

Bromate Reduction to Bromide in a Hydrogen-Oxidizing Bioreactor

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Abstract

Sustained biological bromate (BrO_3^-) reduction was demonstrated in a hydrogen-based membrane biofilm reactor (MBfR). With 1 mg/L bromate and 5 mgN/L nitrate in the influent, the effluent bromate was 0.12 mg/L and the bromate flux was $1.1 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. When influent bromate was increased to 4 mg/L, the effluent bromate was 3.5 mg/L with a flux of $0.92 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. In both experiments, nitrate was fully reduced to below detection, and bromide (Br^-) was produced stoichiometrically from bromate. When nitrate was excluded from the influent, bromate initially was reduced from 4 mg/L to 3.4 mg/L, but gradually fell to below 2 mg/L. Sustained bromate reduction in the absence of nitrate suggests that hydrogen oxidizing, bromate-reducing bacteria may exist. An additional test was run with 100 $\mu\text{g/L}$ bromate, closer to typical bromate concentrations in drinking water, and 5 mgN/L nitrate. The effluent was well below the 10 $\mu\text{g/L}$ drinking water standard, suggesting that the MBfR may be suitable for concurrently reducing bromate and nitrate in drinking water.

Introduction

Bromate (BrO_3^-), a suspected human carcinogen, is produced from bromide (Br^-) during ozonation or advanced oxidation of drinking water (Kurata 1992). Bromate is regulated as a disinfection by-product at 10 $\mu\text{g/l}$ (Clark 2001), and pilot and full-scale drinking water studies show bromate can form at concentrations as high as 150 $\mu\text{g/l}$ (Krasner 1993). Bromate management is important when ozonation and advanced oxidation processes are used for drinking water treatment (Butler 2005).

Granular activated carbon (GAC) has been examined as a potential treatment process for bromate reduction. GAC filters initially were believed to reduce bromate abiotically based on surface charge and electrostatic reactions (Asami et al. 1999; Bao et al. 1999). Batch experiments have since indicated that bromate reduction in GAC occurs mainly due to biological activity, not abiotic processes (Kirisits 1999). High dissolved oxygen (DO) and nitrate concentrations adversely impact bromate reduction in biologically active carbon (BAC), (Kirisits 1999; Kirisits et al. 2001).

Denitrifying bacteria can reduce bromate to innocuous bromide (Hijnen et al. 1995); therefore denitrifying bioreactors may be suitable for treating bromate in drinking water (Hijnen et al. 1999). Bromate can also be co-metabolically reduced with chlorate as the primary electron acceptor and hydrogen as the electron donor (van Ginkel et al. 2005a). Bromate also can serve

as a primary electron acceptor for a mixed microbial community, when acetate is the electron donor (van Ginkel et al. 2005b).

Biological reduction has been demonstrated for a variety of oxidized contaminants in drinking water, such as nitrate, selenate, chlorate, and perchlorate. One reason it is not commonly practiced in water treatment is because an electron donor must be added, and common donors, such as methanol, ethanol, and acetate, can cause biological instability, taste and odor problems, and health concerns. Hydrogen overcomes many of these problems, as it is non-toxic, inexpensive, and unlikely to create biological instability, and also is possible to generate on site. Hydrogen has been known to be an effective electron donor since the 1970s, but a safe and efficient delivery system was lacking.

A new reactor, the hollow-fiber membrane biofilm reactor (MBfR), was developed to safely and efficiently deliver hydrogen to a biofilm for reduction of oxidized contaminants in drinking water. The MBfR has been shown to be effective for drinking water denitrification (Lee 2000; Lee and Rittmann 2002) and for perchlorate reduction (Nerenberg et al. 2002). Preliminary tests also show it can be effective for bromate reduction (Nerenberg and Rittmann, 2004). When 1 mg/L bromate was spiked into a hydrogen-based MBfR continuously supplied with 5 mgN/L of nitrate, approximately 95% bromate reduction was achieved (Nerenberg and Rittmann 2004). However, these tests were of short duration (around 2 hours). It was not known whether bromate reduction can be sustained. Also, potential effects of the bromate concentrations on performance are not known, and it is not clear whether common denitrifiers or specialized bacteria are involved in bromate reduction in an MBfR.

