

The Hydrogen-Based Hollow-Fiber Membrane Biofilm Reactor (HFMBfR) for Removing Oxidized Contaminants

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Abstract

Research with a laboratory prototype and at the pilot scale documents that the hydrogen-based hollow-fiber membrane-biofilm reactor (HFMBfR) is technically and economically feasible for reduction of nitrate and perchlorate. In the HFMBfR, H₂ gas diffuses through the wall of a composite membrane, and an autotrophic biofilm naturally develops on the outside of the membrane, where the bacteria's electron acceptor is an oxidized contaminant (e.g., NO₃⁻ or ClO₄⁻) supplied from the water. The hydrogen pressure to the hollow fibers is a key control parameter that can be adjusted rapidly and easily. For denitrification, partial nitrate removal often is acceptable, and the hydrogen pressure can be low to minimize the costs of H₂ supply and the concentration of H₂ in the effluent. When perchlorate must be reduced, full nitrate removal is essential, since NO₃⁻-N above about 0.2 mg/L slows perchlorate reduction. Perchlorate reduction is sensitive to the hydrogen pressure, which underscores the critical role of H₂ pressure for controlling process performance. Given that H₂-oxidizing microorganisms have the potential to reduce many oxidized contaminants, we hypothesize that and are beginning to test how well the HFMBfR reduces bromate, selenate, chlorinated solvents, and other oxidized contaminants.

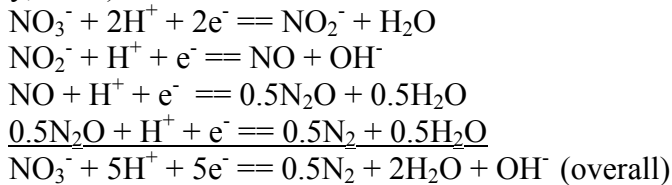
Keywords

Biofilm, denitrification, hollow-fiber membrane, hydrogen reduction, oxidized contaminants, perchlorate reduction, water treatment

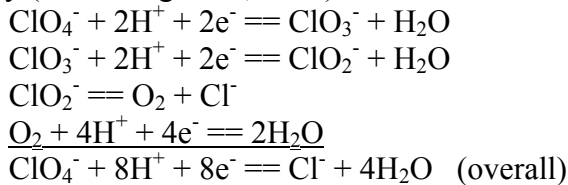
Oxidized Contaminants

Many of the emerging water contaminants share a common characteristic: they are chemically oxidized. The classic examples are nitrate (NO_3^-) and nitrite (NO_2^-), which are increasingly polluting waters subject to agricultural fertilizers. Because nitrate and nitrite cause methemoglobinemia in infants, their U.S. drinking-water standards are 10 and 1 mgN/L, respectively (Rittmann and McCarty, 2001). A more recently discovered oxidized pollutant is perchlorate (ClO_4^-), which mainly comes from rocket fuel. Perchlorate affects thyroid function and has a recommended action level of only 4 $\mu\text{g/L}$ (Nerenberg et al., 2002).

Microbially catalyzed reduction of oxidized pollutants detoxifies them by producing a reduced product that is innocuous. For example, nitrate is stepwise reduced to harmless N_2 gas by denitrification, which requires 5 electron equivalents (e^-) per mole of NO_3^- -N (Rittmann and McCarty, 2001):



Likewise, perchlorate is microbially oxidized to the innocuous Cl^- ion in an 8-electron pathway (Nerenberg et al., 2002):



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 (Banaczak et al., 1999; NRC, 2000; Rittmann and McCarty, 2001):

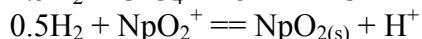
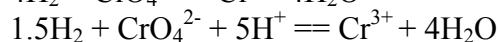
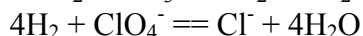
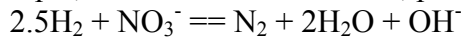
- chlorinated solvents, like trichloroethene (TCE), which can be reductively dehalogenated to ethene and Cl^- ion.
- bromate (BrO_3^-), which is an ozonation byproduct that can be reduced to Br^- ion.
- selenate (SeO_4^{2-}), which occurs naturally in certain mineral deposits and can be reduced to less 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).

