

THE MEMBRANE BIOFILM REACTOR IS A VERSATILE PLATFORM FOR WATER AND WASTEWATER TREATMENT

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Abstract : The membrane biofilm reactor (MBfR) creates a natural partnership of a membrane and biofilm, because a gas-transfer membrane delivers a gaseous substrate to the biofilm that grows on the membrane's outer wall. O₂-based MBfRs (called membrane aerated biofilm reactors, or MABRs) have existed for much longer than H₂-based MBfRs, but the H₂-based MBfR is a versatile platform for reducing oxidized contaminants in many water-treatment settings: drinking water, ground water, wastewater, and agricultural drainage. Extensive bench-scale experimentation has proven that the H₂-based MBfR can reduce many oxidized contaminant to harmless or easily removed forms: e.g., NO₃⁻ to N₂, ClO₄⁻ to H₂O and Cl⁻, SeO₄²⁻ to Se⁰, and trichloroethene (TCE) to ethene and Cl⁻. The MBfR has been tested at the pilot scale for NO₃⁻ and ClO₄⁻ and is now entering field-testing for many of the oxidized contaminants alone or in mixtures. For the MBfR to attain its full promise, several issues must be addressed by bench and field research: understanding interactions with mixtures of oxidized contaminants, treating waters with a high TDS concentration, developing modules that can be used *in situ* to augment pre-denitrification of wastewater, and keeping the capital costs low.

Key Words : Biofilm, Bio-reduction, Hydrogen, Membrane, Oxidized contaminants

INTRODUCTION

The membrane biofilm reactor (MBfR) takes advantage of a natural partnership of a membrane with a biofilm.¹⁾ As illustrated in Figure 1, biofilm grows on the outside of a gas-transfer membrane that has a gas-phase substrate on the inside of the membrane. The substrate diffuses through the wall of the membrane and is consumed by the bacteria in the biofilm. Thus, the biofilm accumulates on an "active" surface, or one that delivers substrate to the bacteria. The substrate can be an electron donor or an electron

acceptor, as long as it is a gas.

The MBfR has its greatest advantage when the delivered substrate is hydrogen gas (H₂), an electron donor that is oxidized by a wide variety of bacteria that reduce one or more oxidized contaminants.¹⁻⁴⁾ Oxygen gas (O₂) also can be delivered as an electron acceptor used to oxidize organic and nitrogenous BOD.⁵⁻⁷⁾ Other gas-phase substrates can be utilized in an MBfR: e.g., the donors methane (CH₄) and ammonia (NH₃) and the acceptor carbon dioxide (CO₂). A very interesting example is the co-metabolic oxidation of trichloroethene (TCE) and tetrachloroethene (PCE) by methanotrophs,⁸⁻¹¹⁾ in which CH₄ and O₂ are delivered together.

The concept underlying the MBfR can be traced

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back to 1960, when Schaffer et al.¹²⁾ utilized permeable plastic films to transfer O₂ and developed slimes on the outside walls. The advent of more advanced membrane materials in the 1970s through 1990s led to development of a range of O₂-based MBfR systems used for oxidation of organic BOD, nitrification, and combined nitrification and denitrification.^{5,6,13-32)} These aerobic systems, often called membrane-aerated biofilm reactors (MABRs),²²⁾ demonstrated the possibility for delivering a substrate directly to a biofilm. However, the MABR has not blossomed into a major technology for improving water quality. The most likely reason that the MABR has not penetrated the market is that O₂ can be delivered to microorganisms in many other well-established ways. Thus, the MABR does not overcome a large obstacle for treatment of water and wastewater.

The H₂-based MBfR has the potential to become a major technological breakthrough, because it overcomes obstacles that prevent environmental biotechnology from meeting pressing needs in water quality. In particular, the H₂-based MBfR makes it possible to bio-reduce a large set of oxidized contaminants. Table 1 lists many oxidized contaminants and indicates why and where they are problems. Except for nitrate and nitrite, the oxidized contaminants fall into the category of "emerging" contaminants, which society has recognized as problems only recently. For most

of these contaminants, no reliable and cost-effective treatment technology is available. Thus, society has a pressing need that is not already being met by means other than the MBfR.

Using H₂ as the electron donor to bio-reduce the oxidized contaminants offers many advantages over other treatment options. Bio-reduction, in general, is preferable to methods that only transfer the contaminant out of the water. For example, ion exchange and reverse osmosis generate brines in which the oxidized contaminants are concentrated. As shown in Table 1, bio-reduction creates products that are either harmless or easily removed from the water as a solid. Using H₂ as the electron donor for bio-reduction significantly enhances the advantages in these ways:

- H₂ is the "universal" electron donor, because H₂-oxidizing bacteria are known to be able to reduce all the oxidized contaminants.³³⁻³⁷⁾ While organic donors work for some of the oxidized contaminants, they do not work for the entire suite of them.
- H₂ is oxidized by autotrophic bacteria, which use inorganic carbon as their carbon source.³⁵⁾ Autotrophy means that no organic carbon source is needed, and the production of excess biomass, which much be removed and disposed of, is minimized by autotrophy.
- In most cases, H₂ has the lowest cost per electron-equivalent delivered for contaminant reduction.^{2,4)}

Table 1. Oxidized contaminants, their effects, and their desirable reduced products

Oxidized Contaminant	Chemical Formula	Effects	Reduced Product
Nitrate and nitrite	NO ₃ ⁻ and NO ₂ ⁻	Methemoglobinemia, eutrophication, hypoxia	N ₂ gas
Perchlorate and chlorate	ClO ₄ ⁻ and ClO ₃ ⁻	Disrupts thyroid function, endocrine disruptor	Cl ⁻ ion and H ₂ O
Bromate	BrO ₃ ⁻	Genotoxic cancer	Br ⁻ ion and H ₂ O
Selenate and selenite	SeO ₄ ²⁻ and SeO ₃ ²⁻	Reproductive problems	Se ⁰ solid
Arsenate	H ₂ AsO ₄ ⁻	Cardiac arrest, gastrointestinal damage, cancer	As ₂ S ₃ solid
Chromate	CrO ₄ ²⁻	Liver and kidney damage	Cr(OH) ₃ solid
TCE and TCA	C ₂ Cl ₃ H and C ₂ Cl ₃ H ₃	Cancer	Cl ⁻ ion and C ₂ H ₄ or C ₂ H ₆
Dichloromethane and Chloroform	CCl ₂ H ₂ and CCl ₃ H	Cancer	Cl ⁻ ion and CH ₄
NDMA	ON(CH ₃) ₂ N	Cancer, mutagenesis, teratogenesis	H ₂ N(CH ₃) ₂ N

- H₂ is widely used in industry,¹⁾ which means that reliable and safe methods for transport and storage are readily available.
- H₂ is non-toxic to humans and presents no unavoidable problems with handling.
- If desired, H₂ can be produced on site and on demand by electrolysis.

The MBfR makes it possible to gain all the advantages of H₂ as the electron donor for bio-reductions. Before the MBfR, delivery of H₂ to microorganisms was impractical for two reasons. The first reason is that H₂ has very low water solubility: ~ 1.2 mgH₂/L in equilibrium with 1 atmosphere of H₂.²⁾ Low water solubility makes H₂ sparging inefficient. Inefficient sparging leads to the second reason: Release of H₂ off gas can create a combustible atmosphere.²⁾

The MBfR overcomes the problems of sparging, because the H₂ is delivered directly to the biofilm by its diffusion through the wall of a gas-transfer membrane. Bubbleless H₂ transfer eliminates the problem of creating a combustible atmosphere. It also makes H₂ delivery nearly 100% efficient and virtually self-regulating.⁴⁾ In essence, the bacteria in the biofilm “pull” the H₂ through the membrane wall when they consume H₂ (in proportion to the reduction rate(s) of the reduced contaminant(s) and generate a H₂ gradient in the biofilm and across the membrane wall.

