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Denitrification of drinking water in a two-stage biofilm membrane bioreactor

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ABSTRACT

A two-stage biofilm membrane bioreactor (BMBR) using a commercially available biocarrier material for treating nitrate-contaminated groundwater was developed. The performance of the anoxic stage (denitrification) and oxic stage (total organic carbon removal) in the pilot BMBR system was evaluated and compared with the performance of other membrane bioreactor systems. With a residence time of 2.6 h, a nitrate concentration in treated water of below 1 mg/L could be achieved in the system without any formation of intermediate nitrite ions. At the same time, the use of biocarriers with specific mechanical properties significantly increases the operational period of the membranes.

Keywords: Biocarrier; Biofilm; Denitrification; Drinking water; Membrane bioreactor

1. Introduction

Groundwater resources in numerous countries are often contaminated with nitrates, mainly due to intensive agricultural activities and the uncontrolled use of fertilizers. Strict water standards for drinking water have been accepted worldwide due to the fact that high nitrate concentrations in drinking water sources represent a direct threat to human health. For example, the European directive 98/83/EC sets the quality standards for drinking water intended for human consumption and states that the maximum allowed concentrations for nitrate and nitrite ions are 50 and 0.5 mg/L, respectively.

Various physico-chemical methods are reported to remove nitrates from water (e.g. ion exchange, reverse osmosis and electrodialysis), but they fail to completely eliminate nitrate ions as they yield concentrated waste brines, which require further treatment or disposal [1,2]. Biological denitrification has been found to be the most promising and versatile approach compared to other processes, since it effectively eliminates the nitrate ion under anoxic conditions by using the chemically bound oxygen in the nitrate as a terminal electron acceptor. An additional electron donor must be supplied to the biological denitrification system in order to achieve the appropriate activity of the micro-organisms as well as the desired extent of nitrate reduction. Unfortunately, traditional activated sludge processes may produce effluents of inadequate quality regarding the concentration of suspended solids and residual donor content. Correspondingly, recent research has

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now focused on combining the biological process with membrane technology in the membrane bioreactor (MBR), which can provide efficient retention of both the microbial biomass and the electron donor. McAdam and Judd [1] reviewed the potential of various trailed MBR configurations that have been applied in drinking water treatment such as pressure-driven MBRs or gas transfer MBRs. Pressure-driven MBRs are based on suspended (heterotrophic) biomass technology with membranes placed within or external to the bioreactor, physically rejecting the biomass. Due to the pressure applied for permeate extraction, denitrifying biomass accumulates on the membrane surface in the form of a filter cake allowing further denitrification to take place, while the treated water passes through the ''biofilm'' and membrane. Ethanol or methanol are mainly used as electron donors in these systems [1,3–7]. Major disadvantage of the pressure-driven MBR systems is membrane fouling, which limits their sustainability and wider use [7]. On the other hand, gas transfer MBRs employ gas-permeable hollow fibres with autotrophic denitrifying biofilm growing on the shell side of the membrane. Hydrogen gas (H_2) is used as an electron donor in these systems [1,8]. The disadvantage of gas transfer MBR systems is that the membrane is not used for direct filtration in order to reject the biomass, but acts only as an electron donor supplier [1]. Recently developed so-called hybrid systems [1] have focused on combining processes from different types of MBR systems. Rezania and coworkers [9] incorporated both gas transfer and submerged pressure-driven membranes into the same reactor. Wang and coworkers [10] presented a fibre-based biofilm reactor with methanol as an electron donor, where the biofilm also acts as a filter for suspended solids. Research work focused on the development of the pressure-driven MBR technology for wastewater treatment shows that by employing a biofilm instead of activated sludge (suspended biomass), beneficial effects could be achieved on the kinetics of the biological processes and membrane operation. Some other advantages of biofilm MBR systems, such as greater flexibility, reliability and easy-to-use operation, are also documented in the literature [11–13]. In the article by Ivanovic and Leiknes [14], the status of biofilm MBR technology for wastewater treatment was reviewed in general. However, specific data concerning drinking water treatment were not included, which indicates a lack of research work in this field.