Microbial Reduction with Hydrogen Gas

The key to microbial reduction is bringing together the oxidized contaminants, bacteria able to reduce them, and an electron-donor substrate that the bacteria can oxidize. The most widely useful electron donor for the wide range of microbial reductions is hydrogen gas (H_2), which releases 2 electrons per mole:



For example, full reductions of nitrate, perchlorate, chromate, and Np(V) with H₂ are



Besides being the electron donor most widely used by microorganisms, hydrogen has four other major advantages as an added electron donor. First, it is by far the least expensive donor per equivalent of electrons supplied (Lee and Rittmann, 2000). Second, it is non-toxic to humans. Third, it evolves from water that has an open surface, thereby eliminating a residual that could cause biological instability or disinfection byproducts in drinking water. Finally, it supports the growth of autotrophic bacteria, which need no organic C source and form minimal excess biomass. When H₂ is used as the electron donor, the system is called autohydrogenotrophic (Lee and Rittmann, 2000; Rittmann and Lee, 2002).

The Hollow-Fiber Membrane-Biofilm Reactor

The Hollow-Fiber Membrane-Biofilm Reactor (HFMBfR) is the optimal environment for bringing together the oxidized contaminant, the capable bacteria, and H₂ as the electron donor. The HFMBfR is different from membrane bioreactors (MBRs) used to treat wastewaters (Manem and Sanderson, 1996; Rittmann, 1998; Rittmann and McCarty, 2001). In an MBR, the membrane is a solids separator that replaces the settler, such as in activated sludge. Water passes through the membrane to yield a solids-free effluent and concentrated sludge for recycling. Thus, the MBR application of a membrane is the same as the in microfiltration and ultrafiltration of drinking water: namely, producing a particle-free permeate.

In the HFMBfR, H₂ gas diffuses through the walls of a special composite membrane, illustrated in Figure 1. The hollow fiber contains a 1- μm thick nonporous, hydrophobic polyurethane layer sandwiched by micro-porous polyethylene walls. The dense polyurethane layer allows slightly pressurized gas to diffuse through the membrane without forming bubbles. Biofilm naturally grows on the outside wall of the membrane fibers, because the H₂ electron donor meets the contaminant electron acceptor at that interface. Because of the counter-current transport of H₂ and the oxidized contaminant in the biofilm, the H₂-utilization efficiency can be nearly 100%, which enhances the economics and prevents forming an explosive atmosphere above the water.

At Northwestern University, we built a laboratory-scale prototype for studies on nitrate and perchlorate reduction by the autohydrogenotrophic HFMBfR (Lee and Rittmann, 2000, 2002a; Rittmann and Lee, 2002; Nerenberg et al., 2002). The membrane fibers were installed in a tube reactor about 1 m long. The laboratory prototype contained 83 fibers that provided 750 cm² of surface area for biofilm attachment (specific surface area was 180 m⁻¹). Feed and recycling flow rates during the experiments were fixed at 10 and 1,750 ml/min, respectively. The recycle controlled the liquid flow velocity for good mass transport and to prevent fiber clumping. The system was seeded initially with *Ralstonia eutropha*, but a diverse mixed culture developed over time.