Our research examines the ability of a denitrifying hydrogen-based MBfR to reduce bromate over an extended period of time. After sustained bromate reduction was verified, various influent levels of bromate were tested, as well as the ability of bromate to serve as a primary electron acceptor.

Methods

The hydrogen-based MBfR used in our research was similar to that used by others (Lee and Rittmann 2002; Nerenberg and Rittmann 2004; Nerenberg et al. 2002). It consisted of a bundle of 16 hollow-fiber membranes housed in glass tubing (Figure 1). The hollow-fiber membranes were made from a composite material consisting of microporous polyethylene encasing a dense, polyurethane core (HFM200TL, Mitsubishi Rayon, Japan). The membrane outside diameter was approximately 280 μm , and the total membrane surface area was 30.5 cm^2 . Hydrogen gas was supplied to the inside of the hollow fiber membranes at a pressure of 5 psi, allowing it to diffuse through the membranes into a hydrogen-oxidizing biofilm that formed on the fibers' outside surface. The total volume of the reactor was 25 cm^3 . Influent flow rate was maintained at 0.5 mL/min, resulting in a hydraulic retention time of 50 minutes. The recirculation rate in the reactor was 150 mL/min, providing well-mixed condition in the reactor. The reactor was inoculated with activated sludge from the local wastewater treatment facility (Mishawaka, IN). Bromate, bromide, nitrate, and nitrite were monitored by ion chromatography (IC2500 with AS11/AG11 column, Dionex Corp, Sunnyvale CA.) with a sodium hydroxide eluant. The feed contained a 16 mM phosphate buffer, but on day 43 the buffer concentration was reduced to 4

mM in order to improve analytical bromate resolution. Prior to day 43, influent bromate concentrations were calculated from the mass of sodium bromate added, and effluent bromate concentrations were based on the effluent bromide concentrations.

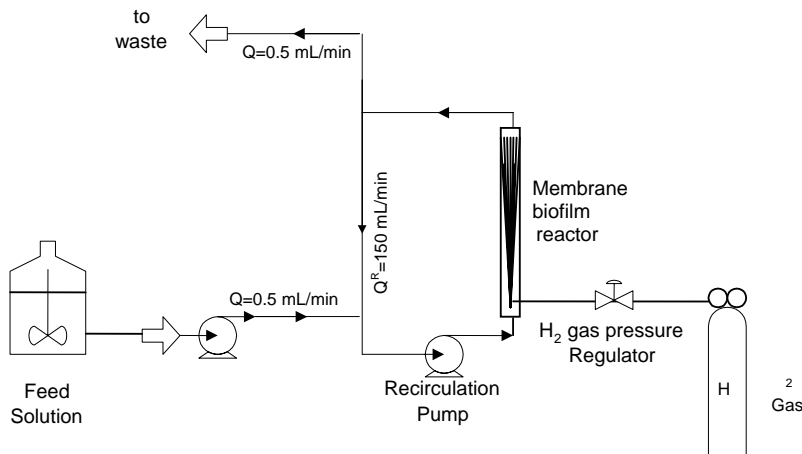


Figure 1 Schematic of the MBfR

Initially, the MBfR was fed nitrate only and operated as a denitrifying bioreactor. Once steady-state denitrification was achieved, the MBfR was tested under four loading conditions. The first tested bromate reduction under denitrifying conditions over an extended period of time. Subsequently, nitrate was removed and bromate was tested as a primary electron acceptor. For the third loading condition, nitrate was added at a lower concentration. Finally, a new MBfR was used to test denitrification and bromate reduction with a typical drinking water bromate concentration, 100 $\mu\text{g/L}$. Loading conditions to the reactor are summarized in Table 1. The influent bottle was open to the atmosphere for the majority of the experiments, and contained an average of 6.5 mg/L of dissolved oxygen (O_2). Sparging of the influent with nitrogen gas (N_2) was performed from day 152 to day 169 in an effort to increase bromate reduction.