One of the strengths of the MBfR is that it is a platform technology that can be used in many settings for waters contaminated with one or more oxidized contaminants: drinking-water sources, ground or surface waters that must be bio-remediated, industrial and agricultural wastewaters, and municipal wastewater requiring advanced nutrient removal. The following sections describe these applications, summarize our experience with them, and identify special challenges that must be overcome.

DRINKING-WATER APPLICATIONS FOR NITRATE AND PERCHLORATE

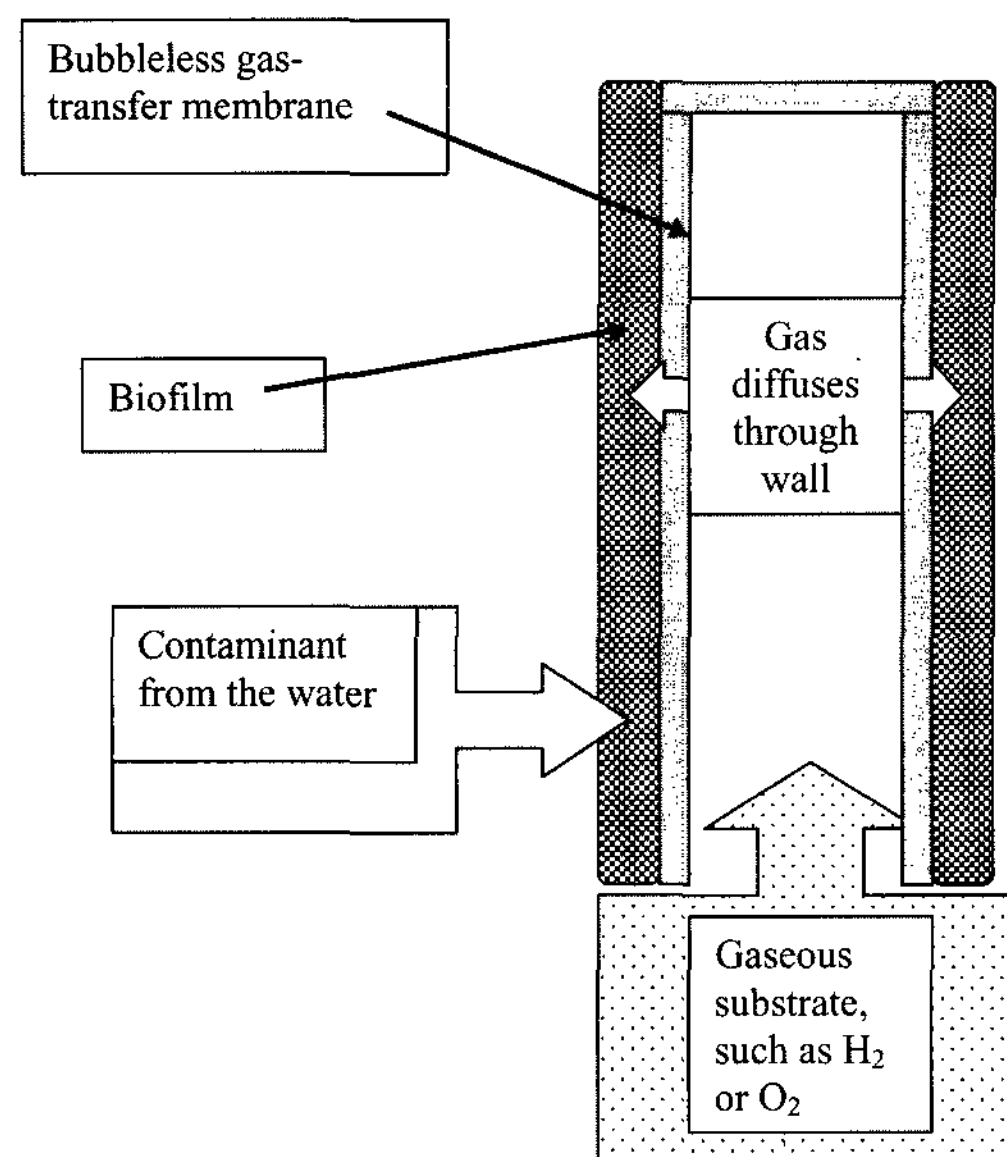
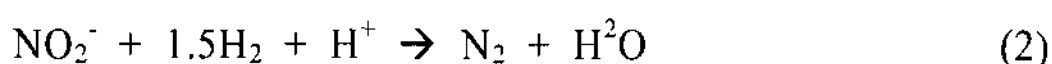
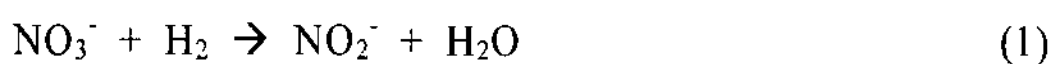


Figure 1. The concept of the membrane biofilm. The biofilm is the natural meeting place for the contaminant from the water and the gaseous substrate that the bacteria in the biofilm utilize to reduce or oxidize the contaminant.

The initial applications of the H₂-based MBfR targeted drinking water contaminated with nitrate, perchlorate, or both.^{2,3,37-43)} Extensive fundamental and applied research has been completed, and these applications are now moving to field testing and initial full-scale implementation.

Nitrate Reduction

Nitrate finds its way into surface and ground waters from agricultural drainage and run off, as well as from wastewater discharges and atmospheric deposition. Denitrification is the dissimilatory reduction of nitrate to nitrite and then to N₂ gas. Eqns. 1 and 2 show the two bio-reduction steps with H₂ as the electron donor:



Complete reduction of NO₃⁻ to N₂ requires 2.5 molH₂/molNO₃⁻, and synthesis of biomass adds a small (~10%) additional H₂ requirement. The second step consumes acidic hydrogen (H⁺),

which increases the water's alkalinity and may result in a pH increase. Denitrifying bacteria are common and almost always reduce O_2 in parallel to reducing NO_3^- . Thus, the denitrifiers naturally create the anoxic conditions that they need to carry out efficient nitrate reduction.

MBfR denitrification has proven to be simple and robust.^{2,37-39} Without needing a special inoculum, significant denitrification begins in a few days and becomes stable in one to two weeks. Lee and Rittmann² carried out extensive experimental studies to define the performance of the MBfR for denitrification in the drinking-water setting. Figure 2 summarizes the performance surface that they obtained. The effluent NO_3^- concentration is controlled by a combination of the NO_3^- surface loading (defined in the figure caption) and the H_2 pressure on the inside of the membrane. The NO_3^- surface loading defines the demand for H_2 delivery through the membrane's wall. The H_2 pressure controls the H_2 availability, or the potential to deliver H_2 as it is demanded. Comparing the curves for different H_2 pressures demonstrates that the capacity to reduce NO_3^- is easily modulated up or down by an increase or decrease in the H_2 pressure for a given surface loading. By the same measure, an increase in surface loading can be compensated by a higher H_2 pressure.

An interesting feature of denitrification in the drinking-water setting is that partial nitrate removal is the desired performance outcome, since a typical NO_3^- standard is 10 mgN/L.⁴⁴ Thus, the treatment goal usually is to keep the effluent NO_3^- concentration safely below 10 mgN/L, but it is not necessary to drive the NO_3^- concentration very low, such as to < 1 mgN/L. Figure 2(a) shows the trade off of surface loading to achieve partial denitrification. For example, when the goal is to achieve an effluent NO_3^- of 3 mgN/L, the combinations of H_2 pressure (psi) and surface loading (gN/m²-day) are 4.7 and 1.0 and 6.2 and 1.25. The H_2 pressure of 8.3 psi keeps the NO_3^- concentration well below 3 mgN/L. Clearly, using a higher H_2 pressures allows a greater surface loading for the same effluent NO_3^- concentration, which translates to lower membrane surface area and capital costs.