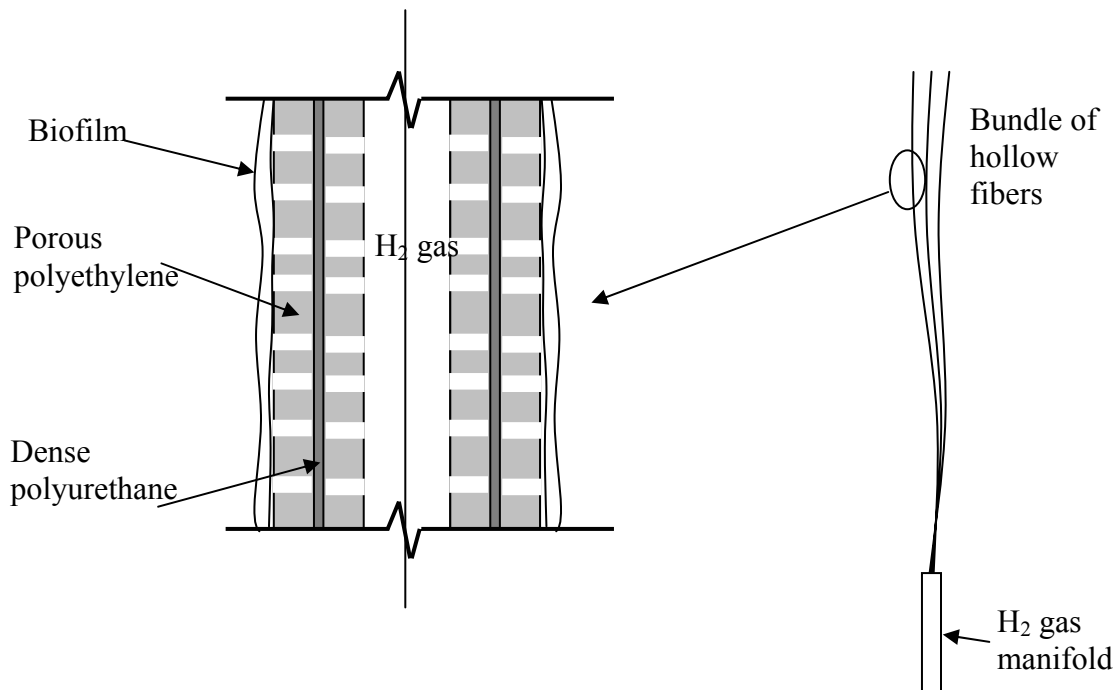


Figure 1. Schematic (left) of how the H₂ diffuses through the sandwich wall of the composite membrane fibers, while biofilm naturally forms on the outer surface, where the oxidized contaminant is available from the water phase. Bundles of hollow fibers are potted together and pressurized with H₂ gas (right).

Experience with Denitrification

We carried out extensive studies at Northwestern University to evaluate the capability of the HFMBfR for drinking-water denitrification. The methods and results were fully reported (Lee and Rittmann, 2000, 2002a,b; Rittmann and Lee, 2002), and we provide a brief summary here.

The influent nitrate concentrations were 10 and 12.5 mg N/l for the first and second steady states, respectively. At steady-state with a liquid retention time of 40 min, we achieved the desired partial removals of nitrate between 76 and 92 % with effluent hydrogen concentration as low as 9 µgH₂/L. The nitrate flux was as high as 1 g N/m²-d due to the “counter-diffusion” type of substrate transfer. We prevented fiber clumping, and the biofilm detachment rate from the fibers was very low, about 0.015/day. Table 1 summarizes key steady-state results.

Table 1. Summary of Steady-State Result for the HFMBfR Treating Nitrate

Parameter	Steady-State 1	Steady-State 2
Influent NO ₃ ⁻ -N, mg/L	10	12.5
H ₂ pressure, psi (atm)	4.5 (0.31)	6.2 (0.42)
NO ₃ ⁻ -N flux, gN/m ² -d	0.8	1.0
Effluent NO ₃ ⁻ -N, mg/L	2.4	1.0
Effluent NO ₂ ⁻ -N, mg/L	0.9	0.7
Effluent H ₂ , µg/L	9	70
Effluent SS, mg/L	0.6	1.1

