

**PERFORMANCE OF HYDROGEN -DRIVEN DENITRIFYING MEMBRANE
BIOFILM REACTOR (MBfR)**

By Dominika Celmer

**A Thesis Submitted to the Faculty of Graduate Studies
in partial fulfillment of the requirements
for the degree of**

Doctor of Philosophy

**Department of Civil Engineering
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Performance of Hydrogen - Driven Denitrifying Membrane Biofilm Reactor (MBfR)

BY

Dominika Celmer

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of
Manitoba in partial fulfillment of the requirement of the degree**

Of

Doctor of Philosophy

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To My Grandpa Stanislaw Maciejewski

ABSTRACT

The goal of this research was to develop and evaluate the method of controlling structure of biofilm and performance of membrane biofilm reactor (MBfR) for hydrogen driven denitrification. The particular nitrate contaminated streams treated in this study include synthetic ground water- used in initial studies on feasibility of MBfRs, and tertiary wastewater obtained from North End Water Pollution Control Centre (NEWPCC) - used for actual evaluation of analyzed methods. The controlling methods were based on hydrogen limitation, application of shear force caused by mixing and nitrogen sparging and introducing ultrasound treatment into operating mode of MBfR.

It was found that starving conditions (restricted hydrogen supply) limit biofilm development and allow maintaining stable denitrification rates ($0.59 \pm 0.04 \text{ gNO}_3\text{-N d}^{-1} \text{ m}^{-2}$). Despite the availability of excess nitrates no significant growth of microorganisms was observed within the biofilm. Larger fluctuations were observed in measured total solids (TS) concentration within biofilm. Increase in TS and overall biofilm density was caused either by precipitation of the buffer substances or an attachment of solids present in the incoming wastewater, which appeared to be the main weakness of this method.

The application of shear force was found to minimize biofilm thickness, and increase biofilm density. The density of the biofilm was still significantly lower than the values obtained in system operated with hydrogen limitation and overall changes in biofilm structure allow obtaining higher removal rates (up to $0.93 \pm 0.14 \text{ g N (d} \cdot \text{m}^2)^{-1}$ for 300 μm thick biofilm). Hydrodynamic shear force was a reliable and efficient tool for controlling biofilm structure and MBfR performance.

The test with ultrasound treatment allowed to increase the denitrification rate up to $1.17 \pm 0.11 \text{ gNO}_3\text{-N m}^{-2} \text{ d}^{-1}$ for the highest tested dosage. The benefit of high removal rates was minimized by the negative impact of ultrasound on biofilm viability observed for high ultrasound dosages. Moderate dosages were recommended as they were found to increase bacteria viability within a biofilm, probably due to removal of excess dead cells. It was found that ultrasound has no significant impact of volatile solids concentration but in high dosages it can cause decrease in protein content and destabilize the biofilm matrix. Similarly, application of ultrasounds seemed to diminish the hydrogen utilization rate (HUE) as values of 15 – 46% were observed while application of mixing and nitrogen sparging used as a shear force resulted in much higher observed HUE (40% to 100%).

The analysis of the cost of introducing of MBfR for tertiary treatment showed that it can be good alternative for heterotrophic denitrification. Hydrogen - driven denitrification within MBfR with full denitrification controlled by high level of mixing would be recommended as it combines good and stable effluent quality with low net present value (NPV) of the created system.

The analysis showed that different operating modes affect the protein, carbohydrates and EPS content within biofilm, as well as biofilm stability and MBfR performance.

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LIST OF ABBREVIATIONS

MBfR – membrane biofilm reactor
NO₃ – N – nitrogen in form of nitrates
SDR – specific denitrification rate
COD – chemical oxygen demand
TCOD – total chemical oxygen demand
SCOD – soluble chemical oxygen demand
DO – dissolved oxygen
TSS – total suspended solids
VSS – volatile suspended solids
HUE – hydrogen utilization efficiency
r – biofilm thickness
R- fibre radius
V – biofilm volume
l - fiber length
TS – total solids concentration within a biofilm (total solids density)
VS – volatile solids concentration within a biofilm (volatile solids density)
VS/TS – ratio of volatile to total solids within a biofilm
EPS – extracellular polymeric substances
p – total proteins content
c- total carbohydrates content
 μ_{\max} – maximum specific growth rate
S – concentration of limiting substrate in the solution
X – biomass concentration
Y – maximum yield coefficient
K_s – half velocity constant
k- max rate of substrate utilization per mass unit
m_s- substrate required for maintenance
 μ - viscosity of the fluid
 τ_w shear stress due to viscous effects
P - normal stresses due to the pressure
F – acting force, centripetal force
A- surface area of the submerged body
m – body mass
v – velocity
r – radius
 ω – angular velocity

