

Evaluation for Biological Reduction of Nitrate and Perchlorate in Brine Water Using the Hydrogen-Based Membrane Biofilm Reactor

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Abstract: Whereas ion exchange is an attractive technology for treating perchlorate and nitrate in drinking water, a major disadvantage is that the resin must be regenerated using a brine, producing wastes with high concentrations of nitrate, perchlorate, and salt. This study investigates the potential for simultaneous nitrate and perchlorate reductions in high-salt conditions using the H₂-based membrane biofilm reactor (MBfR). The autotrophic biological reductions produce harmless N₂ and Cl⁻, making the brine safe for reuse or disposal. A very high-strength brine (~15% salt) from a commercial ion-exchange membrane, Purolite, supported biofilm accumulation and allowed slow reduction rates for nitrate and perchlorate. Reduction rates increased significantly when the Purolite brine was diluted by 50% or more. A synthetic high-strength salt medium containing nitrate, perchlorate, or both supported more rapid reduction rates for as high as 20 g/L (~2%) NaCl, while 40 g/L NaCl slowed reduction by 40% or more, confirming that the microorganisms in the MBfR were inhibited by high salt content. An increase of H₂ pressure gave higher fluxes for 20 g/L NaCl, demonstrating that H₂ availability controlled the reduction kinetics when the system was not salt-inhibited.

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Introduction

Nitrate and perchlorate are found in surface water and groundwater throughout the United States (Clifford and Liu 1993; Mueller and Helsel 1996; Urbansky 1998; Nzenkung et al. 1999) and are highly soluble in the aqueous phase. They are not removed from water during conventional treatment with coagulation, flocculation, sedimentation, and filtration. Advanced treatment techniques, such as reverse osmosis, ion exchange, membrane filtration, and electrodialysis, are effective for removing both anions (Urbansky 1998; Tripp and Clifford 2000; Batista et al. 2000), but produce waste concentrates or brines containing high levels of the target contaminants, in this case perchlorate and nitrate. Typical spent brine from an ion-exchange process treating water having 50–100 µg/L of perchlorate and 3–20 mg N/L of nitrate contains 2.5–10 mg/L of perchlorate, and 150–500 mg N/L of nitrate (Tripp and Clifford 2000; Najm et al. 1999). Further, total salt concentration is typically 3–10%, al-

though some brines are as high as 15%; for comparison, saturated brine is 26.6% (Keller 1998). Disposal of this highly saline waste is a major unsolved problem for these processes (Venkatesh et al. 2000).

To reduce the requirements for salt and spent-brine disposal, several procedures for detoxifying and reusing spent brine have been developed (Van der Hoek et al. 1987; Clifford and Liu 1993; Bae et al. 2002; 2004). Among them, microbial reduction may provide the most suitable alternative, as perchlorate and nitrate are reduced to innocuous Cl⁻ and N₂ (Rittmann et al. 2004). However, microbial reduction must take place in a highly saline environment when brine treatment is the goal.

The effect of high salinity on denitrification is not clear (Lawson 1981; DeVries and Hopstaken 1984; Van der Hoek et al. 1987; Kristensen and Jepsen 1991; Clifford and Liu 1993). DeVries and Hopstaken (1984) and Kristensen and Jensen (1991) found that denitrification could occur fully in a saline environment like that of seawater (~3% of NaCl). On the other hand, Van der Hoek et al. (1987) and Lawson (1981) reported severe inhibition of denitrification for over 2.5% NaCl. Glass and Silverstein (1999) concluded that a decrease in nitrate-reduction kinetics appeared to follow an increase in salinity in the range of 3.6–7.1%. Recently, interest in bacteria that can remove nitrate from hypersaline wastes has grown. A denitrifying, moderately halo-alkalophilic bacterium, *Halomonas camisalis*, was isolated and characterized by Mormile et al. (1999), whereas Gevertz et al. (2000) characterized two nitrate-reducing and sulfide-oxidizing bacteria isolated from oil-field brines.

In the case of perchlorate reduction, most known perchlorate-reducing microorganisms cannot endure high salinity and usually do not grow in more than 2–3% NaCl (Attaway and Smith 1993; Malmqvist et al. 1994; Coates et al. 2000; Michaelidou et al. 2000), although Attaway and Smith (1993) found a culture dominated by *Wolinella* that was tolerant of high salt. Recently, per-

