

Membrane Biofilm Reactors for Water and Wastewater Treatment

Robert Nerenberg
Assistant Professor
University of Notre Dame
Department of Civil Engineering and Geological sciences
163 Fitzpatrick Hall
Notre Dame, IN 46556
574-631-4098
Nerenberg.1@nd.edu

ABSTRACT

Certain gaseous substrates, such as hydrogen, methane, and oxygen, can act as electron donor or acceptors for desired microbial processes. These gases are inexpensive and can lead to effective processes, but their low water solubility can limit their use. The membrane biofilm reactor (MBfR) is a novel system that uses membranes to supply dissolved gas directly to a biofilm growing on the membrane surface. This paper describes the MBfR and discusses applications for water and wastewater treatment.

INTRODUCTION

Many microbial processes in environmental engineering can use dissolved gases as substrates for microbial growth. The most obvious example is dissolved oxygen, which serves as an electron acceptor for aerobic degradation. Other examples include hydrogen, an electron donor for autotrophic denitrification, and methane, which supports cometabolic trichloroethene (TCE) oxidation. Low aqueous solubility limits the use of many gaseous substrates. For example, the BOD of typical wastewaters (100 – 400 mg/L) greatly exceeds oxygen's solubility of 8 mg/L (for air at 1 atmosphere). In activated sludge, the solubility problem is resolved by continuously bubbling air

(sparging) to replenish oxygen. However, sparging is problematic when applied to other gases, such as hydrogen or methane: it is wasteful, due to loss of excess gas to the atmosphere, and can cause safety hazards. In addition, sparging requires large amounts of energy and can vent volatile organic compounds (VOCs) to the atmosphere. The membrane biofilm reactor (MBfR) a novel system that provides dissolved gas directly to a biofilm growing on the membrane surface, avoiding the need for sparging.

MBfRs are *not* membrane bioreactors (MBRs). An MBR is a biological treatment process where a membrane is used to separate biomass from the effluent water, substituting for a clarifier. Because MBRs act as filters, they are susceptible to fouling by biofilms or other materials that accumulate at the membrane surface. In contrast, in MBfRs a gaseous substrate moves across the membrane, while the naturally-forming biofilm on the outer surface catalyzes desired reactions. Since the pores of the membrane are hydrophobic, water and bacteria do not penetrate and block them. The combination of a membrane for gas delivery as well as for biofilm support led to the name Membrane-Biofilm Reactor.

This paper describe MBfRs and discusses several applications for water and wastewater treatment.

MEMBRANE BIOFILM REACTORS

MBfR CONFIGURATION

One of the key elements of an MBfR is the membrane. Membranes may be made from organic or inorganic materials, and can be configured in sheet or hollow-fiber geometries. Hollow-fiber membranes are commonly used for MBfRs because, with

outside diameters as small as 0.1 mm, they provide high surface-to-volume ratios. Hydrophobic materials are preferred because their pores remain dry, and gas molecules diffuse much more quickly through dry pores than through liquid-filled pores (Yang et al. 1986). Dry pores also eliminate the potential for fouling.

A key feature of hydrophobic hollow-fiber membranes is that they can be operated at high gas pressures without bubbling. Higher gas pressures improve mass transfer by providing a greater driving force for dissolution. When membrane pores are fairly large, such as with silicon membranes, bubbles begin to form when the gas pressure slightly exceeds the hydrostatic pressure of the liquid (Ahmed et al. 1992; Mulder 1997). In contrast, when the pores are small, the water surface tension on the pores can provide a significant resistance to the formation of bubbles, allowing much higher applied pressures.

Figure 1 shows a schematic bundle of hollow fiber membranes and a section of a single hollow fiber. As shown on the right side of the figure, the fibers are collected into a gas-supplying manifold at one end and are sealed at the opposite end. On the left side of the figure, pressurized gas in the lumen (interior) of the fiber diffuses through the dry pores and into the biofilm coating the fiber. 100 % of the gas supplied to the MBfR passes into the biofilm.

