DEAMMONIFICATION PROCESS
OF SLUDGE DIGESTER LIQUORS IN BIOFILM SYSTEMS

This study is a review of the new methods of ammonium nitrogen removal from liquids which originate from dewatering of digested sludge based on the rule of deammonification in biofilm systems.

1. INTRODUCTION

Sludge digester liquors generated during sludge treatment and digester processes in WWTP are characterized by high temperature and high content of nutrients generated due to digestion processes. Liquors from anaerobic digestion can contain over 1000 mg·dm⁻³ of ammonium nitrogen and 30–100 mg·dm⁻³ of phosphorus [16]. In treated wastewater the content of sludge digester liquors does not usually exceed 2.5% and the load of nutrients in liquors can reach 30% of the raw wastewater load. The liquors are usually directed to raw wastewater to be treated with it, disturbing the work of settlers and activated sludge chambers. In this case, a decrease in biogen concentration in the liquors is necessary before directing the latter to the main stream of WWTP. Phosphorus compounds are removed from sludge digestor liquors by precipitation method (iron and aluminum salts), whereas ammonium nitrogen reduction is carried out using physicochemical methods (stripping, struvite precipitation). It is also possible to apply bioaugmentation of nitrifiers in side stream (InNitri and BABE processes) [5] or deammonification process.

The paper presents new technologies of ammonium nitrogen removal in a side stream in biofilm systems and indicates the possibilities of their application. The paper also discusses the deammonification process with aerobic-anoxic biofilm in one-reactor systems (CANON and OLAND technologies).
2. PROCESSES OF ANAEROBIC AMMONIUM NITROGEN REMOVAL

The term “deammonification” describes ammonium nitrogen removal from wastewater conducted in a way different from classical nitrification and denitrification [8]. The deammonification process consists in oxidizing ammonium nitrogen to nitrite and then reducing nitrite to gaseous nitrogen without formation of indirect compounds – nitrates. This is a two-stage process which is also known under the name “Anammox” (anaerobic ammonia oxidation) [6], [8]. In this process, two zones are established: aerobic and anaerobic/anoxic. In the first zone, the nitrifying bacteria (nitrifiers) of the first stage oxidize ammonium, whereas in the second one, the so-called Anammox bacteria reduce nitrites. Anammox bacteria belong to the Planctomycetales group (Brocardia anammoxidans and Kuenenia stuttgartiensis) [8]. The mechanism of ammonium nitrogen oxidation by Anammox bacteria was determined by Wyffels et al. [28] who used $^{15}$N nitrogen tracer. The effectiveness of digester sludge liquid deammonification is enhanced by high temperature of treated liquors (20–35 °C) and its influence on the washing away the nitrifying bacteria of the second phase (oxidizing nitrite to nitrate) [8]. The inhibition of the second-stage nitrifiers is also controlled by HRT [10]. The recent studies [11], [19] with FISH analysis confirmed that anaerobic ammonium oxidation in the deammonification process was performed by Anammox bacteria, although Pynaert et al. [19] did not exclude a specific activity of the aerobic ammonium oxidizers.

In recent years, numerous reports have described the possibilities of running deammonification in different combinations of both zones. One and two-reactor systems with activated sludge or a biofilm can be applied. Moreover, this process can be carried out in CSTR or SBR reactors.

![Fig. 1. WWTP scheme with the use of sludge liquor deammonification](image-url)
Depending on the way the process is conducted, we can distinguish SHARON [10], CANON [20], [21], [23] and OLAND [14] technologies and their combinations, e.g., SHARON-Anammox [8]. An example of the use of deammonification of sludge digester liquors for a typical WWTP is presented in figure 1.

3. DEAMMONIFICATION IN A BIOFILM

It is possible to run the process of deammonification in WWTP with a biofilm, provided that a proper biofilm thickness is maintained and that the biofilm has two layers (figure 2).

In an external oxic layer of biofilm, the typical nitrifying bacteria (*Nitrosomonas europaea/eutropha*, *Nitrosomonas oligotropha/uera*, *Nitrosomonas communis*, *Nitrospira* sp.) are found, while in an internal layer there live anoxic microorganisms capable of anaerobic ammonium oxidation (*Anammox* bacteria). The nitrifiers from *Nitrosomonas* genus are responsible for supplying the biofilm with nitrites and for creating proper conditions for *Brocardia anammoxidans* and *Kuenia stuttgartiensis* bacteria [4], [6], [8].

The deammonification in biofilm systems can be carried out on a rotating contactor, a fixed film and fluidized bed reactor, as well as in SBR reactors with biomass carriers (e.g. MBSBBR – moving-bed batch biofilm reactor). The deammonifying biofilm is used in OLAND and CANON processes.
4. THE CANON PROCESS

The letters CANON stand for Completely Autotrophic Nitrogen Removal Over Nitrite. This technology was developed at Delft University of Technology in Holland and is based on the presence of nitrifying and Anammox bacteria in the biofilm [17], [21], [23].