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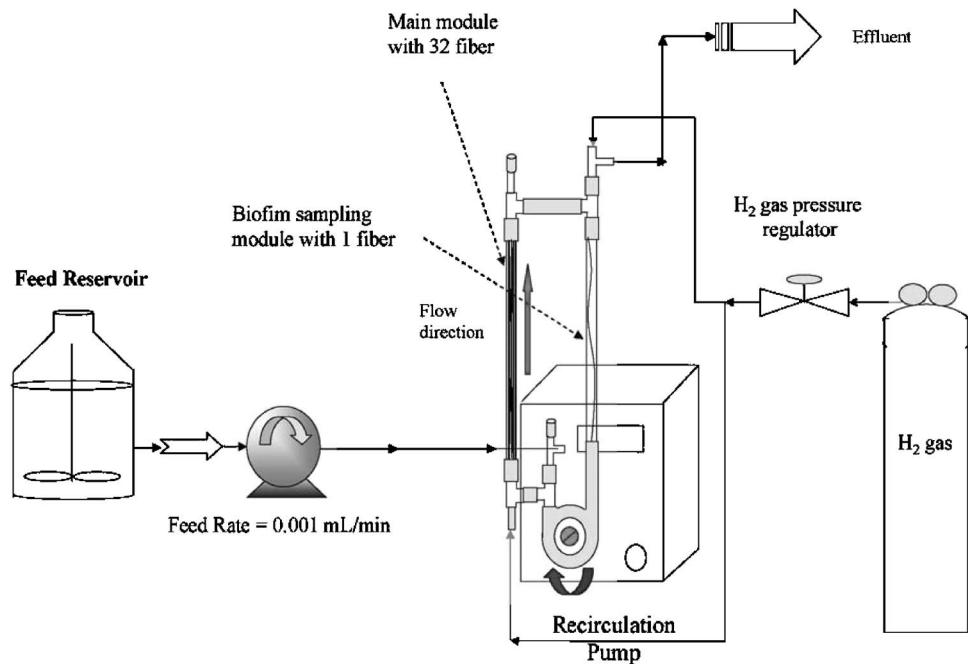


Fig. 1. Schematic of the bench-scale MBfR. The feed reservoir contained either the diluted Purolite brine water or the synthetic high-strength salt medium containing nitrate (200–1,000 mg N/L), perchlorate (100–500 mg/L), or mixed nitrate and perchlorate (same ranges).

chlorate reduction has been found in a high-salinity solution, and this was by a microbial enrichment obtained from an environment containing a high salt concentration (Logan et al. 2001).

Information about bacteria able to reduce perchlorate and nitrate from contaminated regenerant brine also is scarce. Okeke et al. (2002) obtained cultures capable of reducing nitrate and perchlorate in up to 5% NaCl environments, along with salt-tolerant bacterial isolates from cultures, *Citrobacter* sp. Cang et al. (2004) reported that two cultures, developed from marine inocula, are capable of reducing nitrate and perchlorate in high salt solution. One culture was capable of reducing up to 500 mg N/L nitrate and 100 mg/L perchlorate within 5 h in the presence of 30 g/L NaCl. The other was capable of reducing 100 mg/L perchlorate in the presence of 60 g/L NaCl within 24 h.

The hydrogen-based membrane biofilm reactor (MBfR) has shown promise for the direct treatment of nitrate, perchlorate, and other oxidized contaminants (Lee and Rittmann 2000, 2002, 2003; Nerenberg 2003; Nerenberg et al. 2002; Rittmann et al. 2004). Hydrogen gas (H_2) is delivered to a biofilm by diffusion through a bubbleless membrane. A biofilm develops naturally on the outside of the membrane, where autotrophic bacteria oxidize H_2 and transfer the electrons to NO_3^- , ClO_4^- , or other oxidized contaminants. The MBfR makes it technologically feasible to use H_2 gas to drive microbiological reductions. Compared to organic electron donors, H_2 is advantageous because it often is less expensive, leaves no residual in the treated water, is nontoxic to humans, and generates less excess biomass (Rittmann et al. 2004).

Besides direct water treatment, the MBfR may be valuable for removing nitrate and perchlorate from brines produced from treatment by ion exchange or reverse osmosis. The MBfR and autotrophic reduction have not been tested for regenerant brines. Therefore, the objective of this research was to evaluate the MBfR's capability for reducing perchlorate and nitrate at high salinity (up to 15% NaCl).