Perchlorate Reduction

Perchlorate (ClO_4^-) is a major component of rocket fuel, and it also is found in small amounts in certain fertilizers.³⁷ Widespread ClO_4^- contamination in ground water and selected surface water was discovered in the U.S.A. after new analytical methods lowered the detection limit to the μ g/L range. Although no formal standard is in place for ClO_4^- , California has a notification

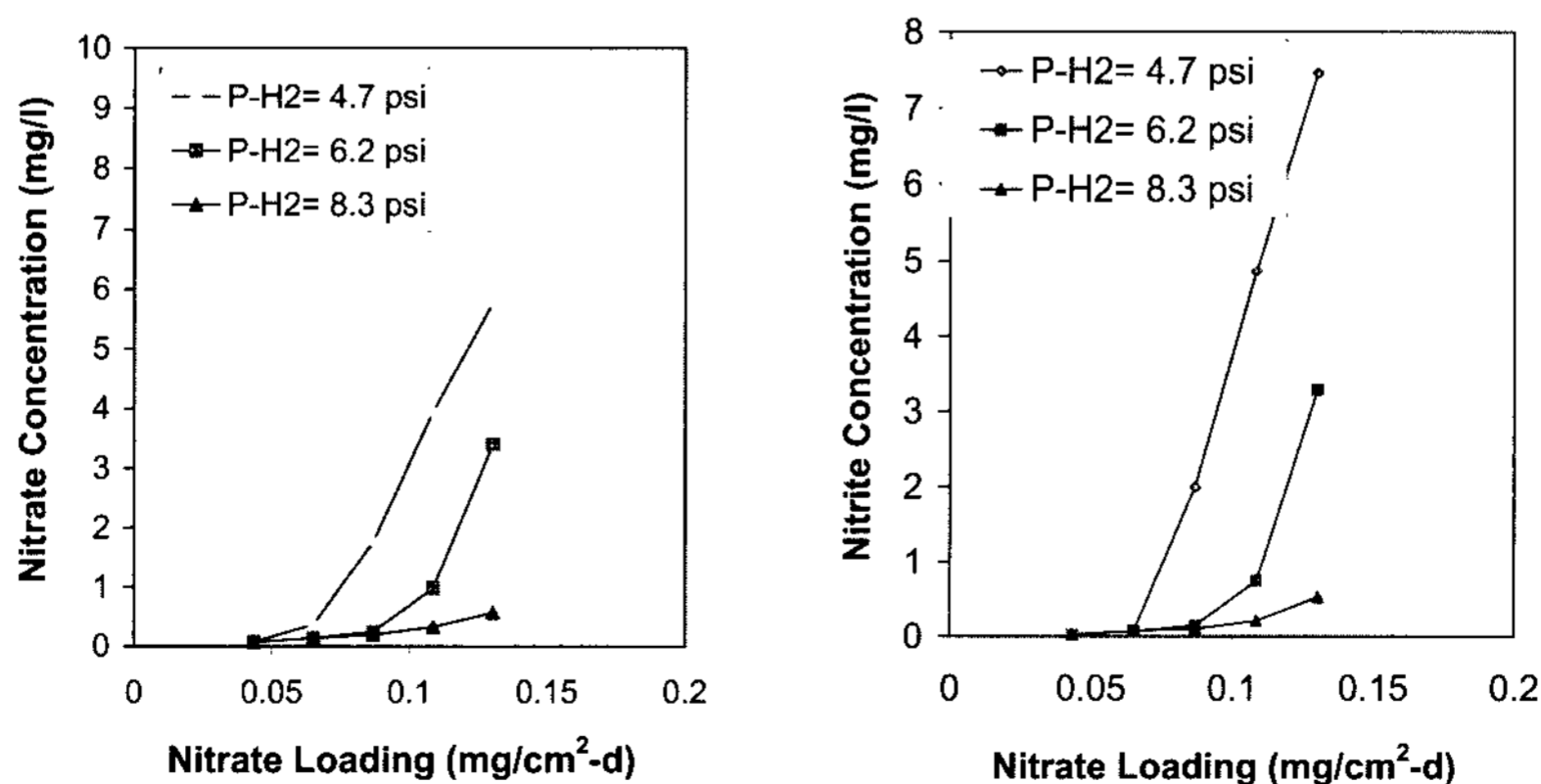
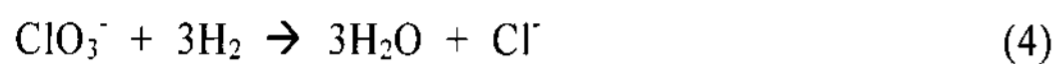
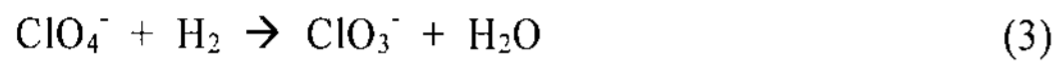


Figure 2. Response surface for how nitrate and nitrite concentrations depend on the nitrate surface loading (mgN/cm²-day) and H_2 pressure (psi).² The nitrate surface loading is defined as QS^0/A_m , in which Q = the influent flow rate, S^0 = the influent NO_3^- -N concentration, and A_m = the surface area of the biofilm-coated membrane. Conversions: 1 mgN/cm²-day = 10 gN/m²-day; 14.7 psi = 1 atm = 101 kPa = 101 kN/m².

level of 6 $\mu\text{g/L}$, and the U.S. Environmental Protection Agency has begun the process of establishing a maximum contaminant level (MCL). Although perchlorate can be removed by ion exchange or reverse osmosis, bio-reduction with H_2 is strongly preferable, since the reduction end products are harmless H_2O and Cl^- , as shown by eqns. 3 and 4.



Complete reduction of ClO_4^- requires 4 mol H_2 /mol ClO_4^- . The first step of ClO_4^- reduction produces chlorate (ClO_3^-), which normally does not accumulate.^{3,41)}

Nerenberg et al.³⁾ carried out the first evaluations of the MBfR for perchlorate reduction. When they challenged an MBfR already active in denitrification with ~ 1.4 mg/L of ClO_4^- , the MBfR gave $\sim 40\%$ ClO_4^- reduction immediately, and ClO_4^- reduction steadily increased to $> 99\%$ over about three weeks. Systematic studies of what controlled ClO_4^- reduction showed that it responded to the H_2 pressure in the same manner as NO_3^- , but even more sensitively. Perchlorate-reduction kinetics were slowed by having more than about 1 mgN/L of nitrate, which suggests that partial denitrification is not a viable option when perchlorate reduction is the goal.

Nerenberg et al.⁴⁶⁾ isolated an autotrophic, H_2 -oxidizing *Dechloromonas* strain that was enriched in the biofilm by addition of more perchlorate in the influent to the MBfR. However, this strain was present even with no ClO_4^- input, and it gained energy from the reductions of NO_3^- and O_2 . Thus, ClO_4^- can be reduced as a secondary electron acceptor, which makes it possible to achieve very low concentrations of perchlorate when NO_3^- , O_2 , or both is present in the influent.^{2,40,46,47)}

Based on excellent results with bench-scale MBfRs, Nerenberg, Rittmann, and colleagues at Montgomery-Watson-Harza^{4,48)} conducted pilot-scale studies at La Puente, California. They treated ground water containing ~ 25 mgN/L NO_3^-

and 60 $\mu\text{g/L}$ ClO_4^- , a typical situation with perchlorate contamination of ground water. The two-stage pilot MBfR treated 1 - 4 L/day continuously. Once the system stabilized, effluent NO_3^- and ClO_4^- were reduced to less than 0.5 mgN/L and 4 μgClO_4^- , respectively. One of the most important findings of the pilot study was that the actual H_2 delivery rate was nearly the same as the H_2 -utilization rate computed from the H_2 stoichiometry required to reduce the input electron acceptors (NO_3^- , ClO_4^- , and O_2). Thus, H_2 delivery to the biofilm was self-regulating, so that H_2 was neither over-dosed nor under-dosed. The pilot studies also identified the important role for biofilm control and achieving high surface loadings, topics discussed in the next section. Perchlorate reduction to below 6 $\mu\text{g/L}$ also was documented with two ground waters from California's San Joaquin Valley.⁴⁹⁾

Challenges for Nitrate and Perchlorate Reductions

The MBfR is now being tested in an expanding series of field trials that involve its licensee, Applied Process Technology, Inc. (www.aptwater.com). Experiences in the early field trials, with the La Puente pilot, and from about 9 years of bench-scale evaluations point out four challenges that must be resolved before the MBfR becomes a commercial success for drinking-water treatment.