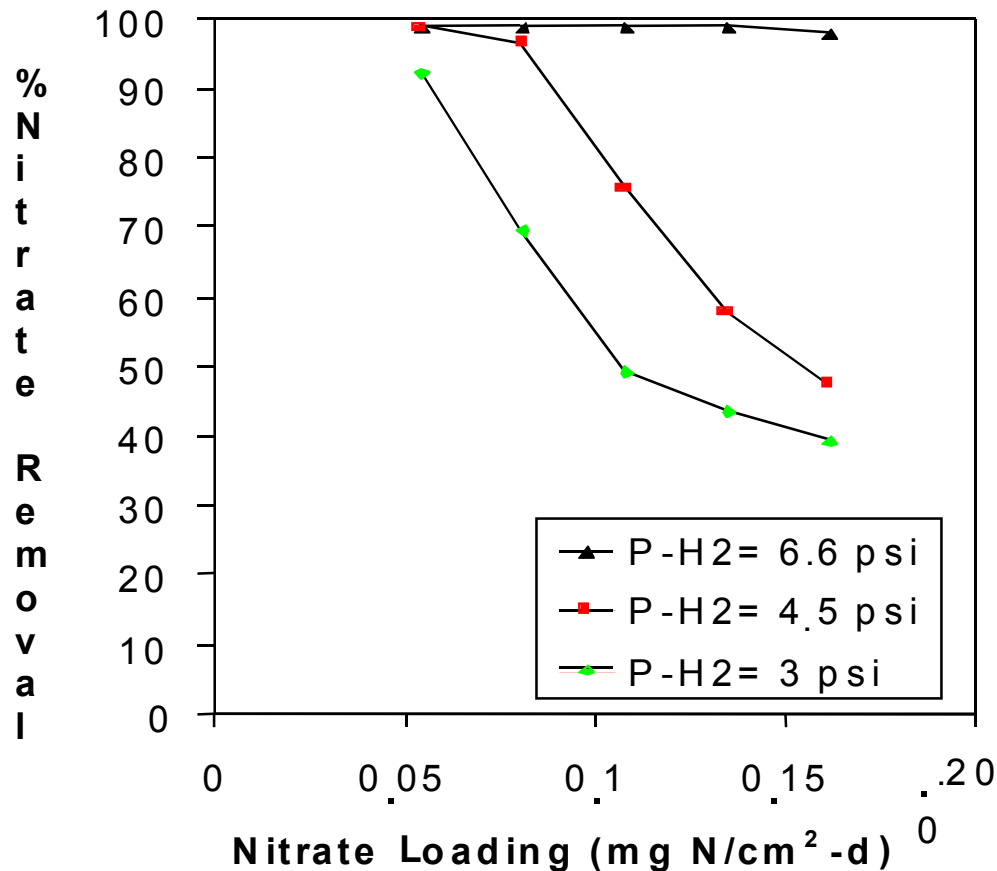


Figure 2. The response of the percent nitrate removal to changes in nitrate loading and hydrogen pressure for short-term experiments during steady-state 1. $0.1 \text{ mgN/cm}^2\text{-d} = 1 \text{ gN/m}^2\text{-d}$. $1 \text{ psi} = 0.068 \text{ atm}$.

For each steady state, we ran many nonsteady-state experiments to test the HFMBR's response to nitrate loading and H₂ pressure (Lee and Rittmann, 2002a; Rittmann and Lee, 2002). Each short-term study lasted for more than three liquid retention times to allow the formation of a pseudo-steady state in the reactor. Figure 2 provides a succinct summary of how the HFMBR responded for steady-state 1. The key conclusion from the nonsteady-state experiments is that adjustments to the H₂ pressure to the hollow fibers easily and rapidly controlled the effluent nitrate concentration and % nitrogen removal. For example, a loading of $0.1 \text{ mgN/cm}^2\text{-d}$ ($= 1 \text{ gN/m}^2\text{-d}$) gave nearly 100% NO₃⁻ removal when the H₂ pressure to the fibers was 6.6 psi (0.45 atm), but reducing the H₂ pressure to 3 psi (0.2 atm) gave partial removal of 50%. For drinking-water treatment, the goal is to keep the effluent NO₃⁻-N below the standard of 10 mgN/L, which makes partial removal feasible and desirable. Other applications may require full nitrate removal and, therefore, higher H₂ pressure.

Experience with Perchlorate Reduction

Following the successful studies with denitrification, we used the same prototype reactor at Northwestern University and added perchlorate to the denitrifying system (Nerenberg et al., 2002). We saw immediate perchlorate removal (roughly 40% removal from 1,600 $\mu\text{g/L}$), and the removal increased over two weeks to nearly 100%. This shows that the autotrophic denitrifiers were capable of reducing perchlorate, but that the growth of bacteria with better capability to remove perchlorate occurred over time.

Perchlorate removal was adversely affected by a high nitrate concentration in the reactor. NO_3^- -N greater than about 0.1 to 0.2 mg/L slowed perchlorate reduction, and NO_3^- -N above about 0.5 mg/L slowed perchlorate reduction by 50% or more. On the other hand, increasing the H_2 pressure increased perchlorate removal, and the effect was much more dramatic than for denitrification. These findings mean that partial denitrification is not an option when perchlorate reduction is required, while controlling hydrogen pressure is a key for good perchlorate removal.

After completing systematic studies with the laboratory prototype, we challenged it with a perchlorate-contaminated groundwater from California. We used the groundwater with its normal ClO_4^- concentration of 6 $\mu\text{g/L}$, and we also spiked the ClO_4^- concentration to 100 or 50 $\mu\text{g/L}$ to provide a more severe test of the HFMBfR. Figure 3 shows that the HFMBfR removed perchlorate to below the 4- $\mu\text{g/L}$ action level in all cases.