Materials and Methods

Experimental Setup

A schematic of the MBfR used in this study is shown in Fig. 1, and reactor characteristics are provided in Table 1. Four MBfR systems were used in this study with different feed media, and each MBfR system consisted of two membrane modules connected in a recirculation loop to give a total system volume of 11.7 mL. The main membrane module contained a bundle of 32 hydrophobic hollow-fiber membranes (Model MHF 200TL, Mitsubishi Rayon) inside a glass shell, whereas the other module contained a single fiber used to take biofilm samples without disrupting the biofilm in the main module. A syringe pump (Harvard Apparatus, Model 55-3206) was used with PVC tubing to give feed rate of 0.001 mL/min. The system behaved as a completely mixed biofilm reactor because of the high recirculation rate (150 mL/min versus a feed rate of 0.001 mL/min), and the high recirculation

Table 1. Physical Characteristics of each MBfR System

	Units	Main tube	Coupon tube	Reactor total
Tube inside diameter	cm	0.6	0.5	—
Number of hollow fibers		32	1	33
Cross-sectional area fibers	cm ²	0.0197	0.0006	0.0203
Feed rate	fed-batch	mL/min	—	0.001
	continuous flow	mL/min	—	0.001
Recirculation rate		mL/min	—	150
Net cross-sectional area	cm ²	0.26	0.20	—
Fiber surface area	cm ²	70.4	2.2	72.6
Liquid velocity	cm/min	570.3	766.3	—
Average hydraulic retention time	fed-batch	min	—	6,520
	continuous flow	min	—	6,520

Table 2. Synthetic High-Strength Salt Medium and Trace Mineral Solution

	Nitrate medium (per L)			Perchlorate medium (per L)			Mixed nitrate and perchlorate medium (per L)		
	10 g	20 g	40 g	10 g	20 g	40 g	10 g	20 g	40 g
NaCl									
KH ₂ PO ₄		0.128 g			0.128 g			0.128 g	
Na ₂ HPO ₄		0.434 g			0.434 g			0.434 g	
MgSO ₄ ·7H ₂ O		0.2 g			0.2 g			0.2 g	
Nitrate stock (10 g N/L)		100 mL						100 mL	
Perchlorate stock (10 g/L)					50 mL			50 mL	
CaCl ₂ ·2H ₂ O		0.001 g			0.001 g			0.001 g	
FeSO ₄ ·7H ₂ O		0.001 g			0.001 g			0.001 g	
Trace mineral solution (mg/L)		1 mL			1 mL			1 mL	
ZnSO ₄ ·7H ₂ O	100								
MnCl ₂ ·4H ₂ O	30								
H ₃ BO ₃	300								
CoCl ₂ ·6H ₂ O	200								
CuCl ₂ ·2H ₂ O	10								
NiCl ₂ ·6H ₂ O	10								
Na ₂ MoO ₄ ·2H ₂ O	30								
Na ₂ SeO ₃	30								

rate helped maintain a consistent biomass accumulation on the hollow fibers. The liquid detention time for the flow rate of 0.001 mL/min was 48 h. The standard H₂ pressure was 3 psi (0.21 atm). The pressure also was increased to 4 or 5 psi in order to observe the effect of H₂ availability.

Inoculation and Start up

Four MBfRs were inoculated with 11.7 mL of high-salinity water (2.8% salinity) obtained from a salt pond on the west side of the San Francisco Bay, near the Dumbarton Bridge. Start up began when H₂ was supplied to the fibers, and the liquid in the reactor was recirculated for 24 h to establish a biofilm. Then, regenerant brine (described in the following) from a Purolite ion-exchange system was fed to one MBfR at an average rate of 0.01 mL/min. A synthetic high-strength salt medium that contained 1,000 mg N/L nitrate and 500 mg/L perchlorate was fed at the same rate to the other three MBfR (described in the following).

Characteristics of the Purolite Brine and Synthetic High-Strength Salt Medium

The Purolite brine contained approximately 2,500 mg N/L nitrate and 170 mg/L perchlorate. Its salt (i.e., total dissolved solids) content was approximately 150 g/L (~15%), a value at the extreme high end of salt concentrations found in ion-exchange brines. The Purolite brine was diluted to lower concentrations for some experiments. The synthetic high-strength salt medium, described in Table 2, was prepared in a 1 L glass bottle (Pyrex) and filter sterilized into another sterile 1 L glass bottle using a capsule filter (Pall SuporCap 100, Pall Corporation, Ann Arbor, Mich.). Three kinds of synthetic high-strength salt medium solutions—nitrate alone (1,000 mg N/L from NaNO₃), perchlorate alone (500 mg/L as ClO₄⁻ from NaClO₄), and perchlorate plus nitrate (same concentrations)—were employed to investigate interactions between nitrate and perchlorate reduc-

tions. The NaCl concentration in the synthetic high-strength salt medium was 10, 20, or 40 g/L. In this work, the salt concentration is gauged by the NaCl concentration, since NaCl dominated the salt content.

Fed-Batch Test Using the Purolite Brine Water

The Purolite-fed MBfR was first operated as a fed-batch reactor by extracting 3 mL samples and by replacing 3 mL of same brine every two days over three months. The feed rate of the fed-batch test was equivalent to feeding continuously at an average rate of 0.001 mL/min, equivalent to a liquid detention time for 48 h.

