

# Hydrogen-Based Membrane Biofilm Reactor for Wastewater Treatment

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**Abstract.** The H<sub>2</sub>-based membrane biofilm reactor (MBfR) delivers H<sub>2</sub> gas to a biofilm that naturally accumulates on the outer surface of bubbleless membranes. Although the MBfR is proven for the reduction of nitrate and perchlorate in drinking-water and groundwater settings, its most extensive application may be for advanced nitrogen removal in wastewater treatment, where existing approaches either fail to achieve the goals of advanced-N removal or have severe problems of cost, reliability, and safety. By utilizing H<sub>2</sub> gas as the electron donor to drive denitrification, the MBfR completely eliminates an added organic electron donor, which overcomes major problems: a large increase in excess biomass generation, over- or under-dosing of donor, safety concerns, and relying on specialized methanotrophs. In addition, the MBfR is simple to operate and can be used for tertiary denitrification or placed within a pre-denitrification process. Preliminary results reported here show that a biofilm of autotrophic denitrifiers accumulates rapidly in the wastewater setting, the MBfR can drive NO<sub>3</sub><sup>-</sup> concentrations below 1 mgN/L, and the H<sub>2</sub> pressure controls the NO<sub>3</sub><sup>-</sup> flux.

**Keywords.** Biofilm, Denitrification, Membrane, Nutrients, Wastewater

## Introduction

One of the emerging challenges for wastewater treatment is achieving very low effluent concentrations of total nitrogen (TN) and total phosphorus (TP). Increasingly severe problems with eutrophication and hypoxia in lakes, reservoirs, estuaries, and the near-shore ocean are forcing environmental regulators to impose more stringent effluent requirements on TN and TP. For example, an effluent standard for TN could be 1 mgN/L when the discharge is to a sensitive water body; it is possible that a receiving-water standard of 0.12 mgN/L could be applied if the wastewater were the dominant water input.

Existing wastewater-treatment technology is capable of taking effluent TN down to the range of 10 – 15 mg/L, but it is neither reliable nor cost-effective for achieving  $\leq 1$  mgN/L. The key for taking TN down to the 1-mg/L level is stable denitrification that drives NO<sub>3</sub><sup>-</sup>-N to a few tenths of a mg/L. Stable nitrification can drive NH<sub>4</sub><sup>+</sup>-N to a few tenths of a mg/L, and filtration can bring organic N to almost zero (Rittmann and McCarty 2001). If soluble organic nitrogen can be held to a few tenths of a mg/L, the total N can be in the region of 1 mg/L: e.g., 0.2 mg/L NH<sub>4</sub><sup>+</sup>-N, 0.3 mg/L NO<sub>3</sub><sup>-</sup>-N, and 0.5 mg/L soluble organic N.

Pre-denitrification is an excellent approach to utilize the influent BOD to fuel denitrification, but realistic constraints on the mixed-liquor recycle rate limit it to about 75% N removal, which

leaves around 10 mg/L TN in the effluent (Rittmann and McCarty 2001). Furthermore, a high influent TKN:BOD ratio can foil the pre-denitrification strategy as a means for total N removal. Return of digester supernatants is a common situation leading to a high influent TKN:BOD ratio.

Tertiary denitrification using an organic electron donor, such as methanol or acetate, could, in principle, drive effluent  $\text{NO}_3^-$  to a few tenths of a mgN/L. However, the dosing of the organic donor cannot be controlled well enough to ensure full  $\text{NO}_3^-$  removal without massive donor overdosing that increases effluent BOD and wastes money. In addition, tertiary denitrification using an organic donor significantly increases excess sludge production and often involves handling chemicals that expensive. Methanol ( $\text{CH}_3\text{OH}$ ) is popular for its relatively low cost, but methanol is a dangerous chemical that is toxic to humans, is regulated, has very difficult handling properties, and is oxidized only by specialized methanotrophs.

A revolutionary new approach that should overcome most of the limitations of traditional denitrification exploits the  $\text{H}_2$ -based membrane biofilm reactor (MBfR), which has been extensively studied for treating drinking water or groundwater contaminated with nitrate, perchlorate, or other oxidized contaminants (Rittmann et al. 2004). The MBfR offer great potential to augment or replace traditional denitrification so that very low TN – in the region of 1 mg/L – can become a reality.

This paper first reviews the MBfR approach and previous experience oriented toward drinking water and groundwater treatment. It then introduces the several ways in which the MBfR can be adapted for treating wastewater to achieve advanced TN removal. Finally, the paper summarizes preliminary results in which the MBfR was applied in a wastewater setting.