The research has shown that under oxygen deficiency limited conditions ammonia is oxidized to nitrites by nitrifying bacteria according to the following reaction:

$$\text{NH}_4^+ + 1.5 \text{ O}_2 \rightarrow \text{NO}_2^- + 2 \text{ H}^+ + \text{H}_2\text{O}. \quad (1)$$

Then nitrites are processed together with the remaining ammonium nitrogen to nitrogen gas by Anammox bacteria that live in an internal biofilm layer and use nitrites as electron acceptors:

$$\text{NH}_4^+ + 1.3 \text{ NO}_2^- \rightarrow 1.02 \text{ N}_2 + 0.26 \text{ NO}_3^- + 2 \text{ H}_2\text{O}. \quad (2)$$

Generally these changes can be presented as follows:

$$\text{NH}_4^+ + 0.85 \text{ O}_2 \rightarrow 0.435 \text{ N}_2 + 0.13 \text{ NO}_3^- + 1.3 \text{ H}_2\text{O} + 1.4 \text{ H}^+. \quad (3)$$

This process is carried in a single reactor with a biofilm on a fixed or rotating contactor. It is possible to use a hybrid reactor with activated sludge and a fixed film. Then aerobic bacteria develop in suspended sludge, while the cultures of Anammox bacteria can be found in the biofilm.

The CANON technology allows the use of Anammox bacteria for nitrogen removal under oxygen-deficiency conditions in a single reactor with a biofilm [20]. This process was also tested in SBR reactors [23]. The maintenance of a suitable concentration of dissolved oxygen in the medium is the basis for running the process and for a proper biofilm quantity. In order to effectively remove nitrogen, the optimum concentration of dissolved oxygen should range from 0.6 mg O$_2$·dm$^{-3}$ [9] to 0.8 mg O$_2$·dm$^{-3}$ [25]. This concentration is lower than that measured by KOCH et al. [13] (2.0 mg O$_2$·dm$^{-3}$). If oxygen concentration in the medium surrounding the biofilm reaches the optimum, its further increase leads to an increase of the population of ammonium oxidizers and the decrease of Anammox bacteria [25]. Nitrite oxidizers should be limited because they compete with ammonium nitrogen oxidizers for oxygen and with Anammox for nitrites. The aeration of the system with a deammonifying biofilm should be controlled, depending on the load of ammonium nitrogen [8].

The maximum uptake of oxygen by biofilm averages 10 g O$_2$·m$^{-2}$·d$^{-1}$ [12], [15] and the consumption of oxygen drops when there is a decrease in oxygen concentration. For the concentration of 1.0 mg O$_2$·dm$^{-3}$, typical of the CANON or OLAND system, the oxygen consumption by biofilm amounts to 3 g O$_2$·m$^{-2}$·d$^{-1}$. Hence, the maximal load which can be treated by aerobic–anoxic biofilm approximates to 350 mg
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$NH_4^+ \cdot dm^{-3} \cdot d^{-1}$, which is tantamount to the surface area of a biofilm of about 200 m$^2$·m$^{-3}$ [25]. A minimal nitrogen load which can be introduced to the reactor for stable removal of nitrogen was determined on a laboratory scale and amounts to 120 mg N·dm$^{-3}$·d$^{-1}$ [23]. The CANON process can be conducted with the reactor load ranging from 2 to 3 kg N·m$^{-3}$·d$^{-1}$.

This process is characterized by high efficiency, which reaches > 90% [24]. The studies show that the CANON run at temperature of 25–30 °C and pH = 7–7.5 leads to the best results [5]. SLIEKERS et al. [21] obtained relatively low, i.e., 42%, nitrogen removal in a gas-lift reactor for the load of 3.7 kg N·m$^{-3}$·d$^{-1}$ and ammonia concentration in influent of 1.545 kg·m$^{-3}$. The oxygen concentration in reactor reached 0.5 mg O$_2$·dm$^{-3}$ and HRT was 10 hours. The ammonium removal rate reached 1.5 kg N·m$^{-3}$·d$^{-1}$. For the sake of comparison, the rate of nitrogen removal in the CANON systems in SBR amounts to 0.07 kg N·m$^{-3}$·d$^{-1}$[20].

5. THE OLAND PROCESS

KUAI and VERSTRAETE [14] were the first to introduce the term OLAND. The letters OLAND stand for Oxygen-Limited Autotrophic Nitrification–Denitrification. This technology was developed in the Laboratory of Microbial Ecology in Gent [27]. At first, this process was attributed to nitrifiers, but further investigation showed that also Anammox bacteria are responsible for ammonium nitrogen removal [19].

So far, the mechanism of the OLAND process has not been fully understood. It is possible that the OLAND process depends on the cooperation between aerobic and anaerobic bacteria oxidizing ammonia or makes use of denitrifying capacity of *Nitrosomonas* in the presence of nitrogen oxides. The mechanism of nitrite dismutation (simultaneous oxidation and reduction) by *Nitrosomonas* species has been described by ABELOVICH and VONSHAK [1]. It is believed that OLAND technology is very similar to the CANON being earlier described. This is corroborated by the term OLAND/CANON [25]. It is supposed that in these methods the processes taking place in the anaerobic zone can be different. In the OLAND process, the denitrification activity of aerobic nitrifiers can be used [2].

