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ANAEROBIC AMMONIUM NITROGEN OXIDATION IN DEAMOX PROCESS

The example of an innovative method for the removal of ammonium nitrogen from dewatered digested sludge, landfill leachates and ammonia-rich industrial wastewaters is provided. The process called DEAMOX, is based on anaerobic oxidation of ammonium (Anammox) and on autotrophic denitrification of sulphur, and is an alternative method of conventional nitrification and denitrification.

1. INTRODUCTION

Sludge digester liquors generated during the processes of treatment and digester sludge subjected to methane fermentation pose problems often occurring on the WWTPs. These difficulties encountered in the treatment systems result from characteristics of such liquors – raised temperature and high content of nutrients released during sludge fermentation [1], [34]. High P-loads can be reduced by their precipitation by iron and aluminum salts, whereas nitrogen reduction is possible in a separate technological line in the side stream. The physicochemical methods of ammonium nitrogen reduction (stripping, struvite precipitation) are seldom applied because of high costs and sludge formation. Thus, new strategies and technologies are needed for the biological treatment of liquids containing a high concentration of ammonium nitrogen. Classical nitrification/denitrification may be replaced with bioaugmentation of nitrifiers in the side stream (InNitri, BABE processes) [1], [34] or such modern processes of removing ammonium nitrogen-rich loads as: nitritation/denitritation (SHARON) and deammonification [1], [10], [25], [33], [34].

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2. ANAEROBIC AMMONIUM NITROGEN OXIDATION

Recently, numerous reports have presented the possibilities of ammonium nitrogen oxidation under anaerobic conditions. The biological removal of ammonium nitrogen in a way different from conventional nitrification/denitrification is called "deammonification". The deammonification process consists in oxidizing ammonium to nitrite and then reducing the nitrite to gaseous nitrogen without the formation of indirect compounds in the form of nitrates. This is a two-stage process, which is known under the term "Anammox" (anaerobic ammonia oxidation) [1], [6], [10], [25], [33], [34]. During this process two zones are established, i.e. aerobic and anaerobic/anoxic, where suitable microorganisms oxidize ammonia compounds with nitrites as the electron acceptors. In the first zone, the nitrifying bacteria (*Nitrosomonas*, nitrifier of the first stage) oxidize ammonium, whereas in the second one, nitrites are reduced by the so-called *anammox* bacteria (*Brocardia anammoxidans* and *Kuenenia stuttgartiensis* [6], [29], [32], as well as newly indentified bacteria *Scalindua wagneri* and *Anammoxoglobus propionicus* [15], [16]).

In a practical context, the studies of the Anammox process lead to the devising of numerous methods of ammonium nitrogen removal not only from sludge digester liquors, but also from landfill leachates and industrial wastewaters [1], [6], [10], [25], [34]. The Anammox process can be conducted in various combinations of the abovementioned zones. One and two-reactor systems with activated sludge or a biofilm as well as a hybrid or a membrane technology can be applied. This process can be carried out in CSTR or SBR reactors. Depending on the way in which the Anammox method is conducted, we can distinguish CANON (Completely Autotrophic Nitrogen Removal Over Nitrite) [22], [31] and OLAND (Oxygen-Limited Autotrophic Nitrification–Denitrification) [17], [22], [28] technologies as well as their combinations with partial nitritation, i.e. SHARON–Anammox [37], SNAP (Single-Stage Nitrogen Removal using Anammox and Partial Nitritation) [19], DEMON [38], DIB [18] and autotrophic denitrification [11], [12], [13].

3. SULPHUR AUTOTROPHIC DENITRIFICATION

Conventional denitrification is a process in which nitrates are reduced to gaseous nitrogen through heterotrophic denitrifying bacteria. These bacteria use organic carbon for metabolic processes. However, there is a considerable group of autotrophic microorganisms, which derive energy from oxidizing some inorganic compounds such as: molecular hydrogen, iron and sulphur salts [3], [24].

Bacteria belonging to *Thiobacillus* and *Thiosphaera* genera oxidize reduced sulphur forms such as S^{2-}, S_2O_3, SO_3^{2-} and elementary sulphur using nitrates as electron acceptors under anoxic/anaerobic conditions [24]. In many reports, a theoretical basis for sulphur autotrophic denitrification has been described [8], [27], [36]. A typical autotrophic denitrifying species is *Thiobacillus denitrificans*, which uses oxygen for the oxidation of inorganic sulphur compounds under aerobic conditions, while under anaerobic conditions, it uses nitrates, transforming them into nitrogen gas. However, in the presence of organic carbon, *Thiobacillus* behaves like heterotrophs [3], [24]. The autotrophic denitrification with reduced sulphur compounds as electron donors can be presented as follows [4], [27]:

$$5\ S + 6\ NO_3^- + 2\ H_2O \rightarrow 3\ N_2 + 5\ SO_4^{2-} + 4\ H^+, \quad (1)$$

$$5\ S_2O_3^{2-} + 8\ NO_3^- + H_2O \rightarrow 4\ N_2 + 10\ SO_4^{2-} + 2\ H^+, \quad (2)$$