The first challenge involves the correlated goals of biofilm control and effluent biomass. The pilot studies at La Puente⁴⁸⁾ underscored that accumulation of too much biomass can result in short-circuiting, poor mass transport, and fouling of the membranes with mineral precipitates and inert biomass. For pilot- and full-scale MBfRs, an in-place scouring and backwash system is the most direct method for removing excess biofilm. Water flushing follows gas (N_2 or air) scour for a few seconds. Most of the detached biofilm is removed from the system in the backwash water, not in the effluent.

Continuous detachment of biofilm always leads to a small concentration of biomass in the effluent. In the bench-scale studies of Lee and

Rittmann,²⁾ backwashing was not practiced, and the effluent suspended solids were less than 1 mg/L. With regular backwashing, the suspended solids in the effluent were much lower.⁴⁸⁾ Nonetheless, the effluent has a small concentration of bacteria that can be assayed by turbidity or heterotrophic plate counts. Thus, the MBfR should be followed by filtration (granular-bed or membrane) and disinfection, which easily bring bacteria to acceptable levels.

The second challenge is achieving partial nitrate removal at the same time that other process goals are attained. As shown in Figure 2(b), NO_2^- accumulates with certain combinations of NO_3^- surface loading and H_2 pressure. Since the typical MCL for NO_2^- is 1 mgN/L, certain combinations that give a satisfactory NO_3^- concentration may yield an unsatisfactory NO_2^- concentration. For example, both conditions that achieved an effluent NO_3^- concentration of 3 mgN/L (Fig. 2(a)) produced NO_2^- concentrations greater than 1 mgN/L. This situation is easily remedied by either lowering the NO_3^- loading or increasing the H_2 pressure. For example, keeping the H_2 pressure at 6.2 psi and lowering the NO_3^- surface loading to 1 gN/m²-day produced effluent NO_2^- and NO_3^- concentrations of approximately 0.5 mgN/L. In a similar vein, past experience suggests that satisfactory perchlorate removal is not consistent with a NO_3^- concentration greater than around 1 mgN/L. The most likely explanation for unsatisfactory reductions of NO_2^- and ClO_4^- is competition for H_2 , which is the common electron-donor substrate for all the reactions. At least for NO_2^- , increasing the H_2 pressure seems to overcome the problem. However, more systematic study is warranted for NO_2^- and ClO_4^- .

The third challenge is avoiding excessive accumulation of mineral precipitates, such as CaCO_3 and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$.⁵⁰⁾ A high calcium (or hardness) concentration is the most critical factor for making an MBfR susceptible to mineral precipitates. The generation of alkalinity during the second step of denitrification accentuates the problem by raising the pH, which shifts the acid/base equilibria towards the precipitating anions CO_3^{2-} ,

HO^- , and PO_4^{3-} .⁵⁰⁾ Excessive accumulation of mineral precipitates contributes to the general problems of having too much biofilm, and it also can make the membrane brittle and more subject to breakage. Practical means to prevent excessive mineral precipitates are preventing a pH rise and controlling the biofilm through regular and effective backwashing.

The fourth challenge is minimizing the capital cost. The initial purchase and replacement of the membranes can dominate the overall treatment costs if not kept in check. Hence, lowering the membrane cost is key to minimizing capital costs. Three strategies are essential for keeping capital costs low.

First, the MBfR should be designed with a high substrate flux of the oxidized contaminant(s), as long as process performance is acceptable. The required membrane area (A_m , in m²) depends on the flux (J , in g/m²-day) according to

$$A_m = Q(S^\circ - S)/J \quad (5)$$

in which Q = the volumetric flow rate (m³/day), S° = the influent concentration (g/m³), and S = effluent concentration (g/m³). Eqn. 5 makes it obvious that A_m is inversely proportional to J , and this is why J is such an important parameter. As shown in Figure 2, S and J are related, and information like that in Figure 2 is needed to establish what J values (coordinated with H_2 pressure) achieve acceptable performance.

Second, the specific surface area of the membranes (a , in m²/m³) should be high, as long as it does not compromise performance. The membrane surface area is the product of the specific surface area and the volume (V , in m³): $A_m = aV$. Clearly, making the specific surface area large allows a smaller and less expensive reactor volume for a given A_m . The specific surface area is maximized by using fibers of small diameter and by having a high packing density of the membrane fibers. These strategies must be balanced against the increased risk that of plugging the void space around the fibers and fiber clumping, both of which cause poor flow distribution

and mass transport.

Third, the material and fabrication costs of the membranes should be modest. All of the bench-scale research carried out by the author's team^{e.g.,2,3,49)} has employed a composite gas-transfer membrane manufactured by Mitsubishi-Rayon (Model HF 200TL). This membrane has a sandwich structure: A dense polyurethane core is sandwiched between microporous, hydrophobic layers of polyethylene. The composite membrane has functioned well, but also is relatively expensive. Non-porous, single-layer membranes are less expensive to manufacture and can be made in a range of diameters. Key to success is that the membrane be bubbleless, or have no continuous pores that transmit gas by advection. The bubbleless feature is essential so that the H₂ pressure on the inside of the membrane can be controlled independently of the water pressure on the outside.

OTHER OXIDIZED CONTAMINANTS

One of the greatest advantages of the H₂-based MBfR is that it is effective for reducing many oxidized contaminants beyond NO₃⁻ and ClO₄⁻. Research over the past 10 to 20 years suggests that H₂ is the "universal electron donor" for microorganisms.³³⁻³⁷⁾ The MBfR is the perfect vehicle

for testing the "universal-donor" hypothesis and, if true, putting it to good use.

Nerenberg and Rittmann³⁴⁾ performed screening studies to test the hypothesis. They operated two MBfRs to steady state with NO₃⁻ or O₂ as the primary electron acceptor. They then challenged both MBfRs with ~1,000 µg/L of 10 oxidized contaminants, applied one at a time for approximately 2 hours. Because the hydraulic detention time was only 24 minutes, the MBfRs reached steady state with regard to the concentration of the oxidized contaminant, but the 2 hours did not allow the biofilm to adapt to the presence of the target compound. As is summarized in Table 2, both MBfRs showed significant bio-reduction of every compound tested. The smallest degree of bio-reduction was 29%, and many compounds were reduced to a concentration below the detection limit. Thus, the H₂-oxidizing communities in the biofilm has widespread capability to bio-reduce many oxidized contaminants without adaptation.

The success with the initial screening study spurred the author's team, led in this effort by Dr. Jinwook Chung, to perform much more extensive tests with these and other oxidized contaminants that are important in contaminated ground water, industrial wastewater, and agricultural drainage. The following sections highlight the results.