Table 1 Loading conditions to the MBfR tested sustained bromate reduction in the presence and absence of nitrate

Loading Condition	Day	Nitrate (mgN/L)	Bromate (mg/L)
1	1 - 73	5	1
1	74 - 78	5	7
1	79 - 118	5	4
2	118 - 169	0	4
3	170 - 183	1	4
4*	1-21	5	0.1

*New MBfR

Results

Steady-state denitrification was achieved after 14 days. When 1 mg/L bromate was added to the influent, the effluent bromate concentration decreased to 0.43 mg/L over three days. The bromate removal flux from day 3 to day 73 averaged $1.10 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$, with effluent bromate ranging from 0.12 mg/L to 0.60 mg/L. Effluent bromide ranged from 0.16 mg/L to 0.50 mg/L. On day 73, the influent bromate was increased to 7 mg/L, while nitrate was kept at 5 mgN/L. Initially, the bromate flux was $4.13 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$, with effluent bromate at 5.4 mg/L. Over 4 days, the effluent bromate increased to 6.9 mg/L, with a bromate flux of $0.14 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. Bromide was produced stoichiometrically from bromate, with 1.8 mg/L bromide on day 74 and 0.1 mg/L by day 78. The lower flux at higher effluent bromate concentrations suggests that bromate is self inhibitory at higher concentrations. Subsequently, the influent bromate was briefly lowered to 1 mg/L, then increased to 4 mg/L from day 85 to day 118. Bromate fluxes averaged $0.92 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ at this higher concentration, with effluent bromate ranging from 3.5 to 3.9 mg/L. Effluent bromide returned to approximately 0.4 mg/L. Full denitrification (>99% removal) was maintained throughout experimentation. Results of this first operating condition are shown in Figure 1.

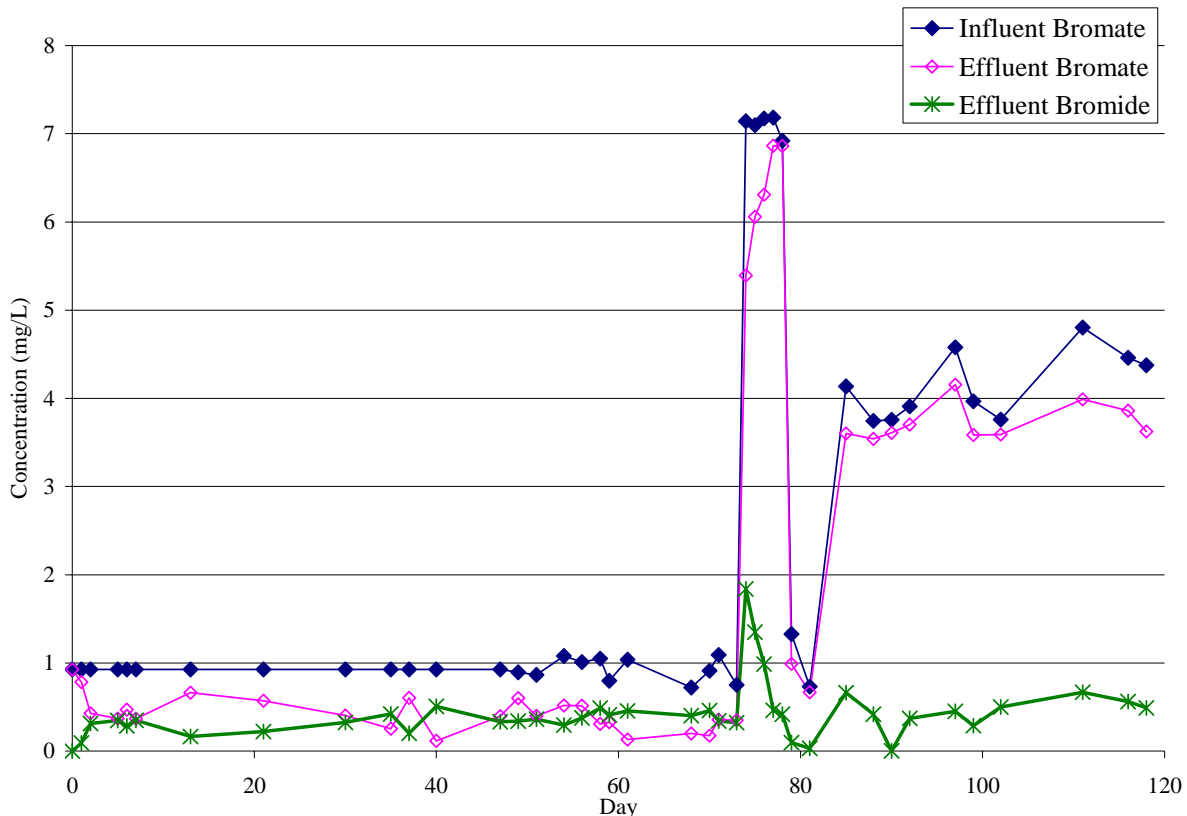


Figure 1. Loading Condition 1: Sustained bromate reduction was achieved with nitrate (5 mgN/L) as the primary electron acceptor