The objective of this study was to investigate the overall performance of the anoxic/oxic biofilm MBR (BMBR) system, employing a commercially available biomass carrier material for the removal of nitrate ions from the polluted groundwater. The advantages of the proposed BMBR system over other types of MBR systems are discussed.

2. Materials and methods

2.1. Experimental set-up and operating conditions

The experimental set-up used in the biological denitrification tests is schematically illustrated in Fig. 1. The main component of the system is a reactor made of Plexiglas divided into anoxic and oxic compartments. The volume of the anoxic part was 5 L, while the active volume of the oxic part (after the membrane module was inserted) was equal to 2.5 L.

Peristaltic pumps (Masterflex) were used for feeding the influent into the unit, and permeate of the effluent through the membrane module. An ultrasonic lever sensor (Flowline, model Echoswitch II) connected to a peristaltic pump controlled the liquid level above the membrane module in the oxic part of the reactor. Aerobic conditions in the fully mixed oxic stage were provided by continuous aeration using a porous flexible plastic tube, which was connected to an air compressor and air flow meter. Intensive aeration also managed to efficiently mix the reactor content (liquid phase and biocarriers). On the other hand, a mechanical stirrer equipped with a Visco Jet® impeller (Heidolph) was used for the efficient mixing of the anoxic stage content. A flat-sheet membrane (cartridge type 203, Kubota Ltd., Japan), made of chlorinated polyethylene with a nominal pore size of 0.4 micron and an effective surface of $0.3\,m^2$, was submerged in the oxic part of the reactor unit. The anoxic and oxic stage of the reactor unit were filled with 2 L (40 vol.%) and 0.8 L

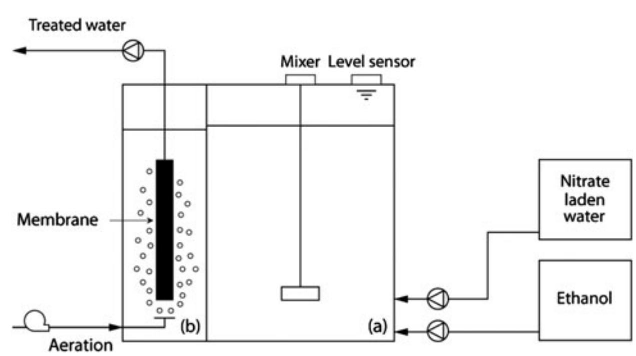

Fig. 1. Schematic display of the experimental set-up with the anoxic (a) and oxic (b) stage filled with Biocontact N biocarriers.

Fig. 2. Images of Biocontact N biocarrier: as received (a) and after inoculation (b) at 25× magnification.

(30 vol.%) of polyurethane-based Biocontact-N carriers (Nisshinbo Chemical, Japan; specific surface area: 1,300 m^2/m^3; void space: 21%), respectively (see Fig. 2(a)). All the experiments were performed at a constant room temperature of 20 ± 2˚C.

2.2. Synthetic water and organic carbon (electron donor) source

The properties and composition of the tap water used in the present study are listed in Table 1. Due to the low chloride concentration, we presumed no effect of the residual disinfectant on the biomass. The synthetic underground polluted water (influent) was prepared daily from tap water (with an average concentration of nitrate ions of 15.3 mg/L) and potassium nitrate (p.a. grade, Merck), which was used as a source of additional nitrate ions. Potassium phosphate (K_2HPO_4, p.a. grade, Merck) served as a source of P (1.0 mg/L P). The employed influent P/N ratio was in the range of 0.03–0.06. The influent solution was kept in a separate 100 L tank, from which it was fed into the anoxic stage of the BMBR system.

