Effect of NaCl on nitrate removal from ion-exchange spent brine in the membrane biofilm reactor (MBfR)

Steven W. Van Ginkel, Bi-o Kim, Ziming Yang, Robby Sittmann, Mark Sholin, Joe Micelli and Bruce E. Rittmann

ABSTRACT

The H2-based membrane biofilm reactor was used to remove nitrate from synthetic ion-exchange brine at NaCl concentrations from ~3 to 30 g/L. NaCl concentrations below 20 g/L did not affect the nitrate removal flux as long as potassium was available to generate osmotic tolerance for high sodium, the H2 pressure was adequate, and membrane fouling was eliminated. Operating pHs of 7–8 and periodic citric acid washes controlled membrane fouling and enabled reactor operation for 650 days. At 30 psig H2 and high nitrate loading rates of 15 to 80 g/m2 d, nitrate removal fluxes ranged from 2.5 to ~6 g/m2 d, which are the highest fluxes observed when treating 30 g/L IX brine.

INTRODUCTION

Release of nitrogen to surface and ground waters is one of the world’s biggest unsolved water-quality problems. The most commonly used process today for removing NO3⁻ from groundwater is ion-exchange (IX), in which NO3⁻ is exchanged for harmless anions as the water passes through a bed of IX resin (e.g., Aldridge et al. 2004; McAdam & Judd 2008). Although IX is efficient at removing NO3⁻ from the water, NO3⁻ is not detoxified. Instead, NO3⁻ accumulates on the IX resin or in the salt-brine used to regenerate the resin. Treatment of the IX brine so that it can be reused or disposed of safely is a major unresolved challenge.

While many studies have addressed heterotrophic denitrification in high-NaCl brines (e.g., Bae et al. 2002; Yoshie et al. 2006; Patel et al. 2008), another approach for treating the brine is bioreduction of NO3⁻ to N2 gas using the autotrophic, H2-based membrane biofilm reactor (MBfR) (Chung et al. 2007; Van Ginkel et al. 2008). The MBfR can remove NO3⁻ from the brine, thereby making it possible to reuse the brine and minimize problems of brine disposal. In addition, recycling the treated brine can lower the salt consumption by about 50% and the salt discharge by about 90% (Liu & Clifford 1996).

Building on the work of Chung et al. (2007), Van Ginkel et al. (2008, 2010a, b, 2011) and Ahn et al. (2009), this work systematically studied the effect of high NaCl concentrations on the NO3⁻ removal flux. As the NO3⁻ concentration of a site’s feed water determines the regeneration frequency of the IX resin, NO3⁻ removal was the major target of this study (Lehman et al. 2009). Our primary goal was to determine the effect of NaCl (~3–30 g/L TDS) on the NO3⁻ removal flux in the MBfR. Past research on heterotrophic denitrification has shown that denitrification is uninhibited by NaCl up to 20 g/L, but higher NaCl concentrations showed significant inhibition. It is unknown how high NaCl concentrations affect autotrophic denitrification. A second goal was to determine the effect of potassium (K⁺) on NaCl tolerance, as past research has shown that bacteria can withstand higher NaCl concentrations if other salts or compatible solutes are available to maintain osmotic tolerance (Ventosa et al. 1998). Our final goal was to determine if we could operate the MBfRs over an extended period of time by maintaining a low-enough pH (<8) to control membrane fouling. Accumulation of mineral precipitates on the membrane surfaces may slow H2 transfer and,
ultimately, the NO$_3^-$ reduction rate (Lee & Rittmann 2003; Rezania et al. 2006).

**MATERIALS AND METHODS**

**Preparation of IX spent brine**

The synthetic IX brine contained (g/L): CaCl$_2$·2H$_2$O (0.1), MgCl$_2$ (0.1), NH$_4$Cl (0.1), NaHCO$_3$ (0.5), Na$_2$SO$_4$ (0.2), NaH$_2$PO$_4$ (1.9), and Na$_2$HPO$_4$ (1.4). Trace nutrients were added as described in Van Ginkel et al. (2008), and the pH was set to 7.0–7.5 using HCl or KOH. NaNO$_3$ was added to give the concentrations shown in Table 1. This medium had a total dissolved solids (TDS) concentration of 2.9 g/L. In order to increase the TDS from 2.9 to 30 g/L, NaCl was added as noted in Table 1. In order to test the effect of withholding K$^+$ from the medium at TDS concentrations of 7.5 and 20 g/L, the potassium phosphate buffer was changed to a sodium phosphate buffer.