After achieving sustained bromate reduction for 118 days, the ability of the MBfR to reduce bromate in the absence of nitrate was examined. Influent bromate concentrations were maintained at approximately 4 mg/L, while nitrate was eliminated. Initially, bromate reduction remained approximately the same, with fluxes averaging $1.66 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. However, after day 140 effluent bromate gradually decreased. By day 150, bromate fluxes increased to $4.23 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$, with an effluent bromate concentration of 2.5 mg/L. In an attempt to further improve bromate reduction, after day 152 the influent was sparged with N_2 gas, reducing the influent DO to 0 mg/L. Oxygen may serve as an alternative electron acceptor to bromate, and eliminating the oxygen was expected to produce more favorable conditions for bromate reduction. The N_2 -sparged influent resulted in improved bromate fluxes, maximizing at $5.53 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. However, after achieving a maximum flux on day 155, the flux decreased. The potential cause of this response is discussed later. Bromate reduction was greatly reduced after day 159. The results from day 118 to day 169 are shown in Figure 2.

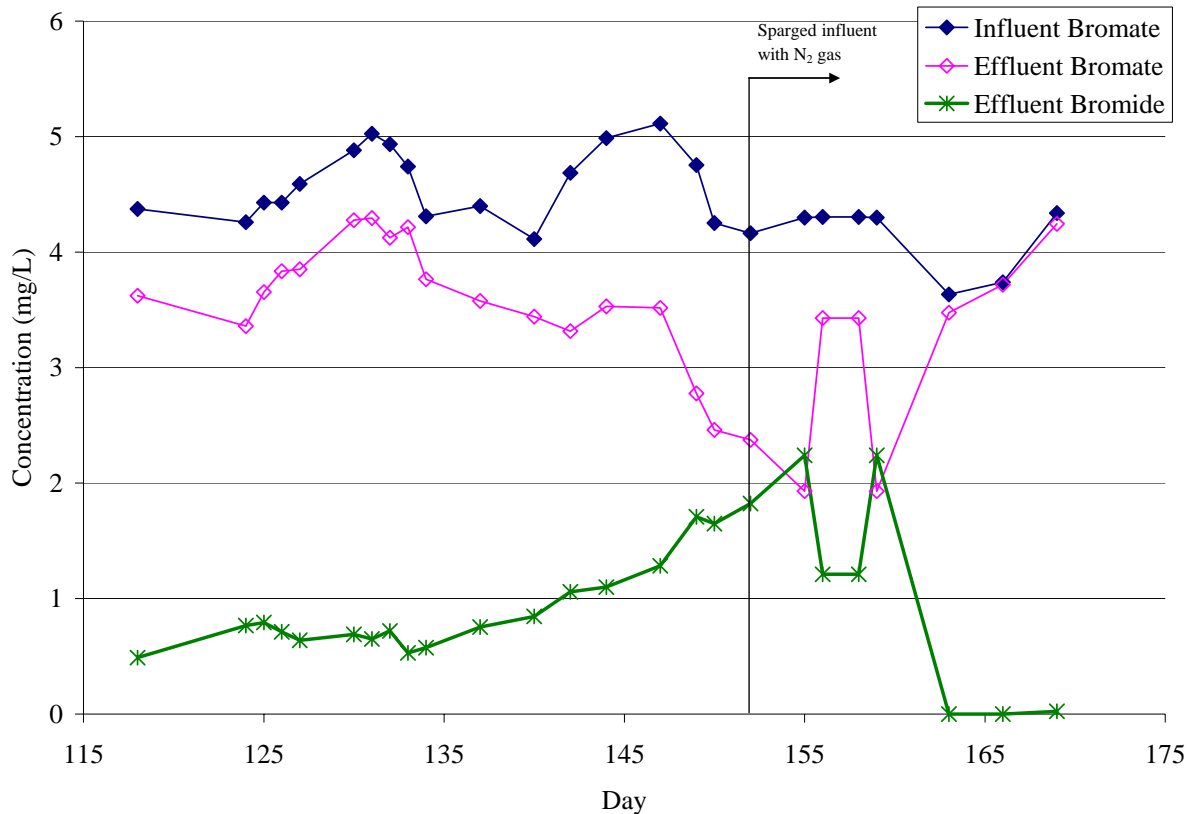