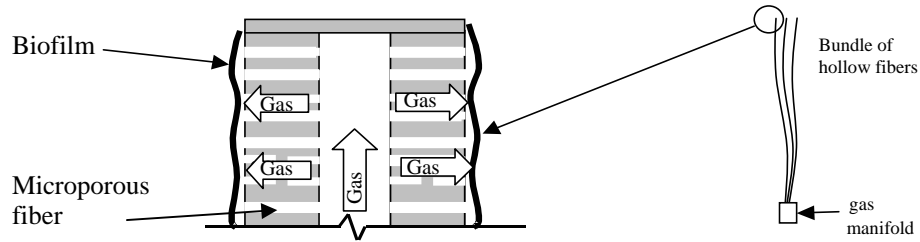


FIGURE 1. Section of fiber (left) and schematic of hollow fiber membrane bundle (right)

Figure 3a shows a scanning electron micrograph (SEM) of the outer surface of a Mitsubishi-Rayon MHF200TL membrane. The average pore diameter is around 0.15 μm , with an elliptical shape, and the surface texture is irregular. Figure 3b is a confocal laser scanning microscopy (CLSM) image showing the cross section of a biofilm growing on a MBfR membrane. In this figure, the biofilm thickness is approximately 50 μm .

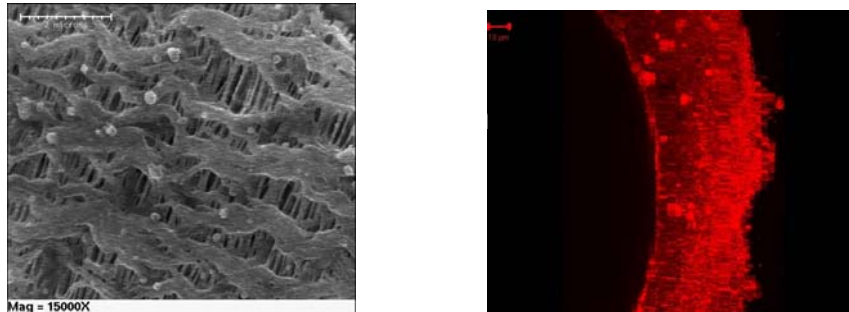


FIGURE 3. (a) Pore structure on the polyethylene surface of a Mitsubishi Rayon MHF200TL16 composite hollow fiber membrane (b) Microscopy image (CLSM) of biofilm growing on hollow-fiber membrane. The red dots are bacteria and the outer wall of the membrane (not visible) is immediately left of the biofilm.

Biofilms accumulate naturally on the fiber surface, which is the interface between the gaseous substrate and the substrate from the bulk liquid. Unlike common biofilm applications, where the electron donor and acceptor diffuse into the biofilm from the bulk

liquid (Figure 2a), in an MBfR one substrate diffused into the biofilm from the membrane and the other from the bulk liquid. This establishes counter-gradients between donor and acceptor (Essila et al. 2000; Lee et al. 2002), as shown in Figure 4b. An advantage of counter gradients is that the gaseous substrate supplied from the membrane is “protected” from entering the bulk liquid by the biofilm and by the liquid diffusion layer. Note the high bulk-liquid gas concentration required in Figure 4a, for conventional biofilms, and the much lower bulk-liquid concentration for the MBfR in Figure 4b. If the MBfR gas supply pressure is selected appropriately, very little gaseous substrate is lost to the bulk liquid, enhancing the cost-effectiveness of the process.