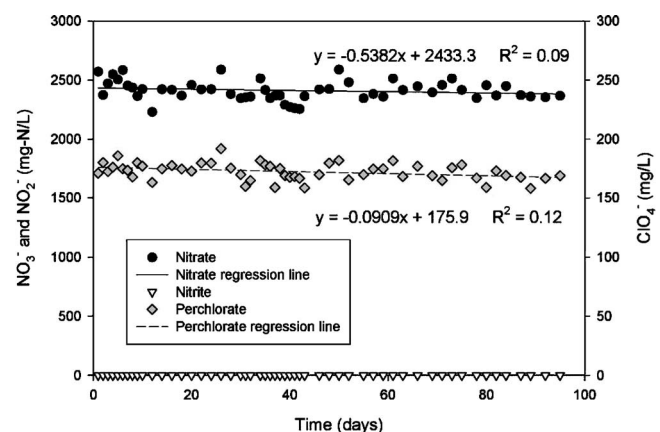


Fig. 2. Nitrate, nitrite, and perchlorate in the samples removed from the MBfR treating the Purolite brine water in a fed-batch mode. The influent concentrations remained constant at 2,500 mg NO₃⁻-N/L and 170 mg ClO₄⁻/L. X axis=time in days; Y axis=nitrate, nitrite, perchlorate in mg/L; circle=nitrate; diamond=perchlorate; and inverted triangle=nitrite.

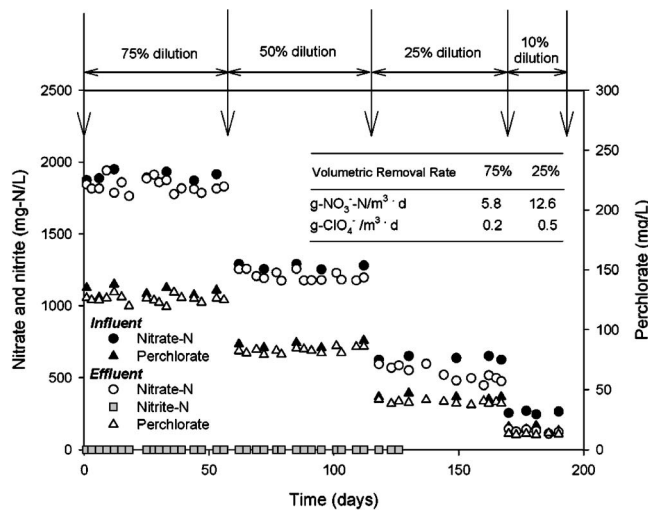


Fig. 3. Nitrate, nitrite, and perchlorate concentrations in effluent from the MBfR treating the diluted Purolite brine as a continuous-flow MBfR at a feed rate of 0.001 mL/min. X axis=time in days; Y axis=nitrate, nitrite, perchlorate in mg/L; circle=nitrate; triangle=perchlorate; and square=nitrite.

Continuous-Flow Tests Using Diluted Purolite Brine and Synthetic High-Strength Salt Medium

After the fed-batch tests were finished, Purolite brine was diluted (with tap water) to 75, 50, 25, and 10% of its original concentration and added continuously at a feed rate of 0.001 mL/min by a syringe pump (Harvard Apparatus, Model 55-3206) in order to investigate how salinity affected the reduction rates. By the same syringe pump equipped with four-syringe rack, synthetic high-strength salt waters with different concentrations of nitrate, perchlorate, and salt were added continuously to three other MBfRs at same feed rate.

Analyses

Analysis for nitrite and chloride was carried out by ion chromatography (Dionex 4500) using an AS-11 column, an AS-11 pre-column, and a 200 μL injection loop, as described in Nerenberg et al. (2002). An AS-11 column also was used to determine perchlorate by ion chromatography after pretreatment to lower the salt concentration (2%). In this case, the ion chromatograph was equipped with an AG11 guard column, a CD25 conductivity de-