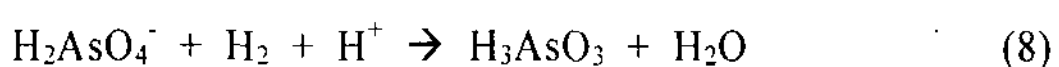
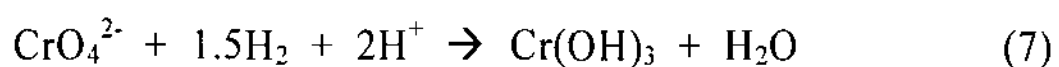
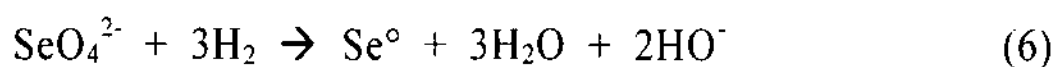
Table 2. Summary of the results of the screening study for a range of oxidized contaminants.³⁴⁾ Removal efficiencies are for short-term feeding of ~1,000 µg/L of each oxidized contaminant fed separately to the unacclimated MBfR biofilm. ">" means that the effluent concentration was below the detection limit

Oxidized Contaminant	Reduction Reaction	Removal Efficiency (%)	
		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	$\text{CrO}_4^{2-} + 1.5\text{H}_2 + 2\text{H}^+ \rightarrow \text{Cr}(\text{OH})_3$	>75	>75
Dichloro-methane	$\text{CCl}_2\text{H}_2 + 2\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}^+ + 2\text{Cl}^-$	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	$\text{SeO}_4^{2-} + 3\text{H}_2 + 2\text{H}^+ \rightarrow \text{Seo} + 4\text{H}_2\text{O}$	67	74
Selenite	$\text{HSeO}_3^- + 2\text{H}_2 + \text{H}^+ \rightarrow \text{Seo} + 3\text{H}_2\text{O}$	93	57

Oxyanions: Selenate, Chromate, and Arsenate

Selenate, chromate, and arsenate are inorganic oxyanions common in one or more of ground water, industrial wastewater, or agricultural drainage. Selenate (SeO_4^{2-} , or Se(VI)) is a serious contaminant in irrigation water in California, and it also is in wastewater from coal-burning power plants, oil refineries, and metal smelters.⁵¹⁾ Selenate causes reproductive problems and has an MCL of 50 $\mu\text{g/L}$ in the U.S.A. Chromate (CrO_4^{2-} , or Cr(VI)) is released from electroplating, mining, and fossil-fuel operations.⁵²⁾ It causes liver and kidney disease and has an MCL of 100 $\mu\text{g/L}$. Arsenate (H_2AsO_4^- , or As(V)) is a significant ground water pollutant that usually comes from dissolution of geological materials.⁵³⁾ It causes gastrointestinal damage, cardiac arrest, and cancer, and its MCL in the U.S.A. recently was lowered to 10 $\mu\text{g/L}$.

Each of these oxyanions can be reduced in an MBfR also active in nitrate reduction. The final reduced products are elemental selenium ($\text{Se}^\circ_{(s)}$), $\text{Cr(OH)}_{3(s)}$, and arsenite (H_3AsO_3). The reduction reactions with H_2 are:



Chung et al.⁵¹⁾ studied what controls Se(VI) reduction to Se° . They found that, upon its introduction to a denitrifying and sulfate-reducing MBfR, Se(VI) was immediately reduced. The initial reduction product was Se(IV), but the reduction progressed to Se° over three weeks. In parallel to the effects seen for nitrate (e.g., Figure 2) and perchlorate, the fractional selenate reduction to Se° increased with higher H_2 pressure and lower selenate surface loading. Selenate reduction also improved with lower nitrate loading, which reduced competition for the common electron donor, H_2 . Se° was retained in the biofilm and exited the reactor with detached biofilm, which was filterable.

Chromate reduction occurred immediately when

it was introduced into a denitrifying MBfR⁵²⁾, and the reduction increased over an 11-day adaptation period. In parallel with other oxidized contaminants, the rate and degree of Cr(VI) reduction increased when the H_2 pressure was raised. $\text{Cr(OH)}_{3(s)}$ precipitated when the pH was above 7.5 and was captured in the biofilm.

A particularly interesting finding is that the Se(VI)- and Cr(VI)-reducing MBfRs had the ability to reduce the other oxidized contaminant immediately when the input oxidized contaminant was switched.^{49,54)} Thus, the microbial communities in the H_2 -oxidizing biofilms had substantial functional redundancy for electron acceptors. The dominant strain in the biofilms was a *Dechloromonas* spp., a genus known for perchlorate reduction and apparently able to reduce chromate and selenate, too.⁵⁴⁾

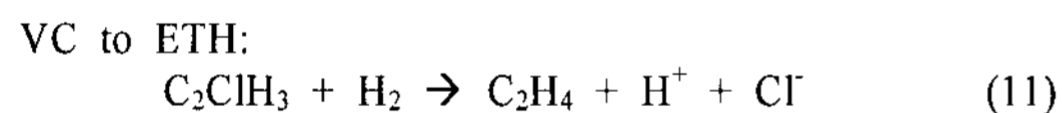
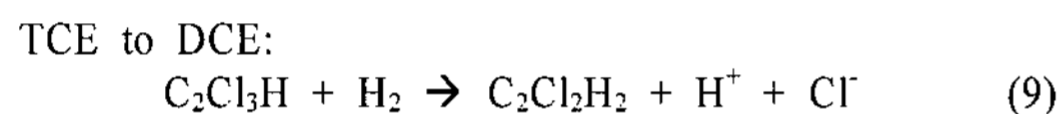
Arsenic is a serious ground water contaminant around the world, because it leaches from As-bearing minerals in the soil. The oxidation state of the As in the contaminated water can be III, V, or a mixture. When As(V) was applied to a denitrifying, sulfate-reducing MBfR,⁵³⁾ As(V) was reduced to As(III), which could be precipitated with sulfide or adsorbed to Fe(II) solids. As(V) reduction was sensitive to the sulfate and nitrate loadings, which suggests competition for H_2 , although higher H_2 pressure did not enhance As(V) reduction in this case. As(V) also was reduced in two ground waters collected from the San Joaquin Valley, California.⁴⁹⁾

Halogenated Organics

The large-scale use of halogenated organics in industry, agriculture, and cleaning operations has led to serious and persistent contamination, mostly of ground water, aquifer solids, and soil. Perhaps the most troublesome of the halogenated organics are the chlorinated solvents, such as trichloroethene (TCE), tetrachloroethene (PCE), trichloroethane (TCA), and chloroform (CF). They are known or suspected carcinogens, significantly water soluble so that they are mobile once dissolved in the water, and not easily biodegraded under natural conditions.³⁶⁾ Another class of trou-

blesome of halogenated organics are the pesticides, which have many chemical structures that often are persistent in the environment.^{35,36)} Among the most widely used and commonly detected halogenated pesticides is dibromochloropropane (DBCP).

While the halogenated organics typically resist biodegradation in natural environments, all of them can be reductively dehalogenated when an appropriate electron donor is provided, and H₂ always is an appropriate donor.^{35,36)} The reductions typically occur in a stepwise manner in which one halogen is removed at the same time that the molecule is reduced by 2 electrons. This stepwise approach is illustrated well by the very important example of TCE reductive dehalogenation with H₂:



TCE reduction proceeds through dichloroethene (DCE) and vinyl chloride (VC, also chloroethene) before being completed with production of ethene (ETH). While ETH is harmless, DCE and VC retain carcinogenicity; thus, it is essential that reductive dehalogenation be complete. Unfortunately, reductive dehalogenation often is not complete. For this reason, understanding the microorganisms and the reductive dehalogenase enzymes responsible for DCE and VC reduction has been a major research activity over the past decade or so.^{55,56)} A key discovery is that the final steps of reductive dehalogenation require the presence of certain *Dehalococcoides* strains that have reductive dehalogenases such as *bvcA*.

Chung et al.⁵⁷⁾ challenged a denitrifying MBfR with ~ 1,000 µg/L of TCE. TCE reduction began immediately and increased continually over 18 weeks. The intermediate reduction products (DCE and VC) appeared transiently, but disappeared so that the TCE was stoichiometrically reduced to

ETH. *Dehalococcoides* strains containing the *bvcA* reductive-dehalogenase genes were present in the MBfR biofilm without any special inoculation, and they increased after TCE application.

Additional studies with denitrifying MBfRs^{58,59)} documented that TCA and CF were reductively dehalogenated alone or in a mixture with TCE. As usual, a higher H₂ pressure increased the rates and extents of reduction, but increased competition for H₂, this time from sulfate reduction, slowed the rates of reduction for the chlorinated solvent.