Till now the investigation relating to the OLAND technology has not made it possible to fully clarify the stoichiometry of the process. According to VERSTRAETE and PHILIPS [27] this process, as also the CANON, consists of two steps: ammonium oxidation to nitrites by nitrifying bacteria (equation (4)) and their reduction to nitrogen gas (equation (5)). Equation (6) describes a combination of these two processes:

\[
0.5 \text{NH}_4^+ + 0.75 \text{O}_2 \rightarrow 0.5 \text{NO}_2^- + 1 \text{H}^+ + 0.5 \text{H}_2\text{O}, \tag{4}
\]

\[
0.5 \text{NH}_4^+ + 0.5 \text{NO}_2^- \rightarrow 0.5 \text{N}_2 + \text{H}_2\text{O}, \tag{5}
\]

\[
0.5 \text{NH}_4^+ + 0.75 \text{O}_2 \rightarrow 0.5 \text{NO}_2^- + 1 \text{H}^+ + 0.5 \text{H}_2\text{O} + 0.5 \text{N}_2 + \text{H}_2\text{O}, \tag{6}
\]
\[ \text{NH}_4^+ + 0.75 \text{O}_2 \rightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2\text{O} + \text{H}^+. \]  

(6)

A more detailed investigation based on isotopic analysis of the gas generated allowed us to present different stoichiometry of the process [28]:

\[ \text{NH}_4^+ + 1.43 \text{NO}_2^- \rightarrow 1.09 \text{N}_2 + 0.008 \text{N}_2\text{O} + 0.13 \text{NO}_3^- + \text{biomass}. \]  

(7)

Nitrogen dioxide (N\textsubscript{2}O), the by-product of the process, is produced in very small quantities. BINSWANGER et al. [3] reported a similar mechanism, according to them some part of nitrites is reduced to N\textsubscript{2}O or N\textsubscript{2}. Different studies concerning the OLAND technology showed that about 40\% of ammonium nitrogen were converted to N\textsubscript{2} or N\textsubscript{2}O [14].

The OLAND process is conducted in single reactors under the same conditions as the CANON. The best results are achieved using a rotating biological contactor, including a rotating disc contactor RDC [8]. The rate of nitrogen conversion obtained using this technology reached 40–75 g N-\textsubscript{NH}_4\cdot m\textsuperscript{-3}d\textsuperscript{-1} at the bioreactor load of 140 g N-\textsubscript{NH}_4\cdot m\textsuperscript{-3}d\textsuperscript{-1} [14]. Along with an increase in the reactor loading it is possible to achieve higher rate of nitrogen processing. PYNAERT et al. [19] testing the OLAND process with a rotating biological contactor (RBC) obtained 86% nitrogen removal at the load of 0.675–1.189 kg N-dm\textsuperscript{-3}d\textsuperscript{-1}, and the respective nitrogen removal of 0.58–1.022 kg N-m\textsuperscript{-3}d\textsuperscript{-1}. The operation of the OLAND system can quickly be initiated by certain load of anaerobic sludge. PYNAERT et al. [18] inoculating the RBC reactor with digester sludge obtained maximum nitrogen removal of 1.5 g N-m\textsuperscript{-2}d\textsuperscript{-1} after 100 days.

6. SUMMARY

The deammonification processes using a biofilm offer a promising tool for treating digester liquids. To comply with technological requirements, the CANON and OLAND processes should be carried out in a single bioreactor in which very low oxygen concentration (micro-aerobic conditions) is maintained, which assures formation of a specific aerobic-anoxic biofilm. In different deammonification processes (Anammox, SHARON) the biofilm is used only for reducing nitrites to nitrogen gas and then it is applied in one-and two-reactor combinations or in hybrid systems [8], [25].

A high flexibility of the deammonifying biofilm to the changes in the ammonium nitrogen load in liquids is the advantage of the process [17]. As a result, the reactors in CANON or OLAND arrangement can operate with changing load. Their loading is smaller than that of SHARON or Anammox bioreactors which can operate at 10–20 kg N-m\textsuperscript{-3}d\textsuperscript{-1}. In comparison with other Anammox processes, for deammonification with a biofilm no additional, external source of carbon is necessary. A drawback of the
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methods, especially of the OLAND technology, may be the formation of considerable quantity of nitrites which can react with aliphatic and aromatic amins to form undesirable nitro- and nitroso-derivatives [22].

So far the processes with deammonifying film have been conducted only on a laboratory scale. There is no information about the use of these processes on a full technical scale. At present investment costs of the CANON/OLAND processes are considered to be on average level, while running costs are unknown. The determination of full technological parameters which determine the efficiency of the CANON and OLAND processes should be undertaken, especially on a half-technical and technical scales.

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DEAMONIFIKACJA WÓD OSADOWYCH W SYSTEMACH Z BIOFILMEM

W pracy dokonano przeglądu nowych metod usuwania azotu amonowego z wód osadowych wytwarzanych w procesach przeróbki osadów ściekowych opartych na deamonifikacji w systemach z biofilmem.