Northwestern University is continuing studies with laboratory-scale HFMBfRs. The main focus is on the microbial ecology and kinetics of perchlorate reducers in the HFMBfRs. We also are conducting screening studies on other oxidized contaminants. For example, we already have seen that bromate is essentially 100% reduced to Br^- for conditions of nitrate and perchlorate reduction.

Pilot-Scale System

Montgomery-Watson-Harza designed, built, and is currently operating a pilot-scale system to treat a perchlorate-contaminated groundwater in La Puente, California. The pilot system has two HFMBfRs in series. The current flow rate is 0.3 gpm, and effluent recycle is provided at 4.5 gpm to improve mass transport and minimize clumping of the fibers. We periodically practice air scouring to remove excess biofilm and reverse clumping.

Although the current results are not yet optimized, they show that the promise of the laboratory studies can be attained at a larger scale. Currently, percent removals of nitrate and perchlorate average around 98% of 24 mg NO_3^- -N/L and 95% of 60 μgClO_4^- /L. The effluent perchlorate concentration is below the 4- $\mu\text{g/L}$ action level. Stoichiometric computations based on the removals of all electron acceptors in the groundwater (i.e., 24 mg/L of NO_3^- -N, 6 mg/L of O_2 , and 60 $\mu\text{g/L}$ of ClO_4^-) show that hydrogen utilization is almost exactly equivalent to acceptor reduction. This is an important finding, because it means that no hydrogen is wasted, a key to good economy and safe operation.

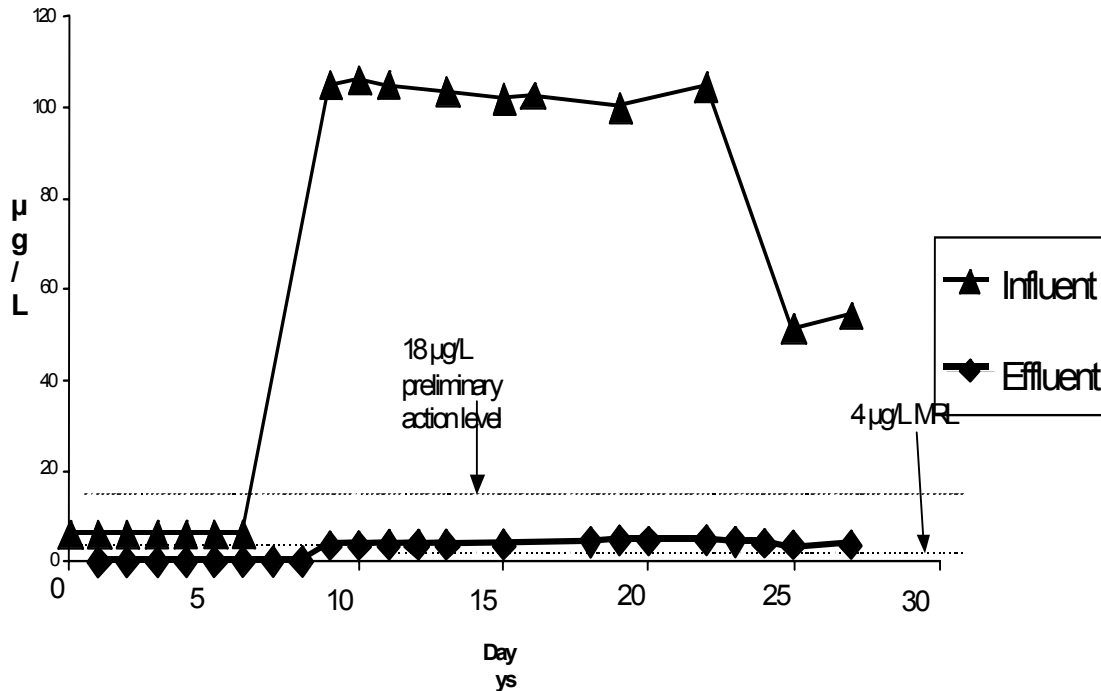


Figure 3. Results of challenging the HFMBfR with a perchlorate-contaminated groundwater from California. The concentration scale is $\mu\text{g/L}$ of ClO_4^- . The natural background perchlorate was $6 \mu\text{g/L}$, and we spiked the groundwater to 100 or $50 \mu\text{g/L}$.

