lead to high N_2O concentrations with simultaneous low dissolved oxygen conditions will result in elevated N_2O emissions being liberated to atmosphere $^{[14]}$. N_2O is a major greenhouse gas and air pollutant. Considered over a 100-year period, it has 298 times more impact 'per unit weight' (Global warming potential) than carbon dioxide $^{[15]}$. Therefore processes that short-circuit nitrification-denitrification will have a higher potential to discharge N_2O to atmosphere in comparison with conventional nitrification-denitrification processes.

Deammonification Processes

Autotrophic N-removal systems or deammonification processes rely on two simultaneous biological processes. These processes are step-wise, but they can be accomplished in two separate stages. The first step is partial nitritation, and then the second step is anaerobic ammonium oxidation (Anammox). These steps can be undertaken in separate stages or in a single stage [16]. To achieve the anammox step, a preceding aerobic step is obligatory. In the first

step ammonium is partially oxidised to nitrite (partial nitritation), which next, as an electron acceptor, reacts with the remaining ammonium to form nitrogen gas (Anammox step). The overall process is called "partial nitritation/Anammox" and comprises of ammonia oxidation under oxic conditions in the first stage, while the Anammox step takes place under anaerobic conditions in the second one.

When the deammonification process was originally developed it was generically known as the CANON process (Complete Autotrophic Nitrogen removal Over Nitrite). However, as the process has developed, and a number of proprietary processes have become commercially available, the generic process has become known the Anammox process, as all the variants use anammox bacteria.

The major suppliers/variants in the UK are:

Anammox®

Single-stage granular sludge process

Paques B.V.

ANITA[™] MOX

Single-stage MBBR deammonification process.

Veolia Water Solutions & Technologies

ANITATM Shunt Process

SBR process for N-removal via the nitrite pathway

Veolia Water Solutions & Technologies

DEMON

Single-stage SBR process with cyclone RAS/SAS separation

Grontmij Nederland B.V.

In the deammonification processes ammonia oxidising bacteria and anammox bacteria can co-exist in the one reactor due to oxygen and oxygen-free zones within the biofilm depth. Ammonia is partially oxidised under oxygen-limited conditions to nitrite and next nitrite together with the remaining ammonia is converted to nitrogen (N_2) gas by the anammox bacteria. This process is particularly suitable for the removal of ammonia from wastewater that does not contain enough organic material to support the conventional nitrification-denitrification process.

Deammonification provides a short circuit in the natural nitrogen cycle. The Anammox process is characterised by removing ammonium (NH_4^+) using nitrite (NO_2^-) rather than nitrate (NO_3^-) requiring less oxygen (O_2) . The Anammox conversion was discovered at a pilot plant of yeast and antibiotics producing company Gist Brocades (now DSM) in Delft. The Anammox process is a fully autotrophic process, meaning it does not require a carbon source. The Anammox process was developed in partnership with the Technical University of Delft and the University of Nijmegen in The Netherlands $^{[17, 18]}$.

The short-circuit or nitrite pathway is achieved by creating conditions under which nitrite oxidising bacteria (NOB) are eliminated from the system, or at least inhibited, while ammonia oxidising bacteria (AOB) are retained or favoured by the operating conditions. Such conditions are high temperature (i.e. $\mu_{\text{max},\text{AOB}} > \mu_{\text{max},\text{NOB}}$); low dissolved oxygen due to the fact that AOB have higher oxygen affinity than NOB; and high levels of free ammonia and free nitrous acid (HNO₂) which inhibit more NOB than AOB. However, in anything other than very dilute, cold solutions, nitrous acid rapidly decomposes into nitrogen dioxide, nitric oxide, and water.

$$2HNO_2 \Rightarrow N_2O + NO + H_2O \tag{11}$$

So as mentioned in the previous section, processes that short-circuit nitrification-denitrification will have a higher potential to discharge N_2O to atmosphere in comparison with conventional nitrification-denitrification processes.

The bacteria responsible for the anammox reaction are autotrophic, and do not need organic carbon to support growth. Although the bacteria are anaerobic, their activity is only reversibly inhibited by oxygen.