Table 1
The properties and composition of tap water, effluent from the anoxic stage and final effluent from the BMBR system

Parameter	Tap water	Effluent from the anoxic stage	Final effluent
Temperature [˚C]	11.5	19.6	19.8
pH [–]	7.1	7.3	7.2
DO [mg/L]	8.1	0.1	7.9
ORP [mV]	235	115	111
Hardness [mg/L] (as $CaCO_3$)	171	175	170
Alkalinity [mg/L] (as $CaCO_3$)	220	233	221
NO_3^- [mg/L]	[a]15.3	[b]0.8	0.7
SO_4^{2-} [mg/L]	18.2	18.7	18.1
Ca^{2+} [mg/L]	53.5	51.5	50.4
Mg^{2+} [mg/L]	15.6	13.2	12.3

[a]Spiked to 150 mg/L in the feed stream.
[b]Average value.

Ethanol solution (p.a. grade, Aldrich) was used as a carbon (i.e. electron donor) source in the denitrification experiments. The solution was prepared daily and kept in a separate 10 L tank, from which it was fed precisely into the anoxic stage of the BMBR system by means of a multi-channel peristaltic pump (Ismatec, model IPC).

2.3. Analytical methods

Nitrate and nitrite ions were analysed using standardized ion chromatography methods (Dionex, model DX-120). The total amount of organic substances in the samples was determined by measuring the total organic carbon (TOC) content. The latter was determined applying a high-temperature catalytic oxidation (HTCO) method carried out at 750˚C using an advanced TOC analyser (Teledyne Tekmar, model Torch).

2.4. Experimental procedure

Prior to the measurements, the pilot BMBR system was inoculated with a suspension of activated sludge extracted from the local municipal wastewater treatment plant. Influent with nitrate ions, ethanol, P and 0.2 g/L of activated sludge was introduced into the system for 14 days until a stable biofilm was formed on the surface of the biocarrier particles in the anoxic and oxic stages (Fig. 2(b)).

A synthetic polluted groundwater (influent) with a nitrate concentration of either 70, 100, 150 or 160 mg/L and a constant C/N ratio of 1.5 was treated in four series of experiments. The pilot BMBR system was operated in continuous mode with a constant influent and effluent (permeate) flow rate of 2 L/h. A 5-day period was implemented for the adaptation of the system after the nitrate loading conditions were changed. The biofilm biomass concentration/nitrate loading balance was established under the given operating conditions during the adaptation period. A system performance was then monitored in the following 14-day period in each series of experiments.

3. Results and discussion

3.1. Nitrate removal

Concentrations of NO_3^- and NO_2^- ions measured in the effluent from the anoxic stage at different influent NO_3^- concentrations and a constant influent flow rate of

2.0 L/h (which corresponds to HRT = 1.7 h) are presented in Fig. 3. At these conditions, the concentration of biomass in the effluent discharged from the anoxic stage was below 100 mg/L in all sets of experiments. It can be seen that the average effluent NO_3^- concentration was below 1 mg/L (Fig. 3(a)) and the NO_2^- concentration was found to be below 0.3 mg/L (which was the level of detection) up to an influent NO_3^- concentration of 150 mg/L and nitrate loading of 1.44 g/(L day) (Fig. 3(b)). The actual denitrification rate equals to 60 mg/(L h) NO_3^-. At an influent NO_3^- concentration of 160 mg/L, the average effluent NO_3^- concentration increased to 4.5 mg/L, which is still well below the maximum allowed concentration of 50 mg/L. At the same time, an average NO_2^- concentration in the discharged effluent of 1.3 mg/L considerably exceeded the limited value of 0.5 mg/L. The sharp increase in the effluent nitrate and nitrite concentrations could be explained by the fact that at the feed nitrate concentration up to 150 mg/L, an optimum balance was obtained between nitrate load, concentration of biomass in the biofilm and carrier concentration (filling ratio) for the required effluent quality in the specific biofilm reactor system. Wang and coworkers [13] observed that the increase in the carrier concentration, in order to increase the concentration of immobilized biomass in the reactor, could lead to an increase of particle-to-particle attrition. At some point, too many micro-organisms are detached from the biofilm and the biomass concentration in the biofilm could decrease, resulting in lower activity.