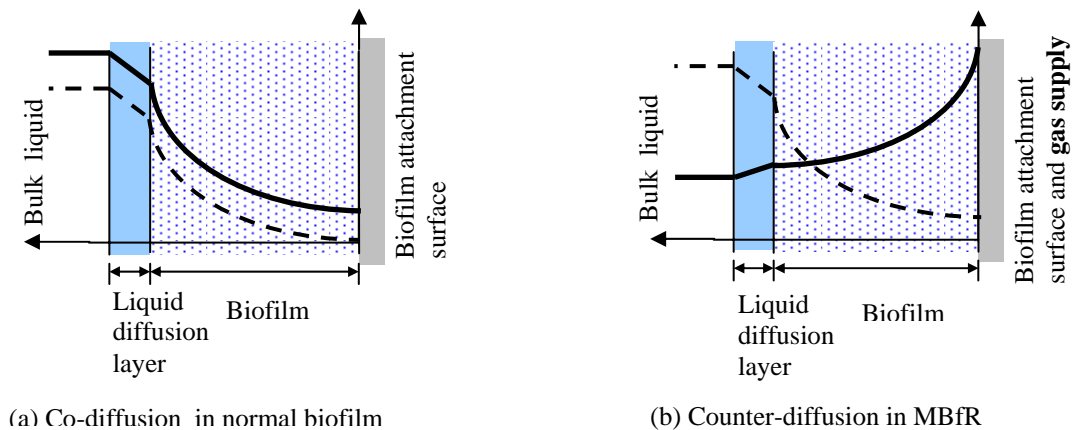


Figure 4. (a) Substrate “co-diffusion” in a normal biofilm and (b) substrate “counter-diffusion” in a hollow-fiber membrane biofilm. The bold line is the dissolved gas concentration, while the dotted line is the substrate from the bulk liquid.

ADVANTAGES OF MBFRS

A major advantage of the MBfR is that virtually all of the gas passing through the membrane can be utilized within the biofilm. This is due to the counter-current transport of dissolved gas and substrate from the bulk liquid, as discussed above. Nearly 100% use

of the gas means no unproductive loss of gas in the effluent. It also avoids potential hazards with explosive or toxic gases.

A second advantage is that the gas moves across the membrane wall when the bacterially catalyzed reaction in the biofilm creates a concentration gradient. If the biochemical demand for dissolved gas declines, the gradient and demand for gas also decline. If the demand increases, the gradient and demand also increase. Thus, to a certain degree the MBfR operates as a self-regulating, on-demand system that modulates its gas supply rate to the contaminant load. This prevents wasting gas or having an under-supply.

A third advantage is that hollow-fiber membranes provide a large specific surface area for biofilm accumulation. A high specific surface area allows a high density of contaminant-reducing bacteria in the MBfR. This means that the detention time for the reactor can be small, thereby minimizing capital costs and the system's footprint. It is ideal for treatment-plant retrofits, as well as for new construction.

HYDROGEN-BASED MBFRS

One of the most exciting applications of the MBfR is to deliver hydrogen gas (H_2) as an electron donor. Many oxidized contaminants can be reduced to less toxic or less mobile species with the addition of an electron donor. The classical example is nitrate, which can be reduced to nitrogen gas by denitrifying bacteria. Historically, organic donors such as methanol, ethanol, and acetate have been used for denitrification. However, H_2 has following inherent advantages over organic electron donors:

- H₂ is a low-cost source of electrons
- H₂ supports autotrophic bacteria, which eliminates the need for an organic carbon source
- H₂ produces less excess biomass (autotrophic growth)
- H₂ cannot leave a significant residuals that increase effluent BOD (low solubility)
- H₂ is non-toxic to humans
- H₂ can be purchased in bulk or generated on-site

Despite these advantages, H₂ has not been widely used, mainly because no efficient and safe delivery system was available. Its low water solubility does not allow it to be supplied in a water stream, and its flammability and cost does not allow H₂ to be sparged.

The MBfR opens the door using H₂ for water and wastewater treatment. In addition to nitrate, a large number of other, relatively new contaminants also fall into the class of being chemically oxidized. Many can be microbially reduced to innocuous or sequestered products:

- Perchlorate (ClO₄⁻), a component of solid rocket fuel that can be reduced to Cl⁻
- Chlorinated solvents, like trichloroethene (TCE), which can be reductively dehalogenated to ethene and Cl⁻ ion.

- Bromate (BrO_3^-), which is an ozonation byproduct that can be reduced to Br^- ion.
- Selenate (SeO_4^{2-}), which occurs naturally in certain mineral deposits and can be reduced to less mobile selenide (S^{2-}) or elemental selenium (Se^0).
- Heavy metals, particularly chromium, which can be reduced from hexavalent chromate (CrO_4^{2-}) to less toxic Cr^{3+} .
- Radionuclide metals uranium and neptunium, which can be reduced to low mobility U(IV) and Np(IV).

The following section describes experience with H_2 -based MBfRs.