Figure 2. Loading Condition 2: Bromate was the primary electron acceptor

After bromate reduction was inhibited on day 169, an attempt was made to reestablish bromate reduction by reintroducing nitrate at a lower concentration and ceasing the nitrogen sparging of the influent. Nitrate was fed at 1 mg/L, while the bromate concentration remained at approximately 4 mg/L. Full denitrification returned immediately. Bromate reduction also reestablished in the reactor, however at lower fluxes. The bromate flux averaged $0.48 \text{ g BrO}_3^- \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ throughout this operating period. Results from day 170 to day 183 are shown in Figure 3.

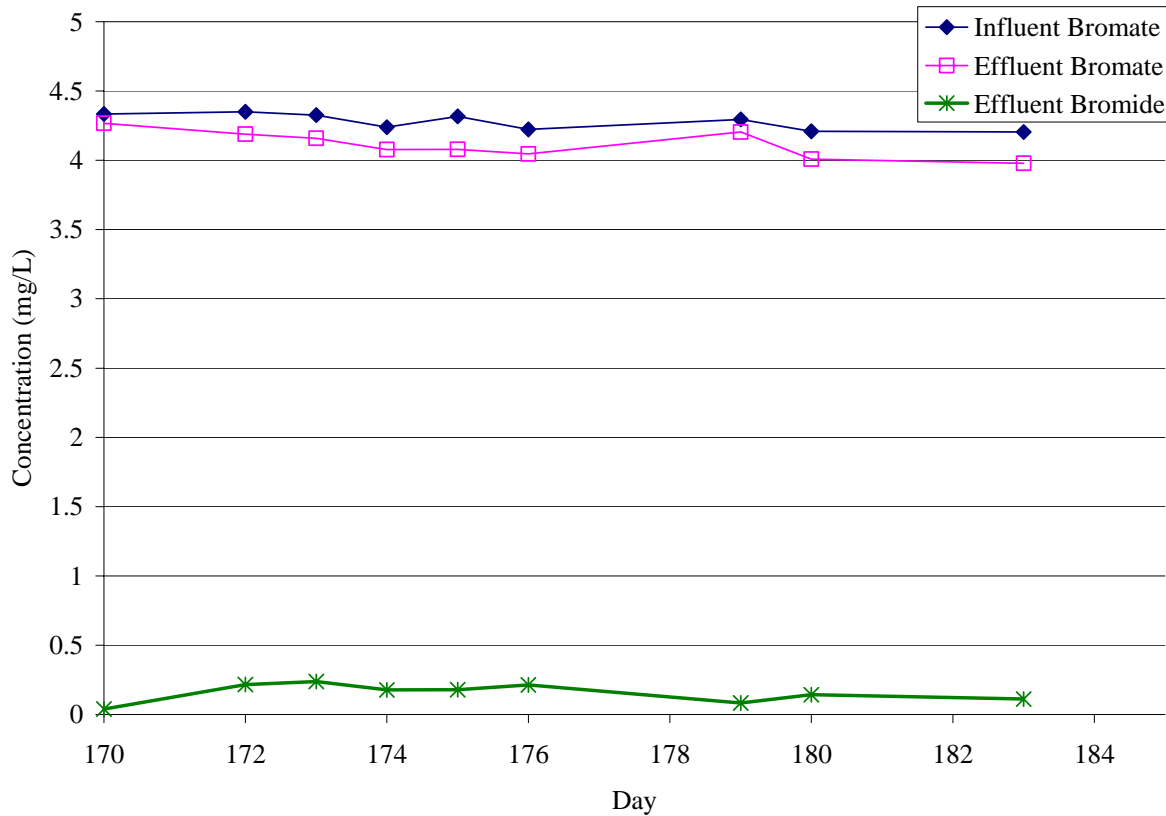


Figure 3. Loading Condition 3: Nitrate was supplied at 1 mgN/L, and some recovery of bromate reduction was established

A new denitrifying MBfR was constructed after loading condition 3 was completed. This reactor had the same configuration as the previous reactor, and full denitrification was achieved within 7 days of startup. After 21 days of operation with an influent containing 5 mgN/L nitrate, 100 µg/L of bromate was added to the influent. Bromate was reduced to below 10 µg/L within 24 hours of addition. Reduction of bromate to below 10 µg/L was maintained for 21 consecutive days.