CHAPTER 1: INTRODUCTION¹

1.1 THE FUTURE OF NUTRIENT REMOVAL

In 1914, Ardern and Lockett introduced activated sludge technology into wastewater treatment facilities (Ardern and Lockett, 1914) and provided a means for larger cities to begin protection of water supplies and prevention of waterborne illness. Research completed since the inception of these process developed a more complete understanding to permit greater control of the bacterial processes involved and hence development of nutrient modifications to activated sludge. Today, the emerging approach of limiting both immision and emission of nutrients stands as the State-of-the Art for wastewater treatment technologies and offers promise of better protection of receiving waters while both causing dispute and opening new avenues of research (Murthy and Oleszkiewicz, 2007).

The new emerging limit of technology (LOT) based regulations combining emission and immision standards, aim at developing sustainable practices of water reclamation and protecting receiving waters from negative changes after effluent discharge. Implementation of LOT creates new areas of research for both nitrogen and phosphorus removal. These include refinement of existing nitrogen and phosphorus removal processes to achieve greater removals and development of new polishing nitrogen and phosphorus removal processes to facilitate very low nitrogen and phosphorus effluent

¹ Part of this chapter were accepted for publication in International Journal of Environment and Waste Management (2007)

Formation of autotrophic nitrogen-removing biofilms on porous and non-porous membranes
D.Celmer , J. -H. Hwang, N.Cicek, J. Oleszkiewicz

concentrations. Such an advanced wastewater treatment is defined as any process designed to produce an effluent of higher quality than normally achieved by secondary treatment processes or containing unit operations not normally found in secondary treatment (Sonune and Ghate, 2004). The increasing space needed for advanced treatment launched the search for alternatives which include biofilm reactors as one of the promising options. Biofilm reactors progressed in the second half of last century with the introduction of plastic media and with increased understanding of the process mechanism. The application of biofilm technology when used to its optimal potential can be applied as a treatment solution for the most stringent requirements.

1.2 PRESENT AND FUTURE OF NITRATE REMOVAL

Nitrate is one of the primary pollution of groundwater, which causes the eutrophication of natural environments and is known to have adverse effects on human health (Blue Baby Syndrom) and livestock health (lower milk production, reduced weight gain, stillborn calves). Due to the effect of nitrate on health the World Health Organization (WHO) set the limit for nitrate in drinking water at $10 \text{ mg NO}_3\text{-N l}^{-1}$, which magnifies the importance of nitrate removal from both wastewater and drinking water. There are several alternatives for nitrate removal including physical (ion exchange, electrodialysis, and reverse osmosis), chemical (reaction with aluminum and ferric) and biological (heterotrophic or autotrophic denitrification) methods. While, physical and chemical methods are mostly used for drinking water, biological denitrification is widely used for wastewater treatment.

1.3 POTENTIAL OF AUTOTROPHIC BIOLOGICAL DENITRIFICATION FOR TREATMENT OF LOW ORGANIC CARBON STREAMS

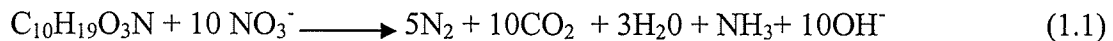
1.3.1 Heterotrophic vs. autotrophic biological denitrification

The biological denitrification process completes nitrogen removal from the stream by converting nitrate and nitrite to nitrogen gas. There are many genera of bacteria which are able to carry out this process. Most of the denitrifiers are heterotrophic bacteria from species such as *Achromobacter*, *Acinetobacter*, *Agrobacterium*, *Alcaligenes*, *Bacillus*, *Chromobacterium* (Lee et al., 2002). Heterotrophic denitrification involves biological oxidation of many organic substrates in wastewater using nitrate or nitrite as the electron acceptor. Electron donors generally come from one of three sources:

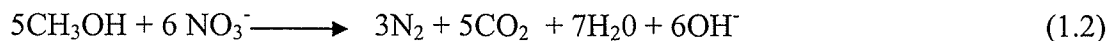
- Biodegradable, soluble COD in the influent stream (wastewater),
- Biodegradable, soluble COD produced during endogenous decay,
- Exogenous COD source such as methanol, ethanol, or acetate.

The stoichiometry of heterotrophic denitrification depends on the type of carbon source utilized [Metcalf & Eddy, ed. IV, 2003].