H_2 -MBFR FOR DRINKING WATER DENITRIFICATION

K.-C. Lee (Lee 1999; Lee et al. 2000; Lee et al. 2002) was one of the first to study MBfRs for drinking water denitrification. A schematic of his bench-scale reactor is shown in Figure 5. The MBfR was inoculated with a pure culture of the H_2 -oxidizing, autotrophic denitrifier, *Ralstonia eutropha*, but was allowed to develop into a mixed culture. Partial denitrification, to 10 mgN/L, was sought and was achieved by limiting the hydrogen supply. Biofilms were allowed to grow to steady state for two different operating conditions. In the first steady state, the influent nitrate was 10 mgN/L, and the membrane hydrogen supply pressure was 0.31 atm (relative to atmospheric pressure). With a hydraulic retention time of 42 minutes, the system achieved 76% nitrate removal and had 0.9 mgN/L nitrite and 0.009 mg H_2 /L hydrogen in the effluent. The average biofilm thickness was 110 μm . The second steady-state had an influent nitrate

concentration of 12.5 mgN/L and a hydrogen supply pressure of 0.42 atm. In this case, the system achieved 92% nitrate removal and had 0.7 mgN/L nitrite and 0.7 mgH₂/L hydrogen. The biofilm thickness was 179 μm and the effluent biodegradable dissolved organic carbon (BDOC) was 0.5 mgC/L. The final pH was buffered to between 7.1 and 7.2 for both steady-states. The nitrate fluxes were 0.08 and 0.1 mgNO₃⁻N/cm² biofilm surface area/day for the two steady states, respectively. These studies showed that high nitrate fluxes could be achieved with low effluent hydrogen concentrations, thus allowing a compact and efficient process. Also, the degree of nitrate removal was easily controlled by managing the H₂ supply pressure.

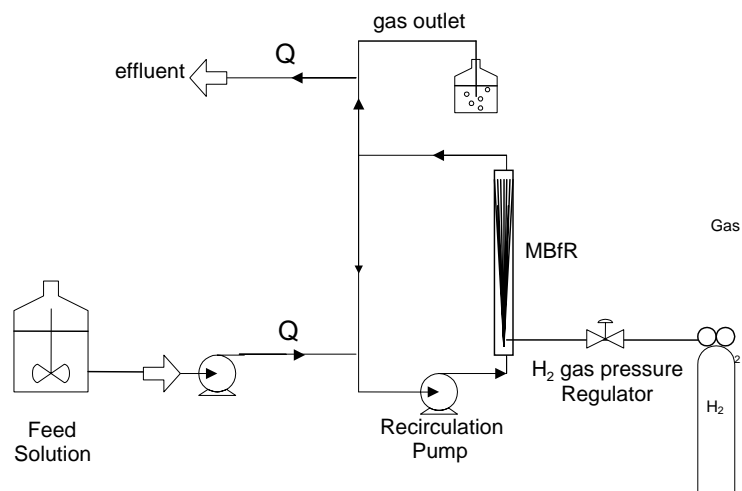


FIGURE 5. Schematic of a bench-scale MBfR

H₂-MBfR FOR PERCHLORATE IN DRINKING WATER

Perchlorate is an emerging oxidized contaminant in areas affected by military bases and rocket manufacturing and testing. Perchlorate affects thyroid function and is considered an endocrine-disrupting compound. Although no federal standard exist yet,

the State of California has an action level of 4 µg/L, and the U.S.E.P.A. anticipates that its health-based standard ultimately will be in the range of 15 - 20 µg/L. Perchlorate can be bacterially respired in a stepwise 8-electron reaction that produces Cl⁻ ion. The overall reaction is $\text{ClO}_4^- + 4\text{H}_2 \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}$.

Bench-scale experiments (Nerenberg et al. 2002; Nerenberg et al. 2002; Nerenberg 2003) proved that an MBfR active in denitrification reliably reduces ClO₄⁻ to below the action level of 4 µg/L, that the H₂ pressure to the membrane is the sensitive control on the capacity of reduce ClO₄⁻, and that prolonged feeding of ClO₄⁻ 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 (Nerenberg et al. 2003; Adham et al. 2004). 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 µg/L of ClO₄⁻ and 5.6 mgN/L of NO₃⁻. After a start-up period in which practical operating problems were overcome, the pilot-scale system achieved excellent ClO₄⁻ removal, typically at or below the 4-µg/L action level. Nitrate also was removed to about 0.2 mgN/L, and O₂ was completely removed. One of the most important contributions of the pilot study was quantifying the H₂ use rate, which could not be measured with the small gas flows in the bench-scale studies. The measured H₂ use rate was very close to 100% of the theoretical use rate based on the consumption rate of the three acceptors entering the MBfR: NO₃⁻, O₂, and ClO₄⁻. The 100% H₂ use

means that the MBfR wastes no electron donor, which is essential for good economy, safety, and effluent quality.