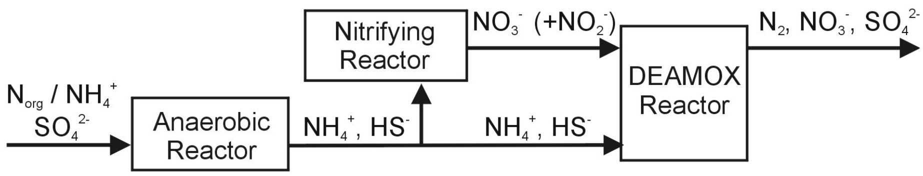
$$1.5\ HS^- + 2.5\ H^+ + 4\ NO_2^- \rightarrow 2\ N_2 + 1.5\ SO_4^{2-} + 2\ H_2O, \quad (3)$$

$$5\ Fe_2S + 14\ NO_3^- + 4H^+ \rightarrow 7\ N_2 + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2\ H_2O. \quad (4)$$

Sulphur autotrophic denitrification can be used in the treatment of water [8], [9], sludge digester liquors [27] and industrial wastewaters [2], [20], [21], [30], [35]. *Thiobacillus* and *Thiosphaera* genera are applied also at a very low C/N ratio or at organic carbon deficiency in treated wastewater in order to promote nitrate denitrification. A disadvantage of sulphur denitrification is high concentration of sulphate produced as a result of this process [3], [21].

4. DEAMOX PROCESS

Recent research on the Anammox process combined with autotrophic denitrification contributed to the development of the DEAMOX (DEnitrifying AMmonium OXidation) technology [23]. In this field of studies, a "denammox" technology, combining classical heterotrophic denitrification with Anammox reaction is also known [26]. MULDER [23] suggests anaerobic oxidation of ammonium nitrogen and nitrites produced as a result of a sulphur autotrophic denitrification in one reactor with anammox bacteria (the figure). This is a specific kind of sulphur denitrification because of a partial reduction of nitrates into nitrites by sulphur bacteria.



Scheme of DEAMOX process

The three-reactor conception of our technology is based on a combined operation of anaerobic reactor, aerobic nitrifying reactor and Deamox reactor. The wastewaters stream containing organic and/or ammonium nitrogen in high concentration and also some sulphates is directed to the anaerobic reactor (AR), from which a part of wastewater is subjected to total nitrification in the nitrifying reactor (NR). Thus, the streams prepared in this way are finally mixed in the last Deamox reactor, where partial denitrification and the Anammox process are carried out within an anaerobic biofilm [7], [11], [12], [13], [14], [23]. The combination of unit processes can be expressed a follows:

$$N_{org} + SO_4^{2-} \rightarrow NH_4^+ + HCO_3^- + CH_4 + HS^- \text{ (AR)}, \quad (5)$$

$$NH_4^+ + O_2 \rightarrow NO_3^- + NO_2^- \text{ (NR)}, \quad (6)$$

$$\left.\begin{array}{ll} 4\,NO_3^- + HS^- \rightarrow 4\,NO_2^- + SO_4^{2-} + H^+, & (7) \\ NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O. & (8) \end{array}\right\} \text{(DEAMOX)}$$

The wastewater composition and a suitable volume of the anaerobic/aerobic stream are an indispensable condition of a stable Deamox process. A theoretical H_2S/NO_3^- ratio calculated on the basis of the process stoichiometry (equation (7)) is 1:4, which corresponds to 0.57 mg S-H_2S/mg N-NO_3 [13].

This new technology was verified by KALYUZHNYI et al. in a laboratory research, with the use of highly concentrated wastewaters from a baker's yeast factory [11], [12], [13], [14]. A compatible system of anaerobic reactors of UASB (Upflow Anaerobic Sludge Bed) type, Deamox and a nitrifying tank (biofilter and activated sludge) allowed one to evaluate the processes suitability for nitrogen removal from strongly concentrated wastewater. The system efficiency depends on the Deamox reactor load. At the load of 1000–1100 mg $N\cdot dm^{-3}\cdot d^{-1}$, the rate of total nitrogen removal reached 880–900 mg $N\cdot dm^{-3}\cdot d^{-1}$ and efficiency ranged from 85 to 90% [11], whereas at the load of 300–748 mg $N\cdot dm^{-3}\cdot d^{-1}$ these parameters dropped to 259–719 mg $N\cdot dm^{-3}\cdot d^{-1}$ and 79–87%, respectively [13]. The studies indicate that nitrogen removal efficiency of around 90% in a Deamox reactor is obtained at the influent N-NO_x/N-NH_4 ratio >1.2 (stoichiometry of the Anammox reaction [6]) and at the influent S-H_2S/N-NO_3 ratio >0.57 mg S/mg N (stoichiometry of the sulphide-driven denitrification of nitrate to nitrite, equation (7)) [11], [12]. A suitable S/N ratios are achieved through the regulation of aerobic and anaerobic feed streams. The Deamox reactor can be supplied with either separated or combined streams [7], [13].