Autotrophic N-removal systems rely on two simultaneous biological processes:

Partial Nitritation carried out by Ammonia Oxidising Bacteria (AOB)

To remove ammonium nitrogen from wastewater using the Anammox bacteria, the correct nitrate-to-ammonium ratio is needed. Nitrite can be produced by aerobic autotrophic ammonia oxidisers according to the following reaction(s):

$$NH_4^+ + 0.77O_2 + 0.05CO_2 \Rightarrow 0.42 NH_4^+ + 0.56NO_2^- + 0.1 biomass + 0.5H_2O + 1.13 H^{+[13]}$$
 (12)

$$2NH_4^+ + 1.5O_2 + 2HCO_3^- \Rightarrow NH_4^+ + NO_2^- + 2CO_2 + 3H_2O^{[16]}$$
(13)

Anaerobic ammonia oxidation carried out by Anammox bacteria

Anaerobic ammonium oxidation (Anammox) is an anaerobic microbiological process in which ammonia, together with nitrite, is converted to nitrogen (N_2) gas. The anammox reaction has been reported according to the reaction(s):

$$0.42NH_4^+ + 0.56NO_2 + 0.03H + + 0.03CO_2 \Rightarrow 0.43N_2 + 0.11NO_3^- + 0.0.3$$
biomass + $0.8H_2O + 1.13 H^{+[13]}$ (14)

$$NH_3 + 1.32NO_2^T + H^+ \Rightarrow 1.02N_2 + 0.26 NO_3^T + 2H_2O^{[16]}$$
 (15)

$$NH_4^+ + 1.32NO_2^- + 0.0066HCO_3^- + 0.13H^+ \Rightarrow 1.02N_2 + 0.26NO_3^- + 0.0666CH_2O_{0.5}NO_{0.15} + 2.03H_2O^{[19]}$$
 (16)

To ensure a stable nitritation from abundant ammonium reject water, the nitrite-to- ammonium ratio should be about 1.3. However, anammox bacteria are inhibited by high nitrite concentrations. Also, some nitrate is formed from nitrite. This reaction is thought to be needed for autotrophic CO_2 -fixation. The bacteria oxidizing ammonia to nitrite need oxygen, whereas the bacteria converting ammonia and nitrite to nitrogen (N_2) are anaerobic. However, similar to anaerobic digestion, both types of bacteria can co-exist in one reactor, provided that the system is kept oxygen limited.

Due to the very slow growth rate of Anammox bacteria, long sludge ages have to be applied meaning that most of the autotrophic N-removal process are biofilm systems, with or without support material, coming in different configurations.

The Anammox® Process

Paques B.V. has developed the so called one-step-Anammox® reactor in which partial nitritation and the anammox reaction as described above occur simultaneously in one single process unit.

As the anammox bacteria have a relatively slow growth rate, effective biomass retention is essential for a sustainable process. The biomass generated in the Paques' one-step-Anammox® process is of a granular nature and has a typical red-brown colour caused by specific enzymes. The granules consist of a mixture of nitritation and anammox bacteria. While the oxygen utilizing nitritation bacteria are concentrated at the outer granule, the anammox bacteria are more concentrated within the centre of the granule. The one-step Anammox® reactor is continuously fed and aerated and can be controlled by measurement of nitrite and ammonium.

The granules have a high settling velocity and are therefore easily retained in the reactor. The one-step Anammox® reactor is equipped with a unique patented biomass separator mounted at the top of the reactor ensuring effective biomass retention [17].

Granular biomass has shown to be to be less susceptible for incidents with high solids or COD. Due to the special settler design solids in the influent and flocculent biomass growth are selectively washed out of the reactor, while the granular biomass is retained. The granules showed to be resilient in coping with potential inhibiting components. Prolonged exposure of granular anammox biomass to nitrite levels up to 50 mg/l did, in contrast to floc-type biomass, not result in inhibition of the bacteria. The granular anammox biomass has been used to inoculate other reactors facilitating the biological start-up. Depending on the amount of

granular anammox biomass used for inoculation start-up times of newly built Anammox® reactors have been reduced significantly.

The ANAMMOX® reactor is aerated and equipped with a biomass retention system. The reactor contains granular biomass. The wastewater is continuously fed to the reactor. The aeration provides for rapid mixing of the influent with the reactor content, intense contact with the biomass and oxygen supply to drive the conversion.

The treated wastewater leaves the reactor by passing the biomass retention system at the top of the reactor. The granular biomass is separated from the cleaned wastewater, assuring high biomass content in the reactor. Together with the dense conversion properties typical for granular biomass, the high biomass content provides for high conversion rates and therefore a small reactor volume.