H₂-MBfR FOR EMERGING CONTAMINANTS IN DRINKING WATER

In addition to perchlorate, several other oxidized contaminants have emerged as drinking water contaminants, including arsenate (H_2AsO_4^-), chromate (CrO_4^{2-}), selenate (SeO_4^{2-}), and bromate (BrO_3^-). In many cases, conventional water treatment processes, as well as oxidative processes such as chlorine-oxidation or ozonation, are ineffective. Advanced separation processes, such as reverse osmosis, ion exchange, membrane filtration, and electrodialysis, can be effective, but are expensive and generate concentrated wastes that require proper disposal. Biological reduction may provide a more suitable treatment alternative, especially when the oxidized contaminant is reduced to a less toxic species (Lovley et al. 1997).

Many oxidized contaminants are reduced in thermodynamically favorable reactions and have been shown to support bacterial growth. However, in some cases the treatment standards may be below bacterial growth thresholds (S_{\min}) (Rittmann et al. 2001). In such cases, reduction may occur in parallel to reduction of more amply available “primary” electron acceptors, such as nitrate or oxygen.

Nerenberg et al. (2003) tested a H_2 -based MBfR for reduction and removal of several oxidized contaminants when nitrate or oxygen served as primary electron acceptors. The influent concentration of the contaminants was 1 mg/L, while influent oxygen and nitrate were 6 mg/L and 5 mgN/L, respectively. The effluent oxygen and nitrate were below detection. The oxygen reactor had previously been exposed to

perchlorate, which explains its higher removals for perchlorate, chlorate, and chlorite. These tests were carried out over a short period of time, without allowing the microbial culture to “adapt” to the new substrate, so long-term efficiencies are likely to be much higher. Results are shown in Table 1.

Table 1. Short-term tests with various oxidized contaminants

Compound	Probable Reduction Reaction(s)	% Removal	
		O ₂ Reactor	NO ₃ ⁻ Reactor
Arsenate	$\text{H}_2\text{AsO}_4^- + \text{H}_2 + \text{H}^+ \rightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$	>50	>50
Bromate	$\text{BrO}_3^- + 3\text{H}_2 \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$	>95	>95
Chlorate	$\text{ClO}_3^- + 3\text{H}_2 \rightarrow \text{Cl}^- + 3\text{H}_2\text{O}$	>95	29
Chlorite	$\text{ClO}_2^- + 2\text{H}_2 \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$	>75	67
Chromate	$\text{CrO}_4^- + 1.5\text{H}_2 + 2\text{H}^+ \rightarrow \text{Cr}(\text{OH})_3$	>75	>75
Dichloro-methane	$\text{DCM} + 2 \text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}^+ + 2 \text{Cl}^-$	38	45
Nitrate	$\text{NO}_3^- + 2.5\text{H}_2 + \text{H}^+ \rightarrow 0.5\text{N}_2 + 3\text{H}_2\text{O}$	Not tested	>99
Perchlorate	$\text{ClO}_4^- + 4\text{H}_2 \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}$	>98	36
Selenate	$\text{SeO}_4^{2-} + 3\text{H}_2 + 2\text{H}^+ \rightarrow \text{Se}^0 + 4\text{H}_2\text{O}$	67	74
Selenite	$\text{HSeO}_3^- + 2\text{H}_2 + \text{H}^+ \rightarrow \text{Se}^0 + 3\text{H}_2\text{O}$	93	57

Both reactors showed significant removals for all tested contaminants. Removals ranged from 29% for chlorate in the NO₃⁻ reactor to over 98% for perchlorate in the O₂ reactor. These results show that many oxidized contaminants can be removed in an MBfR. No specialized inoculum was required, in all cases the required bacteria were present in the mixed culture obtained from an environmental inoculum.

H₂-MBFR FOR WASTEWATER DENITRIFICATION

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. Tertiary denitrification, using an organic electron donor, such as methanol or acetate can drive denitrification. However, the dosing of the organic donor cannot be controlled well enough to ensure full 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 (CH_3OH) 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 new approach that overcomes most of the limitations of traditional denitrification exploits the H_2 -based MBfR. The MBfR offer great potential to augment or replace traditional denitrification so that very low TN can be obtained.