Preliminary Economic Analysis

Montgomery-Watson-Harza took the lead in performing a preliminary engineering design and economic analysis (Rittmann et al., 2001). They evaluated designs for three typical groundwaters contaminated with perchlorate and nitrate. The designs were for complete drinking-water treatment: perchlorate and nitrate reduction with a HFMBfR system, post aeration, rapid filtration for removal of particles and biological instability, and post-chlorination. The key design criteria are summarized in Table 2.

Table 2. Preliminary Design and Cost Criteria for Full Treatment Based on the HFMBfR for Nitrate and Perchlorate Reduction

Unit Process	Selected Key Design and Cost Criteria
HFMBfR	3-stage system, total HRT = 30 min., ClO_4^- flux = $0.23\text{g/m}^2\text{-d}$, specific biofilm surface area = 31 m^{-1} , H_2 consumption stoichiometric to reductions of NO_3^- and ClO_4^- , US\$6/kg H_2
Post-Aeration	$30 \text{ m}^3/\text{min}$ per 1000m^3 volume, 0.08US\$/kW-h
Rapid Filters	Multi-media with hydraulic loading of $12 \text{ m/h} = 5 \text{ gpm/ft}^2$
Post-Chlorination	At least 1 mg/L as Cl_2

The total-treatment unit cost (capital plus operation) was 0.5-0.8US\$/1000 gallons (0.13-0.21US\$/m³) for 1,000 gpm (3.8 m³/min) capacity. This cost compares favorably with the wholesale price of water from the California water project, \$1.3/1000 gallons (0.35US\$/m³). The impact of economies of scale is illustrated in Table 3, which is for a groundwater having 6.5 mg/L of NO₃⁻-N and 90 µg/L of ClO₄⁻. Table 4 shows that the influent nitrate concentration controls the operating costs, since nitrate normally is the dominant electron acceptor and, therefore, its reduction is the largest H₂ consumer. Utility B, which has the highest nitrate concentration, has the highest annual operating cost, which translates to the highest unit cost.

Table 3. Effects of Flow Capacity on the Cost of Full-Treatment Based on the HFMBfR for Influent Conditions of NO₃⁻-N = 6.5 mg/L; ClO₄⁻ = 90 µg/L (1000 gpm = 3.8m³/min)

Flow Capacity	2,500 gpm	1,000 gpm	500 gpm
Total Capital Cost, US\$	2,112,000	933,000	497,000
Annual O&M Cost, US\$/year	481,000	263,000	225,000
<u>Water Production Unit Cost</u>			
US\$/1000 gallons	0.49	0.64	1.10
US\$/m ³	0.13	0.17	0.27

Table 4. The Influent Nitrate Concentration is the Main Water-Quality Factor Affecting Operating Costs. The Flow Capacity is 1000 gpm (3.8 m³/min)

Utility	A	B	C
Influent NO ₃ ⁻ -N, mg/L	6.5	13	0.5
Influent ClO ₄ ⁻ , µg/L	90	30	18
Annualized Capital Costs, US\$1000/year	75	70	65
Annualized Operation Costs, US\$1000/year	263	342	230
<u>Water Production Unit Cost</u>			
US\$/1000 gallons	0.64	0.78	0.56
US\$/m ³	0.17	0.21	0.15

Conclusions

Our research with a laboratory prototype and at the pilot scale documents that the hydrogen-based HFMBfR is technically and economically feasible for reduction of nitrate and perchlorate. The hydrogen pressure to the hollow fibers can be adjusted rapidly and easily to control performance. For denitrification, partial nitrate removal often is acceptable, and the hydrogen pressure can be low to minimize the costs of H₂ supply. When perchlorate must be reduced, full nitrate removal is essential, since NO₃⁻-N above about 0.2 mg/L slows perchlorate reduction, and perchlorate reduction is sensitive to the hydrogen pressure.

Our on-going research is elaborating details of the microbial ecology and kinetics for perchlorate reduction by the HFMBfR and is optimizing process design and refining the economic analyses. Given that H₂-oxidizing microorganisms have the potential to reduce many oxidized contaminants, we are beginning a systematic study of how well the HFMBfR reduces bromate, selenate, chlorinated solvents, and other oxidized contaminants.

Acknowledgements

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