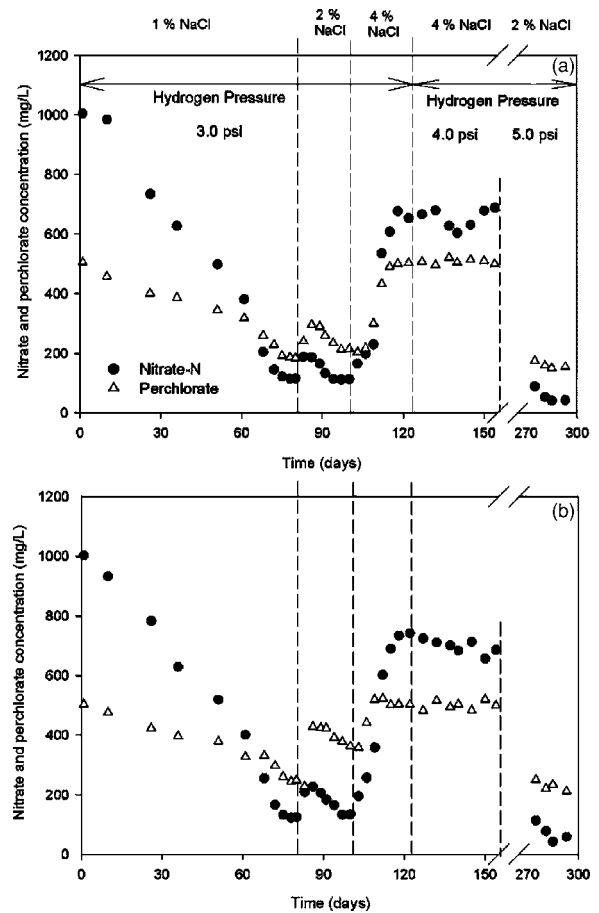


Fig. 4. The nitrate and perchlorate concentrations in effluent from three continuous-flow MBfRs at a feed rate of 0.001 ml/min: (a) nitrate alone and perchlorate alone; (b) mixed nitrate and perchlorate. The influent concentrations were 1,000 mg N/L and 500 mg ClO_4^- /L. X axis=time in days; Y axis=nitrate, nitrite, perchlorate in mg/L; circle=nitrate; and triangle=perchlorate.

tector, and an ASRS-ULTRA suppressor (300 mA). Pretreatment of the sample was with a strong-acid cationic exchange resin loaded with silver (Ag^+). When the sample was exposed to the cationic resin, the sodium exchanged with the silver on the surface of the resin, and then the silver reacted with the chloride to precipitate as AgCl . The pretreated sample with the reduced sodium and chloride concentrations was analyzed by ion chroma-

Table 3. Concentration and Flux Results with the Purolite Brine

		Purolite brine				
Dilution rate (%)		100	75	50	25	10
Nitrate concentration (mg N/L)	Influent	2,530 \pm 12	1,884 \pm 11	1,255 \pm 11	621 \pm 9	259 \pm 8
	Effluent	2,500 \pm 18	1,830 \pm 23	1,180 \pm 10	502 \pm 32	112 \pm 10
Perchlorate concentration (mg/L)	Influent	171 \pm 9	128 \pm 10	87 \pm 8	45 \pm 3	19 \pm 2
	Effluent	170 \pm 14	126 \pm 11	83 \pm 8	40 \pm 5	12 \pm 4
Salt concentration (g/L)		152	114	76	38	15.2
Volumetric removal rate ($g/m^3 \text{ day}$)	Nitrate	—	5.8	7.8	12.6	15.6
	Perchlorate	—	0.2	0.3	0.5	0.7
Flux ^a ($mg/m^2 \text{ day}$)	Nitrate	2.8	—	7.4	—	14.4
	Perchlorate	0.2	—	0.8	—	1.5

^aThe fluxes were computed as the mass-per-time rate of substrate removal normalized to the biofilm surface area.

Table 4. Concentration and Flux Results with the Synthetic High-Strength Salt Medium

Salt concentration (g/L)	Nitrate alone					Perchlorate alone					Nitrate and perchlorate					
	10	20		40		10	20		40		10	20		40		
H ₂ pressure (psi)	3	3	5	3	4	3	3	5	3	4	3	3	5	3	4	
Nitrate concentration (mg N/L)	Influent	1000					0					1000				
	Effluent	116	114	57	677	652	—					124	134	75	734	692
Perchlorate concentration (mg/L)	Influent	0					500					500				
	Effluent	—					184	215	160	499	498	248	357	229	497	499
Flux ^a (g/m ² day)	Nitrate	0.087	0.087	0.093	0.032	0.034	—					0.086	0.085	0.091	0.026	0.03
	Perchlorate	—					0.031	0.028	0.033	0	0	0.025	0.014	0.027	0	0

^aThe fluxes were computed as the mass-per-time rate of substrate removal normalized to the biofilm surface area.

tography. The detection limit for perchlorate was 10 ppb under the lower salt level (2%). To avoid high-salt interference, nitrate was measured with Hach (Loveland, Colo.) NitraVer (0 to 30.0 mg NO₃⁻ N/L) reagent powder pillows. The test is a modified cadmium-reduction method (APHA 1998). The samples size for NitraVer 5 was 1 mL, and the reacted sample was analyzed using a Spectronic 20 spectrophotometer (Milton Roy Co.) at wavelength of 400 nm. All samples were filtered through 13 mm 0.2 μm syringe filter before analysis.