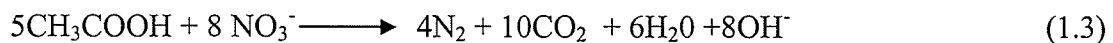
a) Biodegradable organic matter from wastewater:



b) methanol:



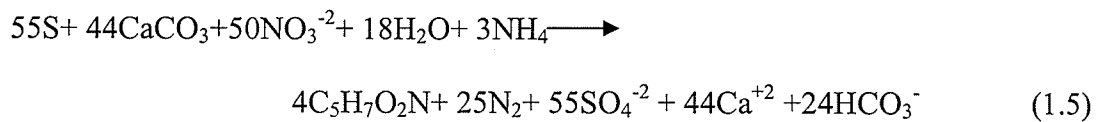
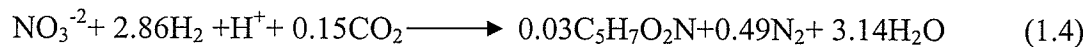
c) acetate :



An alternative option is autotrophic denitrification. The energy source for autotrophic denitrifiers comes from oxidation/reduction reactions with elements such as hydrogen or

sulphur as the electron donor. For that reason, autotrophic denitrification processes have been divided into hydrogen-based and sulphur-based reactions (H_2S , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, SO_3^{2-} , S). Substances present in the water or wastewater, such as CO_2 or HCO_3^- are the inorganic source of carbon for the bacteria.

The stoichiometry of the hydrogen and sulphur driven autotrophic denitrification process is as follows:



The strains of sulphur-based denitrifiers are *Thiobacillus denitrificans* and *Thiomicrospira denitrificans*, while hydrogen driven autotrophic denitrification is carried out by *Ochrobactrum anthropi*, *Pseudomonas strutzeri*, *Paracoccus denitrificans*, and *Paracoccus panthotrophus* (Liessen et al, 1992; Selenka and Dressler, 1990).

As a result of differences in carbon source, autotrophic and heterotrophic bacteria exhibit different kinetic parameters. Autotrophs use more of their energy on cell synthesis than heterotrophs, thus their yield of cell mass and growth rates are lower. The autotrophic vs. heterotrophic biomass yield is 0.24:0.6 or 0.24: 0.9 g $\text{C}_2\text{H}_5\text{O}_2\text{N}$ (g $\text{NO}_3\text{-N}$)⁻¹ removed (Metcalf and Eddy, 2004; Wisniewski et al, 2001; Vasiliadiou et. al., 2006). Process rates (denitrification) are also lower for autotrophic than heterotrophic bacteria. The comparison of the denitrification rates is presented in the Table 1.1.

The treatment of low organic carbon wastewaters is often plagued by inefficient nitrogen removal, due to inhibited heterotrophic denitrification process. Lack of organic electron donor is usually solved by adding expensive external organic carbon source (methanol,

ethanol). An excess of organic carbon in the effluent is a common by-product of such a treatment due to fluctuations in nitrate concentrations. Eliminating the need for organic carbon addition, preventing residual organic carbons in the effluent, low biomass yields, lower chemical cost, can be achieved by application of autotrophic denitrification where carbon dioxide is used as carbon source. Carbon dioxide is present in wastewater in various forms such as H_2CO_3^* or HCO_3^- and hydrogen and sulphur have to be supplied to the wastewater stream.

Table 1.1 The comparison of the denitrification rates for hetero- and autotrophic, hydrogen driven denitrification