### **Review of the MBfR and Previous Experience**

The technological goal of the MBfR is to deliver  $\text{H}_2$  gas as an electron donor to autotrophic bacteria that reduce  $\text{NO}_3^-$  or other oxidized contaminants.  $\text{H}_2$  is the ideal electron donor for fueling denitrification and other reductions because of the following inherent advantages over organic electron donors:

- $\text{H}_2$  is a low-cost source of electrons
- $\text{H}_2$  supports autotrophic bacteria, which totally eliminates the need for an organic C source
- $\text{H}_2$  produces far less excess biomass
- $\text{H}_2$  cannot have a significant residual in the water and cannot increase effluent BOD
- $\text{H}_2$  is non-toxic to humans
- $\text{H}_2$  can be purchased in bulk or generated on-site
- Bacteria use  $\text{H}_2$  to reduce all oxidized contaminants

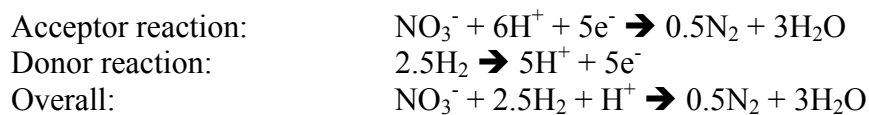
Despite its inherent advantages,  $\text{H}_2$  has not been used an electron donor in the past, because no efficient and safe delivery system was available. Its low water solubility (only 1.2 mg/L in equilibrium with 1 atm) means that it cannot be supplied in a water stream. Its flammability and low water solubility mean that  $\text{H}_2$  cannot be sparged.

The MBfR overcomes the limitations on  $\text{H}_2$  delivery.  $\text{H}_2$  gas is supplied to the interior of special hollow-fiber membranes that are “bubbleless,” or have no continuous pores. We have been using a composite bubbleless membrane produced by Mitsubishi-Rayon, but other membranes

may be suitable.  $H_2$  diffuses through the membrane wall. Molecules of  $H_2$  reaching the outside of the membrane are oxidized by  $H_2$ -oxidizing, autotrophic bacteria that form a naturally occurring biofilm. The biofilm bacteria use most of the electrons to reduce the oxidized contaminants to harmless products: e.g.,  $NO_3^-$  is reduced to  $N_2$  gas, and perchlorate ( $ClO_4^-$ ) is reduced to  $Cl^-$  ion. Supplying  $H_2$  directly to the biofilm results in rapid and nearly 100% utilization of  $H_2$ , both of which enhance process efficiency and safety. In addition, the supply rate of  $H_2$  to the biofilm is self-regulated by the loading of oxidized contaminant to the biofilm. Thus,  $H_2$  delivery with the MBfR is efficient, safe, and simple.

### Denitrification

The original research on the MBfR addressed denitrification in the drinking-water setting (Lee and Rittmann 2000, 2002, 2003). For denitrification,  $NO_3^-$  is the electron acceptor, and  $H_2$  oxidation supplies the electrons:



In drinking-water treatment, the goal is to remove  $NO_3^-$  to below the standard, which typically is 10 mgN/L. Therefore, achieving partial  $NO_3^-$  removal to well below the standard is the goal, as long as partial removal is reliable and no other water-quality problems are introduced. Other problems could include accumulation of nitrite, release of too much biomass, production of biodegradable dissolved organic carbon (BDOC), or a large pH increase.

The extensive research with a bench-scale MBfR (Lee and Rittmann 2000, 2002, 2003) showed that partial or full  $NO_3^-$  removal was possible and easily controllable. Adjusting the  $H_2$  pressure to the interior of the membranes simply and reliably controlled the effluent concentration of  $NO_3^-$ -N. Within the  $H_2$ -pressure range of about 0.15 to 0.6 atmospheres, the effluent  $NO_3^-$  concentration could be controlled systematically from less than 0.1 mgN/L for the higher  $H_2$  pressures and low to moderate surface loading of  $NO_3^-$  to 10 mgN/L for the lower  $H_2$  pressure and a high  $NO_3^-$  surface loading. Increasing the  $H_2$  pressure inside the membranes increased the  $H_2$ -delivery capacity, making it possible to drive the  $NO_3^-$  concentration to very low level, treat a higher surface loading of  $NO_3^-$ , or a combination of both. In most cases, the  $NO_2^-$  concentration was less than 1 mgN/L, and increasing the  $H_2$  pressure made it possible to drive effluent  $NO_2^-$  to less than 0.1 mgN/L.