Results and Discussion

Fed-Batch Test of Purolite Brine Water

The MBfR fed undiluted (15%) Purolite brine had visible biofilm after two weeks and was biologically active. Fig. 2 shows that the nitrate and perchlorate concentrations declined, albeit slowly, over 90 days of fed-batch operation. With a regular influent and effluent flow rate (Q), the volumetric removal rate (R) can be computed from a nonsteady-state mass balance

$$R = -\frac{dS}{dt} + Q\frac{(S^0 - S)}{V} \quad (1)$$

in which S^0 and S are the influent and effluent concentrations of nitrate or perchlorate, V is the MBfR liquid volume, and t is time. Fig. 2 shows the regression lines whose slopes give dS/dt . When combined with $Q=1.4 \times 10^{-6}$ m³/day, $V=14.2 \times 10^{-6}$ m³, and $S^0=2.50$ g NO₃⁻-N/L or 0.17 g ClO₄⁻/L, and the S values shown in Fig. 2, the R values for nitrate and perchlorate increased gradually to maximum values of 2.8 and 0.1 g/m³ day, respectively. Dividing the R values by the membrane specific surface areas gives maximum fluxes (J) of 2.8 and 0.2 mg/m² day for nitrate- N and perchlorate, respectively. These R and J values document that nitrate and perchlorate reductions were possible under extremely high-salt conditions (15%), but they are relatively small values that suggest inhibition, perhaps from the high salinity. The inoculum used in this study was acclimated at 2.8% of salinity before being exposed to the 15% brine. An inoculum, taken from higher salt environment might have performed more efficiently or adapted more quickly. Nonetheless, Fig. 2 documents nitrate and perchlorate reductions at very high salt concentration.

Continuous Tests with Diluted Purolite Brine

In order to explore possible inhibition effects, continuous-feed tests were carried out sequentially with the same Purolite-fed MBfR, but with the Purolite brine diluted to 75, 50, 25, or 10% of

the original brine. Each dilution was run for one to two months, depending on how long it took to get a stable estimate of the rates. The influent concentrations of salt, nitrate, and perchlorate were diluted to the same degree. Data in Fig. 3 show the nitrate, nitrite, and perchlorate concentrations for each test, along with the volumetric removal rates computed from the nonsteady-state mass balance. In all cases, nitrite did not accumulate.

When the Purolite brine was diluted to 75% of its original strength, the volumetric reduction rates hardly increased over those with the full-strength brine: 5.8 g N/m³ day and 0.2 g ClO₄⁻/m³ day. The 50% dilution gave rates noticeably higher reduction rates: 7.8 g N/m³ day and 0.3 g ClO₄⁻/m³ day. However, the 25% dilution gave a significantly faster nitrate reduction, 12.6 g N/m³ day, a rate 1.6 times greater than for the 50% dilution. For perchlorate, the rate at 25% dilution increased about 36%, or to 0.5 g ClO₄⁻/m³ day. Finally, a 10% dilution gave still higher reduction rates: 15.6 g N/m³ day and 0.7 g ClO₄⁻/m³ day.

Table 3 shows the salt concentrations, the concentrations of nitrate-N and perchlorate in the influent and the effluent, and their fluxes for each dilution ratio. Nitrate and perchlorate fluxes increased as the salt concentration decreased to 38 g/L (~4%) or less, suggesting that high salt concentration inhibited both reduction reactions. For a salt concentration of 15 g/L (~1.5%), the nitrate and perchlorate fluxes were 0.014 g N/m² day and 0.007 g ClO₄⁻/m² day, respectively.

Nitrate and Perchlorate Reduction at Varying NaCl Concentration Using the Synthetic High-Strength Salt Medium

The relatively slow intrinsic kinetics with the Purolite brine may have been due to the high salt concentration, to inhibition due to perchlorate or other materials in the brine, or to nutrient limitation. Since all constituents were diluted equally, it was impossible to separate the causes by simply diluting the Purolite brine. Therefore, we performed experiments with a synthetic high-strength salt medium having NaCl concentration ranging from 10 to 40 g/L (1–4%). We included phosphate buffer, N, S, Mg, K, and trace elements to ensure otherwise nonlimiting conditions (Table 2).