DBCP was present in a California ground water that also contained nitrate. A MBfR simultaneously reduced nitrate to less than 0.01 mgN/L and DBCP to less than 0.01 µg/L, which is well below its MCL of 0.2 µg/L.⁴⁹⁾ Chang et al.⁶⁰⁾ showed that 2-chlorophenol was reductively dechlorinated in an MBfR, while Downing and Nerenberg⁶¹⁾ quantified the kinetics of bromate reduction.

Nitro and Nitroso Compounds

The nitro group (-NO₂) is found on a wide range of energetics, such as trinitrotoluene (TNT). Disinfection by-products, such as N-Nitrosodimethylamine (NDMA), contain the nitroso (-NO) group. These compound generally persist in the environment and exhibit carcinogenic, mutagenic, and teratogenic properties.^{35,36,62)} It is well known that the nitro group can be bio-reduced in the energetics,^{35,36)} and bio-reduction of the nitroso group on NDMA seems feasible when H₂ is available as an electron donor. Chung et al.⁶²⁾ tested the hypothesis for NDMA with an MBfR active is nitrate and sulfate reductions. NDMA was bio-reduced by up to 96% in the MBfR, and the rate of reduction responded in the normal manner to H₂ pressure and competing electron acceptors. Although this study was not able to identify the final reduction product(s), it clearly documented that NDMA is susceptible to bio-reduction when H₂ is available as the electron donor.

Challenges for MBfR Reduction of the Other Oxidized Contaminants

The recent results with the wide range of inorganic and organic oxidized contaminants strongly support the promise of the H₂-based MBfR as a platform technology that can solve many emerging water-quality problems. Translating the promise into commercial technology will require that at least four challenges be met.

The first challenge is dealing with mixtures of two or more oxidized contaminants, particularly when the contaminants are of different chemical types. A classic example is having oxyanions, such as chromate and perchlorate, present along with chlorinated organics. While initial results suggest that co-reduction is possible^{49,58,59)}, mixtures have not yet been studied systematically. Important questions need to be answered concerning interactions among the different oxidized contaminants. While it is clear that competition for H₂ is always relevant, more subtle interactions are possible and may be important. These include beneficial secondary utilization of a trace-level acceptor when a more plentiful primary acceptor is co-reduced,^{46,47)} problematic inhibition of one acceptor by another, and competition for space in the biofilm when different species reduce different acceptors.

A second challenge is related to the first challenge, but distinguishable in its own right. It is the need to reduce a primary electron acceptor in order to accumulate enough biomass to fully reduce a low-concentration contaminant that is a secondary acceptor.⁴⁶⁾ Almost every MBfR study conducted up to now has had ample inputs of NO₃⁻, O₂, or both to serve as a primary electron acceptor. Thus, biofilm accumulation has not been a problem, and the target oxyanions or chlorinated organics were well reduced once the NO₃⁻ or O₂ was depleted inside the MBfR. While almost every study has provided evidence of community adaptation to the presence of the target contaminant, the immediate reduction of the target contaminants suggests that the capable bacteria were present and being supported by reduction of the primary acceptor. Nerenberg et al.⁴⁶⁾ quantified the secondary-utilization effect for perchlorate reduction using *Dechloromonas*.

The second challenge has two facets. On the one hand, some contaminated waters may not have a primary acceptor, and this could hamper reduction of the target oxidized contaminant to low-enough concentration. On the other hand, reduction of the primary acceptor increases the cost of H₂ supply; therefore, it is economically wise to provide only as much primary acceptor as is needed to meet treatment goals. Today, little is known about what constitutes enough primary acceptor.

The third challenge is controlling sulfate reduction, since sulfate commonly is present in waters containing oxidized contaminants. In most cases, sulfate reduction is not desired because it increases the demand for H₂ and generates sulfide odors and precipitates. However, sulfate reduction can be desirable in two circumstances: when an objective is to form a sulfide precipitate, such as As₂S_{3(s)} for As(III) removal.⁴⁹⁾ and when sulfate is the necessary primary acceptor. The second situation has not yet been documented, but this could be due only to the reality that the relationships of primary and secondary donors have not been researched thoroughly. Although information on controlling sulfate reduction is sketchy, three factors seem to play a role. The first is the H₂ pressure, and lowering the H₂ pressure can suppress or reverse sulfate reduction. The second is biofilm management to prevent the accumulation of too much biomass. Strong biomass detachment measures suppress or stop sulfate reduction. The third is periodic exposure to O₂, such by air scour during backwashing.

The final challenge is carrying out MBfR treatment in salty water. Industrial wastewaters and agricultural drainage often have total dissolved solids (TDS) concentrations greater than 10,000 mg/L. Brines generated by ion exchange or reverse osmosis have TDS value greater than 30,000 mg/L, and much higher concentrations are frequent. Almost all of the past MBfR research has been in "fresh water," or with TDS values far less than 10,000 mg/L. One exception is a study on nitrate and perchlorate reductions from ion-exchange brines with TDS of 20,000 to

150,000 mg/L.⁵⁹⁾ This study demonstrated MBfR reductions of NO_3^- and ClO_4^- in all cases, but the reduction kinetics slowed dramatically for TDS concentrations of 40,000 mg/L and higher. Thus, the issue of high TDS is kinetics and how to obtain rapid reduction kinetics despite elevated TDS. Increased H_2 pressure improves the bio-reduction rate,⁵⁹⁾ but more tools may be needed if the inhibitory effect of TDS is great.

ADVANCED NITROGEN REMOVAL IN WASTEWATER TREATMENT

Perhaps the most pervasive water-quality problem that the MBfR can address is advanced nutrient removal from wastewaters. Worldwide concern over the effects of eutrophication, including hypoxia in the oceans and estuaries, is leading to the obvious conclusion that nutrient discharges from wastewater treatment plants must be reduced substantially. Advanced nitrogen removal will be phased in over the next years, especially when the discharge ultimately reaches an ocean. The MBfR can play an important role in achieving advanced-N removal.

Although far from universally implemented, pre-denitrification has been a highly successful approach for attaining significant N removal at the same time as energy consumption for aeration is minimized.^{35,64)} In pre-denitrification, part of the influent BOD is utilized as an organic electron donor to drive denitrification and total-N removal. Because the input form of N almost always is the (reduced) ammonium form, the treatment system has an aerobic, nitrification stage to convert NH_4^+ to NO_3^- , as well as to oxidize any BOD not removed by denitrification. The "trick" to pre-denitrification is that the nitrate formed in the aerobic stage is recycled back to an anoxic stage at the beginning of the process so that the influent BOD is available to drive denitrification. While pre-denitrification is remarkably effective for using influent BOD to drive denitrification, practical considerations limit the N removal to around 75%.³⁵⁾ For example, if the

influent Total-N concentration to biological treatment is 60 mg/L, the effluent from a pre-denitrification process will be at least 15 mgN/L, with most of the N in the form of NO_3^- .

While pre-denitrification offers many benefits, it cannot meet an advanced-N standard, which is going to be in the range of 1-3 mg/L total N. This means that the performance of pre-denitrification must be upgraded substantially. Since other forms of N inevitably will exist in the effluent, the upgraded performance must reliably drive NO_3^- to less than 1 mgN/L. The H_2 -based MBfR can provide the needed upgrade is either of two ways: tertiary treatment or *in situ* augmentation. It also can be used as a stand-alone system for total-N removal. Figure 3 shows schematics of the three approaches, which are described in the next sections.

Tertiary Advanced N Removal

The most direct approach for advanced-N removal with the MBfR is tertiary denitrification. In short, the effluent from the pre-denitrification process is routed through an MBfR system so that the NO_3^- concentration is reduced from around 10 - 15 mgN/L to less than 1 mg/L (Fig. 3(a)). It is equally possible to apply tertiary denitrification from a conventional nitrification-only process. The main difference is that the NO_3^- concentration will be substantially higher, ≥ 30 mgN/L.