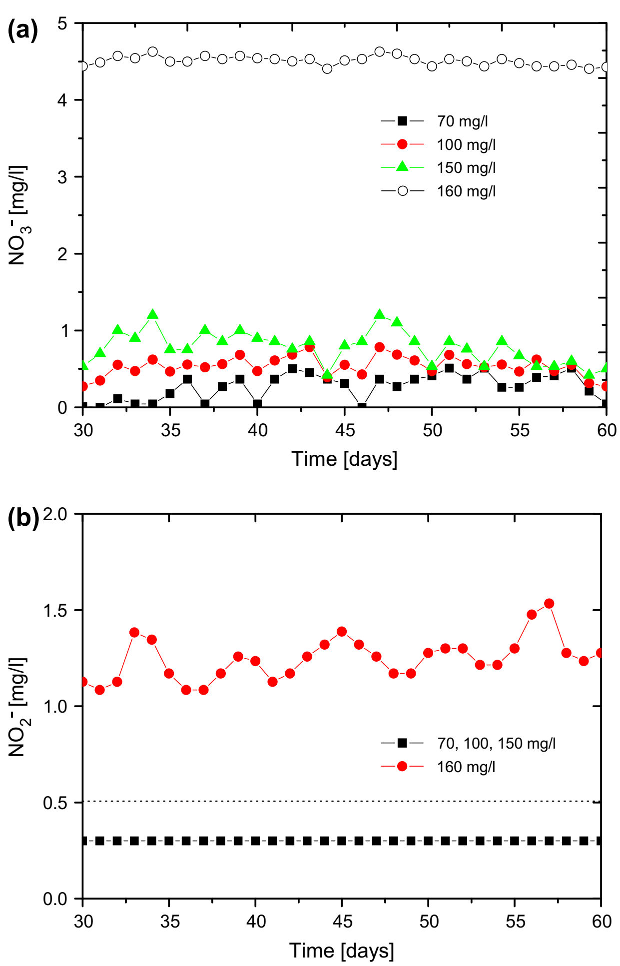

Fig. 3. (a) Nitrate and (b) nitrite concentrations measured in the effluent from the anoxic stage for different nitrate concentrations in the influent stream.

Further, a minimal increase in alkalinity and pH level in comparison to the values typical for tap water was detected in the anoxic stage at an applied nitrate loading of 1.44 g/(L day) (Table 1). As in the literature data, the observed pH value of 7.3 was within the range of 7.0–7.5, which was found suitable for efficient denitrification processes in suspended biomass systems [13,15,16]. The investigated denitrification and membrane filtration process also exhibited a minimal effect on the content of calcium, magnesium and sulphate ions in treated water—final effluent (Table 1).

Results showed that 1.7 h of HRT in the anoxic stage of the pilot BMBR system is needed for the treatment of groundwater polluted with 150 mg/L of nitrate ions in order to provide an effluent with the drinking water quality. It can be also stated that the accumulation of NO_2^- is the limiting factor in the process. This is in agreement with the results of Nuhoglu and coworkers [6], who studied the denitrification process with synthetic drinking water in the suspended biomass MBR system under similar conditions (ethanol was used as a carbon source and P solution was used as an additional nutrient). They found that for all influent nitrate concentrations in the range of 70–550 mg/L, standard limits for NO_3^- were met much earlier than for NO_2^-. For example, due to NO_2^- accumulation in the suspended biomass denitrification reactor, an HRT longer than 20 h was needed for the treatment of polluted water with an influent NO_3^- concentration of 150 mg/L in order to produce effluent with the required quality. Buttiglieri and coworkers [5] studied the denitrification process with polluted lake water in the suspended biomass MBR system (again using ethanol as a carbon source and P solution as an additional nutrient). A minimal HRT of 10 h was needed for the treatment of water with an NO_3^- feed concentration of 130 mg/L in the anoxic stage of the pilot suspended biomass MBR system. The nitrite concentration was found to be below the maximum allowed concentration as long as the HRT was higher than 8 h in a fibre-based biofilm reactor, in which synthetically polluted groundwater was treated using methanol as an electron donor [10]. Furthermore, the poor adaptability of autotrophic bacteria under drinking water denitrification conditions (low nitrate loadings) was demonstrated in gas transfer MBR systems [1]. For example, complete denitrification without nitrite accumulation was accomplished at the nitrate loading of 0.5 g/(L day) in a hydrogen-depended denitrification process with a novel hydrogen delivery system [9]. However, as reported above, a nitrate loading of 1.44 g/(L day) can be applied in a studied BMBR at similar operating conditions.