The reduction of nitrate and perchlorate in the three MBfRs fed with nitrate, perchlorate, or nitrate + perchlorate are demonstrated in Fig. 4. After all MBfRs consistently reduced nitrate and/or perchlorate in the presence of 10 g/L of NaCl (about 80 days), we increased the concentration of NaCl from 10 to 20 g/L and later again to 40 g/L. Data in Fig. 4 shows that all three MBfRs removed of nitrate, perchlorate, or both effectively when the NaCl concentration was 10 g/L. The rates were similar

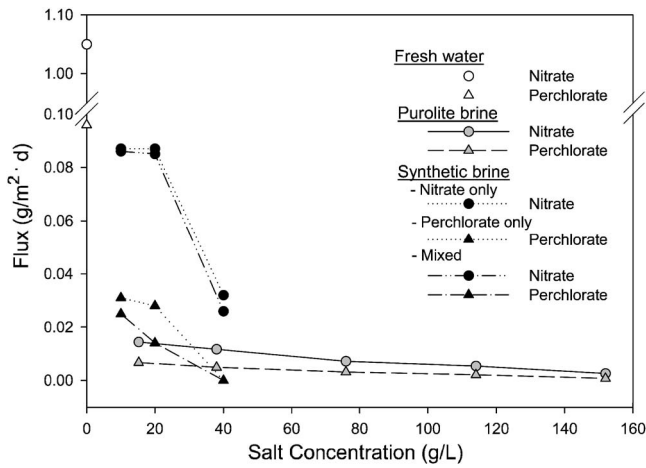


Fig. 5. Fluxes for all experimental tests. X axis=salt concentration (g/L); Y axis=flux (g/m² day); circle=nitrate; and triangle=perchlorate.

when nitrate and perchlorate were separate or together, although mutual inhibition may have occurred when the concentrations were less than about 350 $\mu\text{g/L}$, since both effluent concentrations are slightly higher in the reactor fed both contaminants. Many researchers already reported that nitrate has an inhibitory effect on perchlorate reduction (Chaudhuri et al. 2002), and high levels of perchlorate also can be toxic to denitrifiers (Stouthamer 1967; Anderson et al. 2000). The competition could have been for the common electron donor (H_2) or from inhibition of the reductases. These experiments cannot discriminate between the two possibilities.

All MBfRs adapted to 20 g/L NaCl within a month and achieved almost as good performance as with 10 g/L NaCl. Again, having the two acceptors together gave higher effluent concentrations, more so for perchlorate. When the feed medium contained 40 g/L NaCl, perchlorate reduction nearly stopped after 20 days, whereas nitrate reduction declined to about 40% removal (from >85% removal at 20 g/L). Thus, all MBfR microorganisms were seriously impaired with 40 g/L NaCl, and perchlorate reduction was more strongly affected.

Influence of H_2 Pressure

The hydrogen pressure was increased to 4 psi (0.27 atm) in order to investigate the effect of H_2 bioavailability with the salt con-

dition of 40 g/L. As shown in Fig. 4, nitrate and perchlorate concentrations in the effluent from all MBfRs did not change with an elevated H_2 pressure, indicating that limited H_2 availability was not the cause of slow reduction kinetics. The H_2 pressure and salt concentration were then changed to 5 psi and 20 g/L, respectively. Fig. 4 shows a considerable increase in the consumption rate when H_2 pressure was 5 psi and the salt concentration was substantially less than 40 g/L. Compared with the previous result at 20 g/L and 3.0 psi H_2 pressure, perchlorate and nitrate reduction rates were higher: From 0.085 g/m² day at 3 psi to 0.091 g/m² day for 5 psi for nitrate and from 0.014 to 0.027 g/m² day for perchlorate. This result shows that the reductions of nitrate and perchlorate were sensitive to H_2 availability as long as inhibition from high salt concentration was relieved.

Table 4 summarizes the concentrations and fluxes for the synthetic high-strength salt medium. Nitrate and perchlorate fluxes for all experiments using synthetic high-strength salt medium dramatically decreased as the salt concentration increased to 40 g/L, supporting that both reductions were sensitive to salt content.

Flux Analysis

Fig. 5 compares the effects of salt concentration on the nitrate and perchlorate fluxes obtained with Purolite brine and synthetic high-strength salt medium. Also shown are nitrate and perchlorate fluxes obtained previously for freshwater: 1.05 g NO_3^-/m^2 day by Lee and Rittmann (2002) and 0.096 g $\text{ClO}_4^-/\text{m}^2$ day by Nerenberg et al. (2002). In general, the nitrate fluxes are three to four times larger than the perchlorate fluxes, except for 4% salt in the synthetic high-strength salt medium, when the perchlorate flux was very small. The synthetic high-strength salt medium was able to support larger nitrate and perchlorate fluxes than Purolite brine. Compared to fluxes reported for freshwater, the fluxes for the synthetic high-strength salt medium were lower for nitrate or similar for perchlorate. The diluted Purolite brine did not support as high fluxes. This difference may be related to other constituents in the Purolite brine or to the direction of the change of the salt concentrations. Perhaps starting at the lower salt concentration with the synthetic high-strength salt medium allowed better biofilm accumulations, compared to starting with 15% Purolite brine. This is an issue that deserves future investigation.