The denitrification research also showed that the biofilm that accumulated on the outside of the membranes in the bench-scale MBfR was dense and strong. The specific detachment rate was very low ( $< 0.02/d$ ), and the effluent biomass concentration was correspondingly low (c. 1 mg/L). The autotrophic biofilm produced some soluble microbial products, giving a typical effluent BDOC of 0.5 mg/L, which can be eliminated by downstream biofiltration (Rittmann and McCarty, 2001). The net acid consumption of denitrification required attention to pH buffering, but this situation is true for all denitrification processes.

### Perchlorate Reduction and Pilot Testing

Being a major component of rocket fuel, perchlorate is an emerging oxidized contaminant in areas affected by military bases and rocket manufacturing and testing. Perchlorate affects thyroid function and is an endocrine disruptor. Although no drinking-water standard is yet in place, the State of California has an action level of 4  $\mu\text{g/L}$ , and the U.S.E.P.A. anticipates that its health-based standard ultimately will be in the range of 1 – 4  $\mu\text{g/L}$ . Perchlorate can be bacterially respired in a stepwise 8-electron reaction that produces  $\text{Cl}^-$  ion.

Acceptor reaction:  $\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}$

When 4 moles of  $\text{H}_2$  provide the 8 electrons, the overall reaction is

Overall reaction:  $\text{ClO}_4^- + 4\text{H}_2 \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}$

Bench-scale experiments (Nerenberg et al. 2002, 2004; Nerenberg and Rittmann 2002; Rittmann et al. 2004) proved that an MBfR active in denitrification reliably reduces  $\text{ClO}_4^-$  to below the action level of 4  $\mu\text{g/L}$ , that the  $\text{H}_2$  pressure to the membrane is the sensitive control on the capacity of reduce  $\text{ClO}_4^-$ , and that prolonged feeding of  $\text{ClO}_4^-$  enriches the biofilm in perchlorate-reducing bacteria, although they are present in natural denitrifying populations. The bench-scale work also showed that oxygen and nitrate are good electron acceptors to support perchlorate-reducing bacteria, although their concentrations in the MBfR must be very low to preclude inhibition of perchlorate reduction.

Field-scale pilot testing was carried out at La Puente, California (Rittmann et al. 2004; Nerenberg et al. 2004, Adham et al. 2003). The pilot system consisted of two columns each having ~7,000 hollow-fiber membranes and received a flow rate around 2 L/min. The La Puente groundwater contained approximately 60  $\mu\text{g/L}$  of  $\text{ClO}_4^-$  and 5.6 mgN/L of  $\text{NO}_3^-$ . After a start-up period in which practical operating problems were overcome, the pilot-scale system achieved excellent  $\text{ClO}_4^-$  removal, typically at or below the 4- $\mu\text{g/L}$  action level. Nitrate also was removed to about 0.2 mgN/L, and  $\text{O}_2$  was completely removed. One of the most important contributions of the pilot study was quantifying the  $\text{H}_2$  use rate, which could not be measured with the small gas flows in the bench-scale studies. The measured  $\text{H}_2$  use rate was very close to 100% of the theoretical use rate based on the consumption rate of the three acceptors entering the MBfR:  $\text{NO}_3^-$ ,  $\text{O}_2$ , and  $\text{ClO}_4^-$ . The 100%  $\text{H}_2$  use means that the MBfR wastes no electron donor, which is essential for good economy, safety, and effluent quality.

### Other Oxidized Contaminants

One potential advantage of using  $\text{H}_2$  gas with the MBfR is that all oxidized contaminants should be reduced by microbial catalysis. A screening study (Nerenberg and Rittmann 2004) tested eight new oxidized contaminants in short term tests involving two bench-scale MBfRs that had biofilm grown with  $\text{NO}_3^-$  or  $\text{O}_2$  as the primary electron acceptor. Approximately 1 mg/L of one new contaminant was fed for two hours (enough to give hydraulic steady state), and the removal of the applied contaminant was then measured. Each contaminant showed significant reduction, at least 29%. The oxidized contaminants and their % removals in the nitrate MBfR are summarized here: arsenate ( $\text{H}_2\text{AsO}_4^-$ ) >50%, bromate ( $\text{BrO}_3^-$ ) >95%, chlorate ( $\text{ClO}_3^-$ ) 29%, chlorite ( $\text{ClO}_2^-$ ) 67%, chromate ( $\text{CrO}_4^{2-}$ ) >75%, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) 45%, selenate ( $\text{SeO}_4^{2-}$ )

) 74%, and selenate ( $\text{SeO}_3^{2-}$ ) 57%. Based on the results with perchlorate (Nerenberg et al. 2002), the removal percentages are likely to increase with continuous feeding of the oxidized contaminants; thus, the removals obtained in the screening study probably are minima. More in-depth research is on going.