3.2. Organic carbon removal

Concentrations of soluble organic matter in the effluent from the anoxic and oxic stages are presented in Fig. 4. The TOC values in the effluent from the anoxic stage gradually increased with increasing nitrate loading (Fig. 4(a)). It is seen that biomass in the oxic stage was able to reduce the organic matter content to the TOC level of tap water up to an influent NO_3^- concentration of 150 mg/L. At an influent NO_3^- concentration of 160 mg/L, TOC values higher than 20 mg/L were detected in the effluent from the oxic stage of the pilot BMBR system. Although the TOC concentration is usually not a standard limiting factor, the remaining organic carbon content in treated water higher than 5 mg/L (expressed as TOC) is not acceptable. It should be noted that the degradation of organic matter in the oxic stage was not limited by the concentration of dissolved oxygen, which was near the value of saturation at the given temperature of the liquid phase. Intensive aeration increases the efficiency of oxygen transfer from the gas to the liquid phase, though it could also negatively affect the biofilm formation due to more intensive biocarrier particle-to-particle attrition [9]. Due to the relative large membrane pore size, no measurable effect of the membrane filtration on the additional removal of TOC was noticed during the performed experiments.

The oxic stage of the pilot BMBR system was operated in this work at an HRT of 0.93 h. For example, in the suspended biomass MBR system operating with an influent C/N ratio of 1.8 studied by Buttiglieri and coworkers [5], a minimal HRT of 10 h in the aerobic tank was needed to keep the TOC value at a required level. While the combined HRT needed for the complete treatment of polluted water in the pilot BMBR system was under 3 h, an HRT over 25 h was required for the same task in the suspended biomass MBR system studied by Nuhoglu and coworkers [6]. At a C/N ratio of 1.25 and HRT higher than 8 h, the TOC could

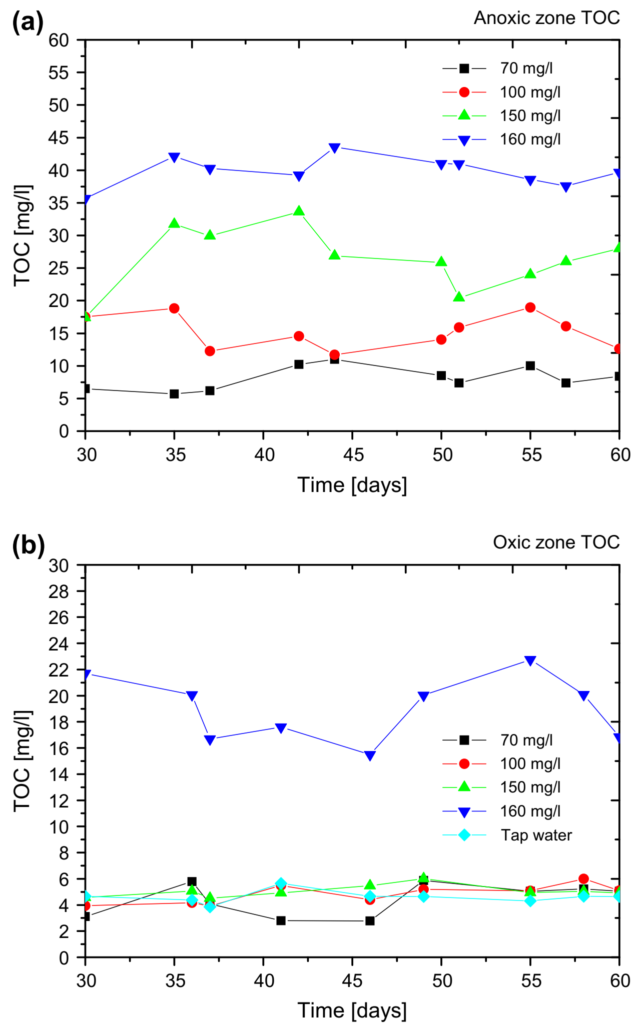

Fig. 4. The TOC concentration measured in the effluent from (a) the anoxic and (b) the oxic stage for different nitrate concentration in the influent stream.