The ANITATM MOX Process

Aerobic granulation can be difficult to control with possible loss of biomass from the systems undermining the long term stability of such anammox processes. Alternatively, the MBBR process is a robust and promising biofilm technology for single-stage deammonification processes, as wash-out of slow growing anammox bacteria can be prevented by a non-clogging media retention grid. The ANITA™ Mox process uses MBBR technology with high protected surface area media for compact design. An advanced aeration control system has been developed to reduce the NOB activity in the biofilm and therefore maximise the amount of nitrite available for the anammox bacteria. This real-time control strategy also reduces the need for mechanical mixing in the MBBR due to the continuous aeration pattern.

ANITA™ Mox MBBR technology uses a reactor with biomass retained on continuously moving, high surface area carrier medium. The biomass carriers have a high specific protected surface area, ranging from 500 to 1,200 m²/m³. The biomass carriers allow the development of a biofilm suitable for simultaneous partial nitrification to nitrite and anammox pathways under continuous aeration condition [20, 21, 22].

Mass transfer limits the dissolved oxygen penetrating the biofilm, creating two zones. The outer layer of the biofilm is aerobic and ammonia is oxidised to nitrite by AOB. The inner layer is anaerobic providing the right conditions for the growth of anammox bacteria. Partial nitrification of ammonia to nitrite and autotrophic N-removal occur simultaneously within the biofilm and an advanced real time aeration control system adjusts the dissolved oxygen concentration in the range of 0.5 - 2.0 mg/l O_2 to avoid further oxidation of nitrite to nitrate by NOB while maintaining high ammonia removal performances in the system.

The ANITA[™] Shunt

ANITA $^{\text{\tiny{M}}}$ Shunt is an SBR process with an advanced control system to improve the process performance and minimise nitrous oxide (N₂O) emissions. It is suitable for the treatment of

ammonia-rich effluents containing some readily biodegradable COD but insufficient to facilitate complete denitrification, with a readily biodegradable COD-to-Nitrogen ratio below 5. Therefore, ANITA Shunt would be an appropriate process for treating the dewatering liquor from anaerobic digestion plants.

The SBR cycle is divided into several sub-cycles each composed of feed (aerated or anoxic based on feed COD content), aeration and anoxic phases. The duration of each phase is controlled to minimise N_2O emissions by on-line ammonium and nitrite monitors which, together with pH and temperature instrumentation, allows calculation of the free nitrous acid concentration that has been found to be the true trigger of N_2O emission rather than nitrite itself.

During the aeration period, dissolved oxygen level is controlled at 0.4 - 1.0 mg/l O_2 to limit NOB activity, and nitrite is allowed to accumulate until a pre-set nitrous acid set point is reached. At this point aeration is stopped and is followed by an anoxic period during which an external carbon source (usually methanol) is dosed for complete denitrification if the feed COD content is limiting. Once the maximum level in the SBR is reached, the sub-cycle is completed and sludge is allowed to settle and the treated effluent is then discharged before a new SBR cycle starts again [24]

The DEMON Process

DEMON is claimed as a cost effective technology for the removal of nitrogen compounds from wastewater with high concentrations of ammonia. The technology is based on a biological process of nitrification and autotrophic denitrification. The process was developed and patented by the University of Innsbruck (Austria) and has evolved into a proven technology ^[25].

Like the other deammonification processes, in a DEMON reactor two separate processes occur; the partial nitrification of ammonia and the subsequent anaerobic oxidation of the residual ammonia by nitrite to nitrogen gas.

Partial Nitritation carried out by Ammonia Oxidising Bacteria (AOB)

$$1.25 \text{ NH}_4^+ + 1.25 \text{O}_2 \Rightarrow 1.25 \text{ NO}_2^{-[25]} \tag{17}$$

Anaerobic ammonia oxidation carried out by Anammox bacteria

$$NH_4^+ + 1.25NO_2 \Rightarrow N_2 + 0.25NO_3 + 2H_2O^{[25]}$$
 (18)

In theory the presence of oxygen (required for partial nitrification) inhibits growth of deammonifying bacteria. Nevertheless the DEMON process allows nitrification and deammonification to occur in one single reactor. This is achieved by maintaining a low dissolved

oxygen set-point of approximately 0.3 mg/l O_2 . This low dissolved oxygen concentration limits the growth rate of nitrite oxidising bacteria (such as *Nitrobacter*) to such levels that they are washed out of the system.