### **Extending the MBfR to the Wastewater Setting**

Adapting the MBfR to wastewater treatment should achieve two major goals.

- Eliminate any organic electron donor, which will to minimize excess sludge production, minimize chemical costs, eliminate the need to use specialized methanotrophs, and eliminate the possibility of donor over-dosing.
- Provide a simple system that is easily integrated into existing wastewater-treatment systems.

The MBfR can be integrated into existing or new activated-sludge designs in two distinct ways.

- Using the MBfR for tertiary denitrification, or post-treatment to remove  $\text{NO}_3^-$  remaining after conventional treatment, such as pre-denitrification.
- Placing the MBfR units directly in a pre-denitrification system to enhance its performance without constructing a tertiary-treatment process.

### Tertiary Denitrification

The goal of tertiary denitrification with the MBfR is to reduce the effluent  $\text{NO}_3^-$  concentration to an advanced-treatment standard (e.g.,  $\leq 1$  mgN/L) when a conventional pre-denitrification process brings the  $\text{NO}_3^-$  concentration down to 10 – 15 mgN/L. Figure 1 illustrates how the tertiary system would be employed a typical post-treatment scenario. This application is similar to the drinking-water settings that have been investigated for denitrification, although two differences are evident. First, the effluent criterion for  $\text{NO}_3^-$  is lower for wastewater treatment:  $\leq 1$  mgN/L versus well below the drinking-water standard of 10 mgN/L. Second, the influent to the MBfR is likely to contain a significant concentration of suspended solids, which are absent or negligible in drinking-water treatment. The physical configuration of the MBfR must be adjusted to accommodate influent solids without fouling the MBfR.

Figure 1. Schematic of how the MBfR can be used for tertiary denitrification to bring the effluent  $\text{NO}_3^-$  concentration from the typical level of pre-denitrification to an advanced-treatment level.

#### Integration into Pre-denitrification

Integrating the MBfR into pre-denitrification obviates the need to construct any tertiary-treatment process. The benefits for capital costs and space are obvious. Figure 2 illustrates how MBfR units could be integrated into a multiple-pass, pre-denitrification system to augment the capacity for  $\text{NO}_3^-$  removal. Integration creates a hybrid biofilm/suspended-growth system in which the biofilm is dominated by  $\text{H}_2$ -oxidizing autotrophs, while the suspended bacteria are BOD-oxidizing heterotrophs and autotrophic nitrifiers. Achieving integration involves a number of technical challenges: preventing fouling of the membranes from the suspended biomass and influent solids, good mass transfer to the membranes, biofilm control on the membranes, controlling the oxygen concentration to allow good nitrification but not create a large  $\text{H}_2$  demand to reduce  $\text{O}_2$ , and locating the MBfR units in the best place to gain really low effluent  $\text{NO}_3^-$  concentration while using the influent BOD as much as possible for denitrification.