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 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.

Preliminary studies were carried out as preparation for pilot studies on wastewater denitrification with the MBfR (Rittmann et al. 2004). The preliminary studies utilized a novel “open matrix” MBfR having 206 cm^2 of membrane area in a volume of 300 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 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 immediately and achieved a high level of denitrification within a few days. Effluent NO_3^- was driven to well below 1 mgN/L, and H_2 pressure gave sensitive control of the denitrification capacity. For example, when the H_2 pressure was only 2 psi (0.14 atm) and influent NO_3^- was 13 mgN/L, the effluent NO_3^- was 0.85 mgN/L, giving a NO_3^- flux of $1.4 \text{ gN/m}^2\text{-d}$. Increasing the H_2 pressure to 5 psi (0.34 atm) when the influent NO_3^- was 16.4 mgN/L gave effluent NO_3^- of only 0.4 mgN/L, with a 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 H₂ pressure of 5 psi (0.34 atm) gave a nominal NO₃⁻ flux of 1 gN/m²-d and had effluent NO₃⁻ and NO₂⁻ 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. This needs to be addressed in future studies.

OXYGEN-BASED MBFRS

Researchers have tested O₂-based MBFRs for nitrification for drinking water (Brindle et al. 1996). Cowman (2004) combined an oxygen-based MBFR with a hydrogen-based MBFR in-parallel to provide concurrent nitrification and denitrification of drinking water. With a 50 mgN/L influent NH₄⁺ concentration, approximately 97% total nitrogen was removed. The process was highly sensitive to the applied oxygen pressure, requiring a balance between providing enough oxygen for nitrification with providing excessive oxygen that inhibited denitrification. The optimal gas pressures were 2.1 psig for O₂ and 2.0 psig for H₂.

An exciting new strategy is to use the O₂-based MBFR for concurrent nitrification, denitrification, and BOD removal. For example, Terada et al. (2002) achieved simultaneous nitrification and denitrification in a single reactor vessel using an O₂-based MBFR treating swine wastewater. Total N removal efficiencies of 85% were achieved. For municipal wastewater treatment, the MBFR could be inserted into an activated sludge

tank to deliver O_2 to nitrifying bacteria. If the bulk liquid O_2 concentration were sufficiently low, denitrifying bacteria growing in suspension or in the outer portions of the biofilm could use BOD as a “free” electron donor to reduce nitrate produced by the nitrifying bacteria. Several researchers have tested this approach in the laboratory with promising results (Hibiya et al. 2003; Terada et al. 2003; Satoh et al. 2004).

OTHER MBFR APPLICATIONS

Several researchers have used methane-based MBfRs to cometabolically degrade trichloroethylene (TCE) (Aziz et al. 1995; Clapp et al. 1999). Others have used MBfRs to treat gaseous contaminants that are passed through the lumen. For example, (Min et al. 2002) used a nitrifying MBfR to oxidize nitric oxide (NO) from combustion gases to NO_3^- . O_2 -based MBfRs can also be used to degrade a wide range of reduced contaminants. (Grimberg et al. 2000) used an O_2 -based MBfR to supply pure oxygen to oxidize trinitrophenol, achieving removals of 85 – 99%. Many other applications are possible, and are likely to be developed as this technology becomes more well-known.

COMMERCIAL SCALE UP

While MBfRs have been tested at the bench and pilot scale, no full-scale applications have been built to date. More research is needed to determine the optimal membrane materials, diameter, packing density, and bulk liquid mixing strategy. A key need is for effective management of biofilm growth, as excessive growth reduces reactor efficiency.

A number of physical and chemical means are available to control biofilm growth. Research currently is being carried out in these areas.

CONCLUSIONS

The MBfR is an effective means to deliver gaseous substrates for biological processes, opening the door to a myriad of new applications in water and wastewater treatment. Key applications include nitrification/denitrification and removal of emerging oxidized contaminants. Almost all the supplied gas is delivered to the biofilm, where it is used for desired biochemical reactions, so little waste occurs. The process has a self regulating feature, where increased gas demand from the biofilm creates a greater driving force for gas supply from the membrane. Also, the hollow-fiber membrane configuration also provides high specific surface areas, allowing for compact reactors. The MBfR has been shown to be effective for numerous applications at the bench and pilot scale. Research is being carried out to develop full-scale configurations.

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