Due to the relatively low growth rate of deammonifying bacteria, a DEMON system is operated with a sludge age of approximately 20 days; thus sludge retention is required. A cyclone is used to separate deammonifying bacteria from waste activated sludge. The deammonifying bacteria are subsequently returned to the DEMON reactor, effectively creating longer sludge ages for deammonifying than for ammonia oxidising bacteria and nitrite oxidising bacteria. The combination of low DO values and the use of a cyclone ensure that nitrite oxidising bacteria will not be able to accumulate in the DEMON reactor [25].

As well as the development of conventional nitrification-denitrification and deammonification processes, there are some novel liquor treatment processes emerging from the biowaste or commercial anaerobic digestion sector, that may offer alternatives to biological treatment of ammonia rich reject water.

Novel Physico-Chemical Processes

Like dewatering liquors, the processing of digestate from commercial biogas plants has become of increasing concern ^[26]. This has given rise to some novel approaches to treating the process reject water.

With regard to composition of digestate and its use in the agricultural sector, the following three groups of constituents are of interest.

- 1. The nutrients as valuable ingredients determining the fertiliser value
- 2. The concentration of organic compounds with its associated soli-improving effect
- 3. The potential content of pollutants, which may prevent an agricultural application.

In the biomass sector, the principle objectives of digestate treatment are; i) a reduction of volume to improve the manageability and to reduce transportation cost and ii) the recovery of nutrients in concentrated ^[26].

Most frequently the first step is mechanical dewatering using a decanter centrifuge. The major fraction deriving from the dewatering process is the reject water. In cases where sufficient waste heat from the combined heat and power (CHP) plant is available, concentration of the liquid phase through evaporation is a possible treatment option [27, 28].

The biomass sector, consider biological treatment processes for treating reject water unattractive due to their significant capex and opex cost ^[26]. Full purification of the liquid phase to obtain direct discharge quality is currently only achieved by means of membrane processes. In a typical configuration the solid-liquid separation is followed by an additional solids removal

step such as flotation. Subsequently, ultrafiltration follows to remove all remaining particles and the colloidal dispersed fraction. The final step is reverse osmosis. Whilst membrane processes are capable of producing water of the highest quality, considerable quantities of reject/retentate are produced. Figure 2 below, shows a typical nutrient flow in the course of the digestate treatment process.

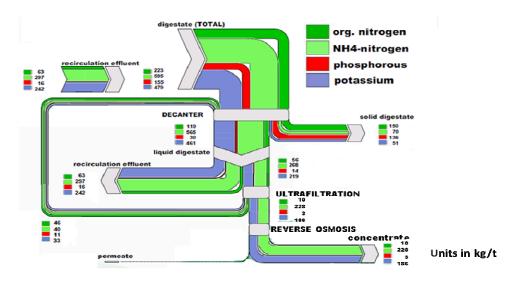


Figure 2: Nutrient flows in digestate treatment (Centrifuge, ultrafiltration, reverse osmosis).

In a typical physico-chemical filtration process, the first stage of the advanced filtration system is represented by an ultrafiltration unit, featuring ceramic membranes and composed by 6+6 parallel sub-units, operating at a pressure of 200 kPa. The first membrane separation determines the production of the concentrated fraction or first-stage retentate. This is recirculated to the centrifuge polymer dosing tank, and the permeate is passed on to the final step, the reverse osmosis. The reverse osmosis unit comprises of a low pressure section (900 kPa) followed by a high-pressure section (3,900 kPa) sequentially operating on a n.4 filtering columns. The outputs of the final stage are a final-stage concentrated retentate fraction, which is sent to storage tank; and the final treated permeate [29].

The ability to treat high-strength ammonia reject liquors using direct ultrafiltration is still relatively unproven in the UK, and early trials have suggested that it is not capable of meeting high-quality effluent standards in terms of nitrogen without reverse osmosis and ion exchange.

Discussion

Over the last 20 years a number of biological processes for treating high-strength ammonia process reject water have emerged. These processes have varied from conventional nitrification-denitrification processes such as the SKM Enviros leachate treatment plant; high-

rate nitrification-denitrification processes such as the AMTREAT process; nitritation-denitritation processes such as SHARON; and deammonification processes such as Anammox, ANITA MOX, ANITA Shunt, and DEMON.

Although all the processes above can treat high-strength ammonia liquors, each process have advantages or disadvantages over the other technologies. There is no panacea when it comes to liquor treatment; the appropriate technology should be selected on a site-by-site basis.

The conventional and high-rate nitrification processes offer the most process robustness and flexibility, and are the simplest to operate. Whereas the deammonification processes offer the greatest capex and opex saving, but they are the most restrictive processes, and the most complicated to operate.