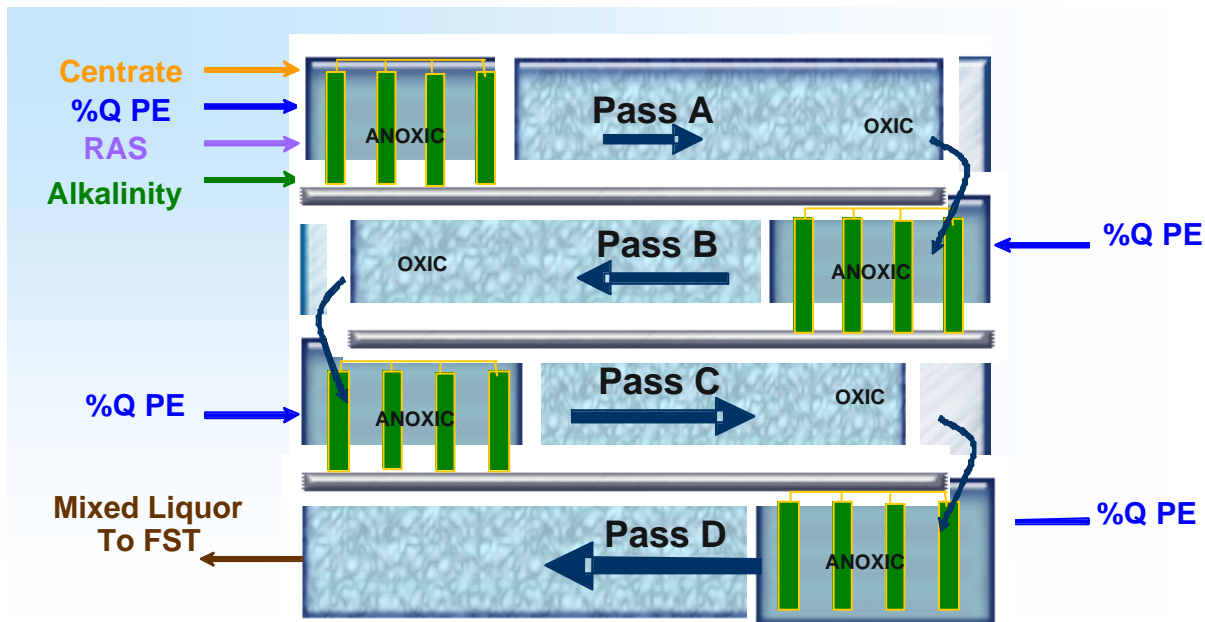


Figure 2. Illustration of how MBfR units could be integrated into a pre-denitrification system to augment the removal of  $\text{NO}_3^-$ .

### Experience in the Wastewater Setting

Preliminary studies were carried out as preparation for pilot studies on wastewater denitrification with the MBfR. The preliminary studies utilized a novel “open matrix” MBfR having  $206 \text{ cm}^2$  of membrane area in a volume of  $300 \text{ cm}^3$ , which gives a specific surface area of  $0.69 \text{ cm}^{-1} = 69 \text{ m}^{-1}$ . The concept of the “open matrix” is to allow mixed liquor to move between the membrane fibers without being filtered out or fouling the membrane surface. The influent contained the effluent from the first-stage of the multiple-stage pre-denitrification plant in New York City. The influent to the MBfR had a  $\text{NO}_3^-$  concentration of 10 - 20 mgN/L. The flow rate was 2.3 L/d, giving an empty-bed hydraulic retention time of 3 h. No inoculum was provided before feeding the wastewater to the MBfR.

Denitrification in the MBfR started up immediately and achieved a high level of denitrification within a few days. Effluent  $\text{NO}_3^-$  was driven to well below 1 mgN/L, and  $\text{H}_2$  pressure gave sensitive control of the denitrification capacity. For example, when the  $\text{H}_2$  pressure was only 2 psi (0.14 atm) and influent  $\text{NO}_3^-$  was 13 mgN/L, the effluent  $\text{NO}_3^-$  was 0.85 mgN/L, giving a  $\text{NO}_3^-$  flux of  $1.4 \text{ gN/m}^2\text{-d}$ . Increasing the  $\text{H}_2$  pressure to 5 psi (0.34 atm) when the influent  $\text{NO}_3^-$  was 16.4 mgN/L gave effluent  $\text{NO}_3^-$  of only 0.4 mgN/L, with a  $\text{NO}_3^-$  flux of  $1.8 \text{ gN/m}^2\text{-d}$ .

Despite the open-matrix configuration, extended operation led to excess biofilm or suspended-solids accumulation, which caused some membrane fibers to clump together. Clumping reduced the biofilm surface area and the mass-transport rate to the biofilm. For example, a  $\text{H}_2$  pressure of 5 psi (0.34 atm) gave a nominal  $\text{NO}_3^-$  flux of  $1 \text{ gN/m}^2\text{-d}$  and had effluent  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations of 3.6 and 1.6 mgN/L, respectively, after clumping. The deficiency of the open-matrix design in the 300-mL reactor was too-low turbulence and mixing around the membranes, and this will be a primary design goal for forthcoming pilot studies.

## Conclusions

The H<sub>2</sub>-based MBfR has been proven for the reduction of nitrate and perchlorate in drinking water and groundwater settings, and it shows promise for a range of other oxidized contaminants in water. Perhaps its most extensive application will be for advanced nitrogen removal in wastewater treatment, where existing approaches fail to achieve the goals of advanced-N removal; have severe problems of cost, reliability, and safety; or both. By utilizing H<sub>2</sub> gas as the electron donor to drive denitrification, the MBfR completely eliminates an added organic electron donor, which overcomes major problems: a large increase in excess biomass generation, over- or under-dosing of donor, safety concerns, and relying on specialized methanotrophs. In addition, the MBfR is simple to operate, and it can be used for tertiary denitrification or integrated into a pre-denitrification process. Preliminary results show that autotrophic denitrifiers accumulate rapidly in the wastewater setting, the MBfR can drive NO<sub>3</sub><sup>-</sup> concentrations below 1 mgN/L, and the H<sub>2</sub> pressure controls the NO<sub>3</sub><sup>-</sup> flux. Some special features will be needed to deal with suspended solids and excess biofilm accumulation in the wastewater setting.

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