For the synthetic high-strength salt medium, all fluxes dramatically declined when the salt concentration was 40 g/L. In the MBfR fed with nitrate and perchlorate together, the nitrate-reduction flux decreased from 0.085 to 0.026 g NO_3^-/m^2 day as salinity increased from 20 to 40 g/L. The perchlorate flux in that

Table 5. Concentration-Normalized Fluxes (10^{-4} m/day) Based on Effluent Concentration for All Experimental Results

Feed composition	Fresh water		Purolite brine					Synthetic high-strength salt medium								
	Nitrate	Perchlorate	15	38	76	114	152	Nitrate alone			Perchlorate alone			Nitrate and perchlorate		
Salt concentration	<1	<1	15	38	76	114	152	10	20	40	10	20	40	10	20	40
Concentration-normalized flux (10^{-4} m/day) ^a	Nitrate	44,000 ^b	1.3	0.23	0.061	0.030	0.011	7.5	7.6	0.5	—	—	—	6.9	6.3	0.4
	Perchlorate	—	0.136	0.024	0.007	0.003	0.001	—	—	—	1.7	1.3	0	2.2	0.4	0
									(16.3)		(2.1)			(12.1)	(1.1)	

Note: Parentheses indicate flux when the H_2 pressure was increased from 3.0 to 5.0 psi.

^aObtained by Lee and Rittmann (2002).

^bObtained by Nerenberg et al. (2002).

^cThe concentration-normalized fluxes were computed fluxes by dividing the effluent substrate concentration.

reactor declined from 0.014 to 2.9×10^{-4} g $\text{ClO}_4^-/\text{m}^2$ day. Thus, keeping the salinity below 40 g/L was important for achieving good reduction kinetics in these experiments.

While flux shows the potential for reducing perchlorate or nitrate, it does not indicate the treatment efficiency, which is reflected by the effluent concentration. A high flux could be supported by a high concentration, which is not consistent with achieving a low effluent concentration. A low concentration together with a high flux demands rapid kinetics. The substrate flux normalized by the effluent concentration is a measure of the kinetics for nitrate or perchlorate reduction. Computation of a normalized flux corresponds to a simple representation of flux (J) in terms of substrate concentration (S): $J=kS$, where k is the normalized flux, which is a rate parameter that has units meters per day.

Table 5 gives the normalized nitrate and perchlorate fluxes for all fluxes shown in Fig. 5. The normalized fluxes are much lower for the Purolite brine than for the synthetic high-strength salt medium, and this suggests that the overall reduction kinetics are inherently slower with the Purolite brine at the salt concentrations in the range tested. Again, these results cannot determine whether the difference is from brine constituents or the direction in which the salt concentration was changed. The normalized fluxes for the synthetic high-strength salt medium were roughly 1000-fold lower than for freshwater. Lower normalized flux means that either brine treatment will demand either higher concentrations or lower fluxes than freshwater treatment unless the reduction kinetics can be increased by a higher H_2 pressure, a larger accumulation of active biomass, an enhancement of the intrinsic kinetics of the microorganisms, or a combination. These are important issues for future research.

Conclusions

We investigated the possibility of simultaneous nitrate and perchlorate removal in brine water using the H_2 -based MBfR. A very high-strength Purolite brine ($\sim 15\%$ salt) supported biofilm accumulation and slow reduction rates for nitrate and perchlorate. Reduction rates increased significantly when the Purolite brine was diluted 50% or more, placing the salt concentration in the more normal range of ion-exchange brines. A synthetic high-strength salt medium containing nitrate, perchlorate, or both supported much more rapid reduction rates for as high as 20 g/L NaCl ($\sim 2\%$). However, 40 g/L NaCl ($\sim 4\%$) slowed reduction by 40% or more, confirming that the microorganisms in the MBfR were inhibited by high salt content and indicating that NaCl higher than about 20 g/L limited the reductions of nitrate and perchlorate. An increase of H_2 pressure gave higher fluxes for 20 g/L NaCl, demonstrating that H_2 availability controlled the reduction kinetics when the system was not salt-inhibited. The concentration-normalized flux is a measure of the kinetic characteristics for the reduction reactions. The normalized fluxes for the synthetic high-strength salt medium were roughly 1,000 times smaller than for previously reported results with fresh water. Thus, it will be important to improve the reduction kinetics by strategies that include using a lower salt concentration or higher H_2 pressure, accumulating more active biomass, enhancing the intrinsic kinetics of the microorganisms, or a combination.

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