High biomass concentration in the Deamox reactor (>20 g $VSS\cdot dm^{-3}$, VSS-volatile suspended solids) allows for a stable coexistence of diversified groups of microorganisms. The species analysis of biomass revealed the presence of denitrifying autotrophs and *Brocardia anammoxidans*, *Kuenenia stuttgartiensis* species as well as nitrifying and methane bacteria [12]. An elevated temperature of approx. +35 °C obtained due to wastewater outflow from the anaerobic reactor inhibits the growth of *Nitrobacter* (nitrifiers of the second stage) [6]. In that case, an oxidation of nitrite into nitrate did not occur. The *anammox* activity reached 18.7 mg $N\text{-}NH_4 \cdot g^{-1} VSS \cdot d^{-1}$ [11] and 24.0 mg $N\text{-}NH_4 \cdot g^{-1}$ $VSS \cdot d^{-1}$ [13]. Moreover, the influence of heterotrophic denitrification was insignificant due to a low content of easily available volatile fatty acids (VFA) and a high content of hardly biodegradable organic compounds [13].

Ammonia nitrogen removal by anaerobic oxidation with sulphates as an electron donor and by the Anammox process was observed also by FDZ-POLANCO et al. in a methanogenic fermentation of distillery wastewater with high load of ammonia nitrogen and sulphur [5]. The authors consider the nitrogen changes to be analogous to those in the Anammox process. However, full stoichiometry of the new process is totally different from a Deamox equation.

5. SUMMARY AND CONCLUSIONS

A new process, called DEAMOX, allows a considerable decrease of a total nitrogen concentration in treated wastewater containing simultaneously ammonium nitrogen and sulphur in high concentration (e.g. sulphates). This process can also be applied in the case of the deficiency of organic content indispensable to complete or partial denitrification. This new solution is based on combining two processes: sulphur autotrophic denitrification and the Anammox process in one-reactor within anaerobic biofilm.

In comparison with the systems based on the Anammox (CANON, SHARON-Anammox etc.), the Deamox technology has the following advantages:

- easy control of nitrites production fed to the Deamox reactor,
- low concentration of nitrites which can be a source of NO and N_2O generated by *anammox* bacteria,
- anoxic conditions in the Deamox tank favour the growth of sludge granules, which stimulates the development of *anammox* species,
- raised temperature in the Deamox reactor inhibits the growth of the second stage nitrifiers,
- possibility of a smooth change of the Deamox reactor loading by controlling the load of ammonium nitrogen.

A drawback of the technology under analysis is a low process capacity: <0.9 kg $N \cdot m^{-3} \cdot d^{-1}$ with reference to the systems based on the Anammox processes. The nitrogen removal rate in an OLAND system amounts to 1.05 kg $N \cdot m^{-3} d^{-1}$ [28], in CANON – 1.5 kg $N \cdot m^{-3} d^{-1}$ [31], and in Anammox – about 8.9 kg $N \cdot m^{-3} d^{-1}$ [31]. The SHARON–Anammox system allows a lower efficiency, i.e. 0.75 kg $N \cdot m^{-3} d^{-1}$, to be achieved [37].The formation of a considerable amount of sulphates is another disadvantage of the Deamox system.

The Deamox technology is an easy method of obtaining a suitable composition of treated wastewater, which is achieved through the control of aerobic and anaerobic streams feeding reactors. This assures flexibility in simultaneous removal of nitrogen and sulphur content. Using a nitrifying reactor (e.g. biofilter) before Deamox tank is advisable in order to assure nitrification of a part of wastewater stream [11], [12]. A dosage of sulphur compounds or non-toxic industrial wastewater with sulphates (e.g. wastewater from cellulose production) is admissible due to insufficient amount of sulphates in wastewaters. Iron salts (e.g. $FeSO_4$) used for phosphorus precipitation in wastewater can also be a source of sulphates in the DEAMOX process. This technology can be modified by a direct supply of sulphide load together with industrial wastewater to the Deamox reactor.

The DEAMOX process can successfully be applied to the treatment of wastewater rich in nitrogen and produced during dewatering of digested sludge and industrial wastewaters (distillery, paper and cellulose industry), as well as landfill leachate with increased content of ammonia and sulphates, provided that nitrification inhibitors (e.g. high metals) are absent or removed. There is, however, no information about the use of the DEAMOX technology on a full or half-technical scale. This new technology requires further studies in order to determine its utility.

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ANAEROBOWE UTLENIANIE AZOTU AMONOWEGO W PROCESIE DEAMOX

Zaprezentowano przykład nowatorskiej metody usuwania azotu amonowego z wód osadowych wytwarzanych w wyniku przeróbki osadów ściekowych, odcieków ze składowisk odpadów oraz silnie skażonych amoniakiem ścieków przemysłowych. Analizowany proces DEAMOX opiera się na anaerobowym utlenianiu amoniaku (Anammox) oraz autotroficznej denitryfikacji siarkowej i stanowi alternatywę dla klasycznej nitryfikacji/denitryfikacji.