Anammox bacteria are slow growing and require relatively constant conditions to operate successfully. The deammonification process has to operate with restricted dissolved oxygen, and anammox bacteria are inhibited is the influent COD is to high, the total phosphorous is too high, and the bulk liquid nitrite concentration is too high. Therefore, where the influent flow is variable, the deammonification process may require a preceding treatment step to protect the anammox bacteria.

Therefore, flow to the deammonification process has to be balanced; the process will not be suitable to treat pre-digestion thickening liquors, and depending on the fate of phosphorus in the digestion process, deammonification may not be suitable without a phosphorus removal stage.

Process Instrumentation

The conventional nitrification-denitrification plants require much less sophisticated instrumentation than the nitritation-denitritation and deammonification plants. The leachate treatment plants and the AMTREAT plant require pH control and dissolved oxygen control, though the plants can operate just on pH.

The nitritation-denitritation plants require nitrate and nitrite instrumentation as the plant is controlled so such that nitratation does not occur.

The deammonification plants require nitrite instrumentation to control the dissolved oxygen level to restrict/inhibit the production of nitrite. Anammox bacteria are inhibited by high nitrite concentrations.

Heating / Cooling

Nitrification and denitrification are exothermic processes. Therefore, as the plants treat the high-strength ammonia liquor, the treatment process will generate heat. Processes that nitrify and denitrify will generate more heat than the nitritation-denitritation processes, which will in turn generate more heat than the deammonification processes. For influent ammoniacal-N concentrations up to approximately 700 mg/l the treatment process will require process

heating. For influent ammoniacal-N concentrations above about 1,000 mg/l, the treatment process may require cooling. This will be dependent on whether or not the tanks have rooves, the material of construction, whether the tanks are clad, wind speed, ambient temperature etc. There is a band in the middle where neither heating nor cooling is required. However, it is just as likely that both heating and cooling would be required. The leachate treatment plants are operated without heating or cooling, and the AMTREAT plant at Ashford is operated without heating or cooling. The SHARON plant at Whitlingham is operated with process cooling, whereas the Anammox plant at Minworth is operated with process heating.

Conclusions

Over the last 30 years a number of biological processes for treating high-strength ammonia process reject water have been developed. As more Advanced Anaerobic Digestion plants and stand alone Biowaste Anaerobic Digestion plants have been installed, the need to treat high-strength reject liquor has increased accordingly. This has led to the development of high-rate nitrification-denitrification processes such as the AMTREAT process; nitritation-denitritation processes such as SHARON; and deammonification processes such as Anammox, ANITA MOX, ANITA Shunt, and DEMON.

All the various technologies listed above are capable of treating high-strength ammonia reject liquors. It is the nature, composition, and variability of the liquor to be treated, the complexity of the plant, and the skills of the plant operators that will dictate the selection of the appropriate process to treat the reject liquor.

- The AMTREAT Process is capable of treating a variety of high-strength process reject liquors arising from a variety of sources including pre-digestion thickening, postdigestion dewatering, and condensate from a sludge drying plants.
- The AMTREAT Process can treat liquors that are highly variable, with this variance including, the influent flow, the ammonia concentration, the COD concentration, the phosphorus concentration, and the influent temperature.
- The deammonification processes (Anammox, ANITA, DEMON) that short-circuit
 nitrification and denitrification offer significant savings in terms of reduced aeration and
 reduced carbon dosing, but this is at the expense of reduced process flexibility.
- Although the processes that short-circuit nitrification and denitrification offer significant savings in terms of reduced aeration and reduced carbon dosing, the nitrous oxide (N₂), emissions, which is a greenhouse gas, will be significantly higher in comparison with more conventional nitrification-denitrification processes.
- The robustness and flexibility of the conventional nitrification-denitrification processes may outweigh the stoichiometric benefits of the nitrite pathway processes, especially if the liquor to be treated contains COD or phosphorus.

- The high biomass concentration in the AMTREAT plant facilitates removal of non-readily biodegradable COD.
- Irrespective of the variability of the feed, the AMTREAT process reliably produces a highquality effluent.
- All the recent liquor treatment processes have advantages or disadvantages over the other technologies. There is no panacea when it comes to liquor treatment; the appropriate technology should be selected on a site-by-site basis.

Acknowledgements

The opinions expressed in this report are those of the author, and do not necessarily reflect the views of the organisations involved.

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