Using the MBfR for tertiary denitrification overcomes two large drawbacks of tertiary denitrification with addition of an organic electron donor, such as methanol. The first drawback is that over-dosing or under-dosing of the organic donor is common. Under-dosing causes the system to fail in its job of total-N removal. Over-dosing causes a breakthrough of rapidly degradable BOD, which can violate the discharge standard for BOD and cause serious fouling for downstream processes. The self-regulation of H_2 delivery with the MBfR should eliminate dosing inaccuracy. The second drawback is the high waste sludge production from the growth of heterotrophs that oxidize the added organic donor.

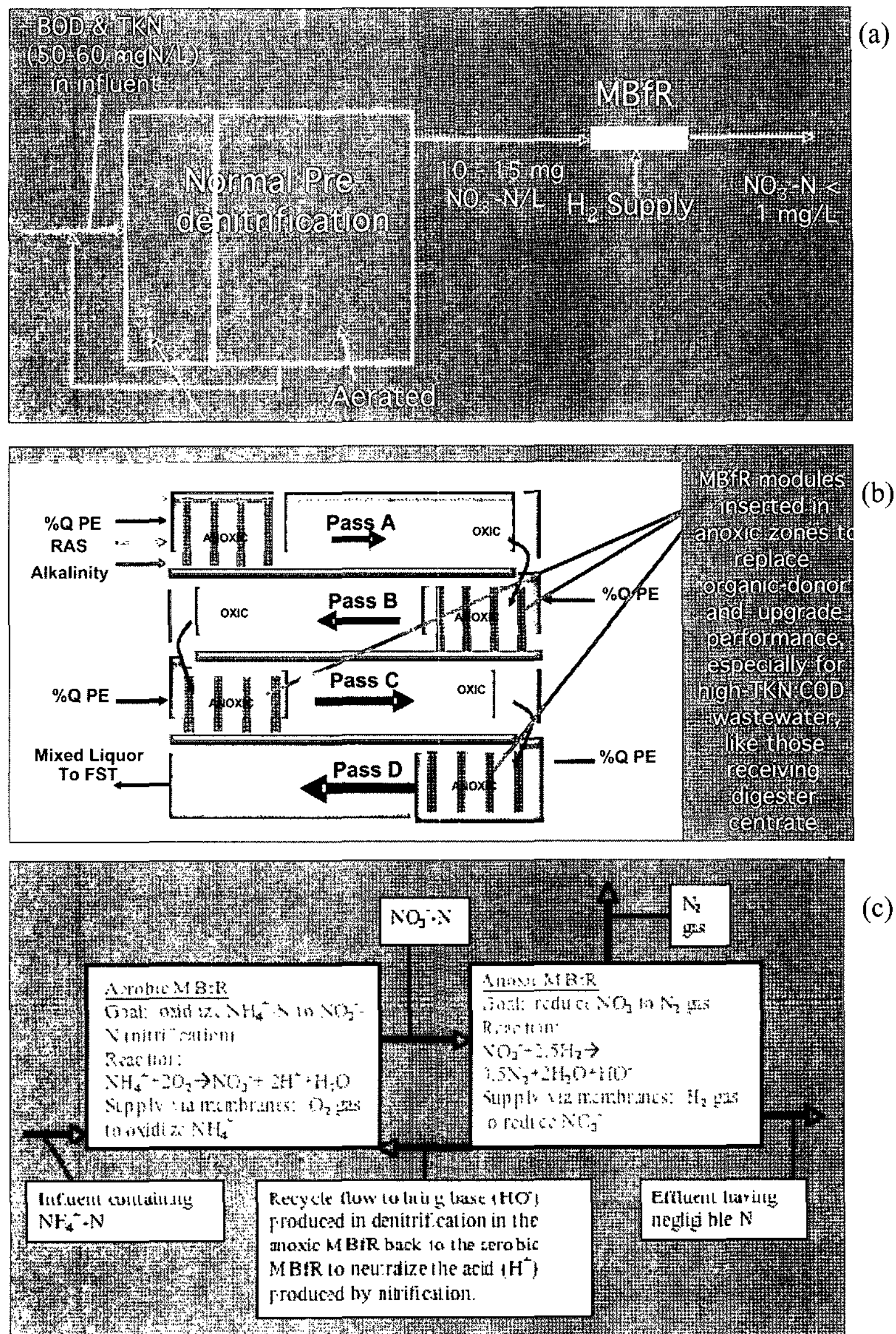


Figure 3. Three approaches for using the H₂-based MBfR for advanced total-N removal: (a) tertiary denitrification following pre-denitrification, (b) *in situ* augmentation of staged pre-denitrification, and (c) the completely autotrophic aerobic/anoxic MBfR.^{7,65,68-70)}

The excess-sludge production with the MBfR should be 3 to 4 times less than with a heterotrophic system.

Because the tertiary approach resembles how the MBfR is used for treating drinking water, all the experience gained with MBfR denitrification in the past²⁾ can be applied directly. Likewise, the MBfR configuration can be similar to that used for drinking water. A likely adjustment is

that the MBfRs used for tertiary denitrification may require more robust means to prevent excess accumulation of biomass, since its influent will contain suspended solids and some BOD.

Rittmann et al.⁶⁴⁾ tested the tertiary-treatment concept by passing effluent from an activated sludge process through an MBfR having a special “matrix” design to minimize fouling by suspended solids. The influent to the MBfR had

a NO_3^- concentration of 13 - 16.4 mgN/L, and the H_2 pressure was adjusted to control denitrification performance. Denitrification began quickly, and steady-state performance was achieved with a H_2 pressure of only 2 psi (0.14 atm): The NO_3^- concentration decreased from 13 mgN/L to 0.85 mgN/L at a NO_3^- flux of 1.4 gN/m²-day. The system performance responded as usual to the H_2 pressure. For example, increasing the H_2 pressure to 5 psi (0.34 atm) brought the effluent NO_3^- concentration down to 0.4 mgN/L, even though the influent concentration increased to 16.4 mgN/L and the NO_3^- flux increased to 1.8 gN/m²-day. This work established the feasibility of tertiary denitrification, and a pilot-scale demonstration is now in progress in Arrowhead, California.

***In Situ* Augmentation of Pre-denitrification**

The alternative to tertiary denitrification is to augment the performance of a pre-denitrification system by placing MBfR modules directly in the anoxic zones of the pre-denitrification system (Fig. 3(b)).⁶⁴⁾ Thus, it is an *in situ* approach that obviates the need to construct any new tanks. The *in situ* approach requires that the pre-denitrification system have more than one anoxic zone, and the MBfR modules are placed in the second, third, etc. anoxic zones. The first zone is used for denitrification with influent BOD. Augmented *in situ* pre-denitrification with MBfR modules overcomes the same two drawbacks of augmentation using organic donors: inaccurate dosing and high excess-sludge production.

At this time, *in situ* modules are not yet tested. In principle, they can be constructed in a manner similar to the immersed membrane separators used in membrane biofilm reactors (MBRs).^{65,66)} As with MBRs, membrane fouling must be prevented through a combination of membrane cleaning, removing fouling materials from the influent, and controlling the NO_3^- loading.

Aerobic/Anoxic MBfR for Total-N Removal

It is possible to achieve total-N removal using a stand-alone MBfR technology.^{7,67-69)} This MBfR-only approach, called the aerobic/anoxic MBfR,⁷⁾

couples an O_2 -based MBfR that nitrifies influent NH_4^+ -level N to NO_3^- with a H_2 -based MBfR for NO_3^- reduction (Fig. 3(c)). If the wastewater contains BOD, it is oxidized in the aerobic MBfR. The two MBfRs should be linked together with a recycle loop so that the based produced by denitrification is able to neutralize some of the acid generated by nitrification.

Cowman et al.⁷⁾ demonstrated the aerobic/anoxic MBfR by treating a synthetic wastewater containing 50 mgN/L of NH_4^+ and no NO_3^- or NO_2^- . They were able to drive the total-N concentration to 1.5 mg/L (97% removal) when the O_2 and H_2 pressures were similar to each other and around 2 psi (0.14 atm). Shin et al.⁶⁷⁻⁶⁹⁾ also achieved excellent total-N removal (98%) with fluxes up to 2.1 gN/m²-day for nitrification and 1.7 gN/m²-day for denitrification.