no longer be detected in the effluent from a fibre-based biofilm reactor with methanol used as an electron donor [10]. Drinking water treated in the gas transfer MBR systems with hydrogen as an electron donor is prone to biomass sloughed from a biofilm increasing dissolved organic carbon (DOC) concentration in the effluent [1]. An increase in the effluent DOC from 11 to 31 mg/L was observed during the treatment of drinking water in the hydrogenotrophic hollow fibre MBR [8], which means that further treatment is necessary to remove biological products from the water stream prior to distribution.

3.3. Membrane module operation

The process pressure was increased by 1.5 kPa (10% of the initial value) at the end of experimental period in order to maintain a constant permeate (final effluent) flow of 2 L/h. The average concentration of suspended micro-organisms in the oxic stage of the BMBR system was found to be 420,000 CFU/mL, which was then reduced by filtration through the membrane module to an average value of 5,300 CFU/mL in the permeate (TSS below 1 mg/L). This demonstrates the relevant membrane retention capacity to keep back suspended biomass over 0.4 microns. No chemical cleaning of the membrane surface was performed during the experimental period. The membrane operational period (i.e. the period between subsequent membrane hydrocleaning steps) in the pilot BMBR system was estimated to be about 1,100 h.

The membrane fouling phenomenon is a rather complex process, which is still not completely understood despite more than a decade of worldwide research [17]. In suspended biomass (activated sludge) MBR systems, it is commonly understood that membrane operation at lower concentrations of biomass is beneficial due to lower viscosities and lower DO diffusion resistance [8]. In the suspended biomass MBR system studied by Buttiglieri and coworkers [5], air flow in the oxic stage was used to control the process pressure. In their case, the trans-membrane pressure was restored with the increasing air flow, which, on the other hand, means higher energy consumption. Contrary to the above general statement, Nuhoglu and coworkers [6] found that a higher suspended biomass concentration is more advantageous in terms of obtaining higher permeate flow rates due to the formation of larger suspended bioparticles. However, a higher suspended biomass concentration, as they report, would lead to smaller specific denitrification rates and higher energy requirements for mixing and aeration. In the pressure-driven fibre-based biofilm reactor presented by Wang and coworkers [10], the biofilm also acted as a filter for suspended solids. Consequently, less than 3 mg/L of suspended solids were detected in the final effluent and no clogging problems occurred during the experimental period; however, there were no data reported on the effect of filtration on the denitrification process and overall system performance.

The size of the biocarriers and filling fraction exhibit an important effect on suspended biomass particle size distribution and concentration [18]. In the presence of filamentous bacteria which enhance the formation of extracellular polymeric substances (EPS), reduction of the suspended biomass concentration by the implementation of biocarriers in the MBR systems might not lead to better membrane performance [11]. In principle, the use of larger biocarrier particles and lower filling fractions result in the formation of larger flocs that detach from the biofilm resulting in lower fouling rates [18]. Due to the specific mechanical properties of the biocarrier material used in the experiments, collisions of floating biocarrier particles with the outer membrane surface (though without damaging it) considerably increase the shear force, which is otherwise generated by the aeration itself. Because of this, the deposition of bacteria on the membrane surface (i.e. cake formation) was significantly decreased, which in turn considerably reduced the fouling rate.

4. Conclusions

The obtained results of drinking water denitrification containing up to 150 mg/L of nitrates, show that the required water quality regarding NO_3^- and NO_2^- concentrations, as well as the TOC values, could be achieved in the anoxic/oxic two-stage BMBR system with substantially shorter HRT's or at higher nitrate loadings than in comparable MBR systems. At the same time, the use of commercially available biocarriers with specific mechanical properties significantly increases the operational period of the membranes. This means that more compact reactors could be used on the industrial scale, which further increases the economical and practical potentials of biological processes in drinking water treatment technologies.

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