Discussion

Bromate reduction occurred over an extended period of time in a denitrifying MBfR in the presence and absence of nitrate. The results with both nitrate and bromate suggest that denitrifying bacteria may be reducing bromate cometabolically. Influent bromate concentrations of 1 and 4 mg/L resulted in similar bromate fluxes of around 1 g BrO₃⁻-m⁻²-day⁻¹, even though the effluent bromate concentrations were 0.5 and 3.5 mg/L, respectively. Higher effluent concentrations normally improve fluxes through through increased biomass, if dissimilatory reduction occurs. However, the lack of improved fluxes also may result from bromate inhibition at the higher effluent concentration.

In the absence of nitrate, bromate fluxes initially remained constant. If co-metabolic bromate reduction by denitrifying bacteria were solely responsible for the flux, a steady decline in bromate reduction would be expected as common denitrifiers decay. However, the bromate fluxes remained constant from day 118 to day 147. In fact, the fluxes began to increase after day 147. This may indicate that bromate reducing bacteria were present in the MBfR, but were present in small numbers or inhibited by nitrate. When the nitrate was removed, the bromate reducers were able to establish themselves in the biofilm as the denitrifying bacteria population declined, and bromate reduction increased. This increase in bromate reduction in the absence of nitrate provides strong evidence that hydrogen oxidizing, bromate reducing bacteria were present in the MBfR.

The response of the reactor after removing DO from the influent may have resulted from one of two activities. One is that sulfate reducing bacteria proliferated in the reactor in the absence of oxygen, and caused reactor failure. Black precipitate was evident on day 154, indicating the presence of sulfide production. It is unlikely that sulfate reducing bacteria were the sole cause of the loss of bromate reduction, as sulfate reducing bacteria are typically slow growers and other bacteria should be able to coexist in a biofilm with sulfate reducers. Sulfate reducers were also shown to have little impact in bromate reduction in BAC filters (Kirisits et al. 2001). Nevertheless, the presence of a large population of sulfate reducing bacteria could have produced adverse effects.

The loss of bromate reduction may also be related to other factors. The results on Day 156 and 157 were anomalous, with a sudden decrease and then increase in bromate reduction. The cause of this is unknown.

Results from loading condition 3 suggest that the bromate-reducing population was greatly affected by the loss of bromate reduction at the end of loading condition 2. Denitrification recovered quickly, but bromate reduction improved more slowly towards what it had been under loading condition 1.

The final test explored the ability of a denitrifying MBfR to reduce bromate below the 10- $\mu\text{g/L}$ regulatory standard. The influent bromate concentration was 100 $\mu\text{g/L}$, a typical value for the drinking water environment. The tests lasted approximately 3 weeks, and the effluent bromate concentrations were consistently below 10 $\mu\text{g/L}$.

Conclusions

The hydrogen-based MBfR was shown to be capable of reducing both nitrate and bromate over an extended period of time. Bromate removal of 88% was achieved with 1 mg/L of bromate and 5 mg/L of nitrate in the influent. Bromate reduction was also shown to occur in the absence of nitrate for 40 days. The exact mechanism for bromate reduction by the mixed population of hydrogen-oxidizing bacteria present in the MBfR is not known. It appears that bromate is cometabolically reduced by denitrifying bacteria in the presence of nitrate. The results also indicate that a hydrogen-oxidizing bacteria capable of growth using bromate as an electron acceptor may exist. Most importantly, tests show a denitrifying, hydrogen-based MBfR is

capable of 100 µg/L bromate to below the 10 µg/L standard. This suggests the MBfR may be a useful technology for concurrently removing bromate and nitrate from drinking water.

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