The aerobic/anoxic approach seems most pertinent to new installations and when the wastewater has a high N/BOD ratio. These conditions make it possible to gain space benefits from using an MBfR approach instead of activated sludge. Being strictly autotrophic, the aerobic/anoxic MBfR also generates the minimum excess sludge for disposal. The concept of the aerobic/anoxic MBfR is proven,^{7,67-69)} but it has not been tested beyond the bench scale. Important unresolved issues include: the best O_2 and H_2 pressures, the influence of BOD oxidation and heterotrophs on nitrification in the aerobic MBfR, the relative surface loadings for NH_4^+ in the aerobic MBfR and for NO_3^- in the anoxic MBfR, and the recycle between the two MBfRs.

Layered Heterotrophic Denitrification with Nitrification

An O_2 -based MBfR also can be used to achieve total-N removal.⁷⁰⁻⁷⁶⁾ As illustrated in Figure 4, the organic electron donors (i.e., the BOD) present in the wastewater drives denitrification in a biofilm that grows on a membrane that supplies O_2 . The nitrifying bacteria, which produce the NO_3^- and NO_2^- that serve as electron acceptors for denitrification, accumulate near the membrane surface, since this is the source of

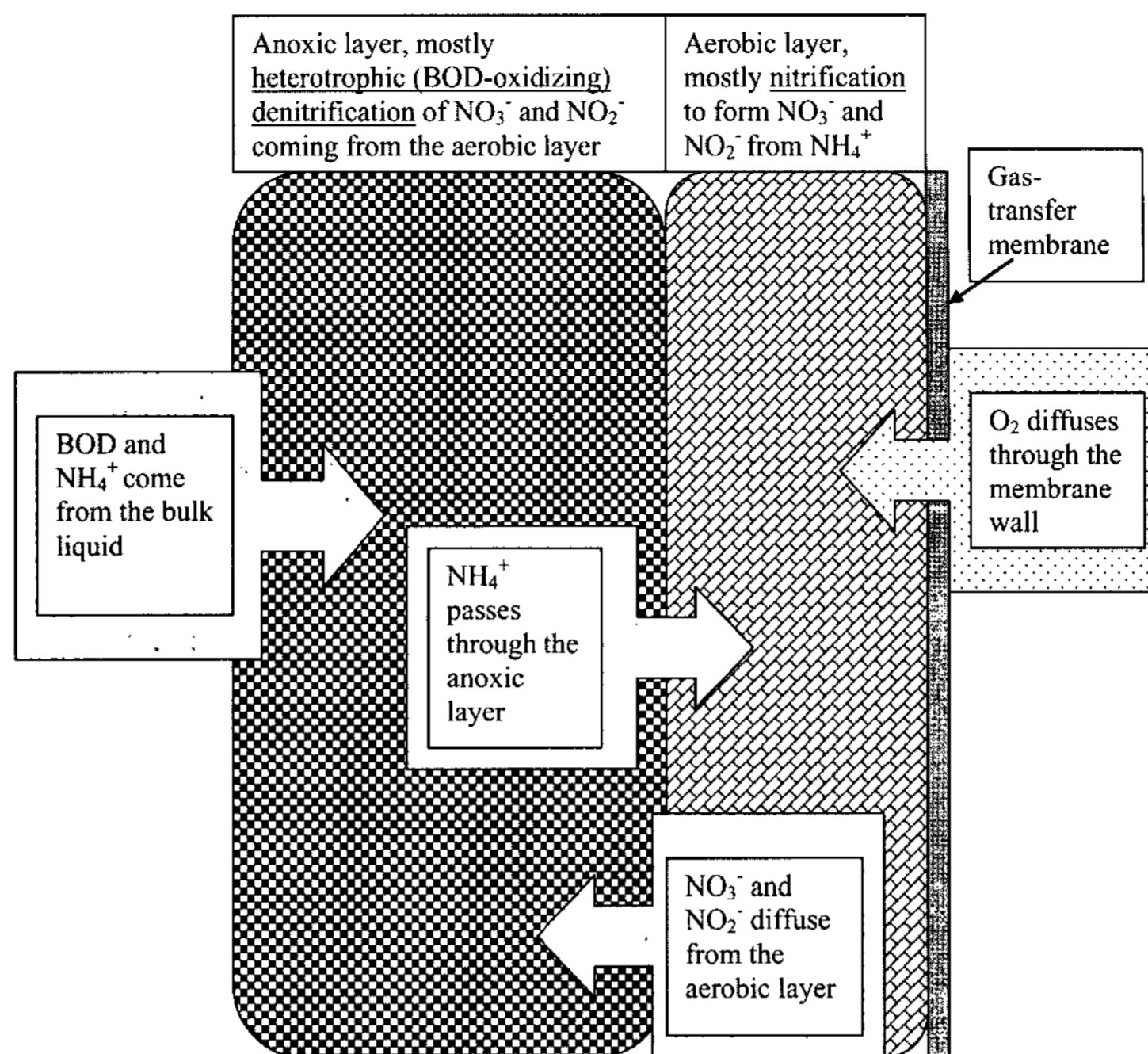


Figure 4. Schematic of the idealized situation for multi-layer nitrification and heterotrophic denitrification in an MABR.

their electron acceptor (O_2). In addition, accumulation of the slow-growing nitrifiers is enhanced because they are protected from detachment and predation, which are most important at the outer surface of the biofilm. Multi-layer denitrification with nitrification has been amply demonstrated of MABRs,⁷⁰⁻⁷⁶⁾ although the translation to a commercial technology has yet to be attained.

CONCLUSIONS

The MBfR is a natural partnership of a membrane and biofilm, because the membrane delivers a gaseous substrate to the biofilm. The substrate usually is O_2 or H_2 . While O_2 -based MBfRs have existed for much longer than H_2 -based MBfRs, the H_2 -based approach has greater potential to solve emerging problems in water quality and become a commercial success.

The H_2 -based MBfR is a versatile platform for reducing oxidized contaminants in many water-treatment settings: drinking water, ground water, wastewater, and agricultural drainage. Extensive bench-scale experimentations over the past

ten years has proven that the H_2 -based MBfR can transform one or several oxidized contaminant to harmless or easily removed forms. The contaminants include inorganic oxyanions (e.g., NO_3^- , NO_2^- , ClO_4^- , ClO_3^- , SeO_4^{2-} , $HSeO_3^-$, AsO_3^- , CrO_4^{2-} , and BrO_3^-), halogenated organics (e.g., TCE, TCA, CF, and DBCP), and nitroso organics (e.g., NDMA). The MBfR has been tested at the pilot scale for NO_3^- and ClO_4^- and is now entering field testing for most of the oxidized contaminants.

In order to achieve commercial success, the several issues must be resolved by bench and field testing. Among the most crucial issues are the understanding interactions with mixtures of oxidized contaminants, treating waters with a high TDS concentration, developing modules that can be use *in situ* to augment pre-denitrification, and keeping the capital costs low.

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NOMENCLATURE

Parameter Symbols

a = specific surface area, m^{-1} or m^2/m^3

A_m = membrane area, m^2

J = substrate flux, g/m^2 -day

Q = volumetric flow rate, m^3/day

S = effluent and reactor concentration, g/m^3

S° = influent concentration, g/m^3

V = reactor volume, m^3

Acronyms

BOD = biochemical oxygen demand

CF = chloroform

DBCP = dibromochloropropane

DCE = dichloroethene

ETH = ethene

MABR = membrane-aerated biofilm reactor

MBfR = membrane biofilm reactor

MBR = membrane bioreactor

MCL = maximum contaminant level

NDMA = N-Nitrosodimethylamine

PCE = tetrachloroethene, also perchloroethylene

TCA = trichloroethane

TCE = trichloroethene, also trichloroethylene

TDS = total dissolved solids

TNT = trinitrotoluene

Total-N = total nitrogen

VC = vinyl chloride

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