external source of electron donor	specific denitrification rate	literature
	[mg N/ g VSS* h]	
methanol	34	Hagman et al., 2008
methanol	3.2	Peng et al., 2007
methanol	3	Nyberg et al., 1996
ethanol	15	Hagman et al., 2008
ethanol	9.6	Peng et al., 2007
ethanol	10	Nyberg et al., 1996
acetic acid	4.5	Patel J. And Nakhla G., 2006
acetic acid	1-3	Kujawa K., 1999
acetic acid	6.2	Hagman et al., 2008
acetic acid	12	Peng et al., 2007
acetic acid	1.6	Pala A. And Bolukbas O., 2005
acetate+ ethanol	14-40	Hagman et al., 2008
butiric acid	3.2	Patel J. And Nakhla G., 2006
propionic acid	1.6	Patel J. And Nakhla G., 2006
glucose	1.2	Pala A. And Bolukbas O., 2005
MWW	1.2	Patel J. And Nakhla G., 2006
MWW	0.6-1	Kujawa K., 1999
primary effluent	1.2	Patel J. And Nakhla G., 2006
endogenous COD	0.2-0.6	Kujawa K., 1999
lactate	6.9	Sage et al., 2006
lactose	5.1	Sage et al., 2006
casein	3.7	Sage et al., 2006
whey protein	2.6	Sage et al., 2006
molasses	2.9-3.6	Quan Z.X. Et al., 2005
fatty acids from PS	0.46	Elefsiniotis P. et al., 2004
hydrogen	17-22	Rezania et al., 2005
hydrogen	9.16-15.41	Kurt et al., 1987
hydrogen	110	Vasilidiou et al., 2006
	[g N/ m ² d ⁻¹]	
methanol	0.24	Liessen et al., 1992
methanol	4	Mansell and Schroeder, 1992
hydrogen	2.7-3.5	Mansell and Schroeder, 2002
hydrogen	0.32	Kurt et al., 1987
hydrogen	0.79	Islam et al., 1993
hydrogen	2	Gantzer et al., 1995
hydrogen	1.39	Benedict et al., 1997
hydrogen	0.001	Lee and Ritman, 2000
hydrogen	2.2	Ergas and Reuss, 2001

MWW – municipal wastewater

PS – primary sludge

1.3.2 Hydrogen driven vs. sulphur driven denitrification

In sulphur-driven autotrophic denitrification, electrons come from sulphur particles used as packing media in the reactor. Limited pilot-scale experiments have proven that the process can give the best solution for medium level nitrate wastewater with low organic content. Application of elemental sulphur, however, was found to be inefficient. Powdered elemental sulphur, under normal circumstances, is insoluble and tends to conglomerate and float (Lampe and Zhang, 1996). Thiosulfate, as a soluble substance, is a much more efficient electron donor in the process of denitrification. Still, due to the creation of sulphates and hydrogen ions (eq. 1.5), sulphur driven autotrophic denitrification causes a significant decrease in pH, which can inhibit the denitrification at $\text{pH} = 5.5$. In order to keep the pH in the proper range, buffering agents have to be added to the system. Dolomite, slaked lime, unslaked lime, limestone, marble stone and crushed oyster shells have been evaluated as the buffering substances (Sengupta et.al, 2007). Crushed oysters were found to be efficient buffer agents as they allowed to obtain higher denitrification rate, pH and alkalinity in effluent, higher alkalinity release and resulted in lower nitrite accumulation as well as lower turbidity in effluent (Sengupta et al, 2007).

Hydrogenotrophic denitrification offers two major advantages over sulphur driven denitrification and heterotrophic denitrification. First, it is practically impossible to have a residual of the supplemented donor, since H_2 evaporates to the atmosphere once the water (wastewater) is exposed to an open surface. Second, it does not leave any by-products which affect quality of the effluent.

1.3.3 Advantages of hydrogen driven denitrification

Hydrogen driven denitrification is an attractive option for removing nitrate from low organic carbon streams. As already mentioned it does not leave any residuals or by-products of the reaction, produces less biomass compared to heterotrophic denitrification and results in lower cost of supplied electron donor per unit of nitrate removed when compared to heterotrophic denitrification.

The analysis of the reactions of heterotrophic, methanol- driven (eq. 1.2) and hydrogenotrophic denitrification (eq.1.4) show that activation energy (defined as the energy that must be overcome in order for a chemical reaction to occur) of the latter one is lower. In case of hydrogen driven denitrification the activation energy equals -72 kJ/e , while for methanol driven denitrification it is -37 kJ/e (Ersever et al.,2007). The requirement for electron donor for hydrogenotrophic denitrification would be lower as well, as the number of molecules with the energy equal or greater than the activation energy will be lower.

The comparison of requirements for methanol and hydrogen in heterotrophic and autotrophic denitrification respectively shows that methanol requirement is equal to $\sim 1.2 - 3 \text{ kg CH}_3\text{OH (kg NO}_3\text{-N)}^{-1}$ removed (Schlekovski and Mavinic, 1998; Brauer and Annachhatre, 2004) while H_2 requirement equals only to $\sim 0.42 \text{ kg H}_2 \text{ (kg NO}_3\text{-N)}^{-1}$ removed. Higher methanol consumption is affected not only by denitrification but also by dissolved oxygen (DO) which is usually carried from previous treatment zones and by non-ideal flow conditions which lead to downstream methanol leakage. Lower H_2 requirement and thus technical and economical viability of hydrogen – driven