**Inocula and MBfR operation**

An MBfR (denoted M1) was inoculated with a mixture of three MBfR cultures previously adapted to a synthetic brine of 45-g/L NaCl (Van Ginkel et al. 2008, 2010a). These MBfR cultures were originally derived from sediments from the Great Salt Lake, UT; the Salton Sea, CA; and the coast of Freeport, TX; after the Van Ginkel et al. (2008) study was completed, these MBfR cultures were combined and placed into batch bottles and given H$_2$, NO$_3^-$, and acetate for several weeks. Then, these batch cultures were pumped into M1, which was fed actual IX brine for approximately 150 days (Van Ginkel et al. 2011). After the study of Van Ginkel et al. (2011) was completed, the biofilm culture was sheared off the fibers and used as the inoculum in the present study.

An MBfR contains H$_2$-pressurized hollow-fiber membranes on which biofilm grows when using H$_2$ as the electron donor and one or more oxidized contaminants as electron acceptors. The configuration and physical characteristics of the MBfRs used in this study are described in Chung et al. (2007). The M1 fibers were composite hollow-fiber membranes consisting of an inner core of polyurethane and an outer layer of polyethylene (OD = 280 μm, Model MHF 200TL, Mitsubishi Rayon, Japan) with a total surface area of 78 cm$^2$. In order to mitigate against membrane fouling, which was likely the cause of the low removal fluxes in Van Ginkel et al. (2008), on two occasions (days 547 and 647), precipitates were cleaned off the fibers by draining M1 of liquid, filling it with a 2% citric acid solution, and recirculating the solution for ~5 min. Then, M1 was drained and refilled with new medium (Table 1). The influent flow rate was varied as shown in Table 1. On days 647 to 650, M1 was operated at high NO$_3^-$ loading rates (15 to 80 g/m$^2$ d); the duration of these tests were >10 hydraulic retention times, which was long enough to attain hydraulic steady state, but without significant membrane fouling.

**Analyses**

Influent and effluent samples were first diluted one hundred times in deionized water and then filtered through a 0.22-μm membrane filter. All anions and cations were measured using ion chromatography (Dionex DX2500, Sunnyvale, California). NO$_3^-$, NO$_2^-$, and SO$_4^{2-}$ were measured using an IonPac AG18 column using EPA Method 300.0 (US EPA 1995). Cations were measured using an IonPac CS12A column (Dionex 2011). The influent and effluent pH values were measured periodically using a pH meter (Symphony, Model# SB70P). Ca$^{2+}$ and Mg$^{2+}$ precipitation was computed from the difference between influent and effluent concentrations.

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**Table 1 | Operational Conditions, NO$_3^-$ removal flux, and percent NO$_3^-$ removals**

<table>
<thead>
<tr>
<th>Day</th>
<th>TDS (g/L)</th>
<th>H$_2$ pressure (psig)</th>
<th>Influent NO$_3^-$ (mg N/L)</th>
<th>NO$_3^-$ loading rate (mg/m$^2$ d)</th>
<th>NO$_3^-$ removal flux (mg/m$^2$ d)</th>
<th>% removal</th>
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<td>0</td>
<td>2.9</td>
<td>5</td>
<td>170</td>
<td>600</td>
<td>590</td>
<td>97</td>
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<tr>
<td>133</td>
<td>5.8</td>
<td>5</td>
<td>150</td>
<td>420</td>
<td>390</td>
<td>91</td>
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<tr>
<td>158</td>
<td>7.5</td>
<td>5</td>
<td>160</td>
<td>470</td>
<td>450</td>
<td>94</td>
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<tr>
<td>270</td>
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<td>15</td>
<td>110</td>
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<td>99</td>
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<td>15</td>
<td>90</td>
<td>800</td>
<td>760</td>
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<td>800</td>
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<tr>
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<td>30</td>
<td>500</td>
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<td>2,500</td>
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<tr>
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<td>3,900</td>
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<td>30</td>
<td>1,500</td>
<td>80,000</td>
<td>6,200</td>
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RESULTS AND DISCUSSION

Effect of NaCl and H₂ pressure on NO₃⁻ reduction

Table 1 summarizes NO₃⁻ loadings, removal fluxes, and percent removals for all experiments. In order to compare MBfR performance during continuous flow, the NO₃⁻ removal fluxes \( J, \text{g/m}^2 \text{d} \) were computed from

\[
J = \frac{(S^0 - S)Q}{A}
\]

where \( S^0 \) and \( S \) are the influent and effluent NO₃⁻ + NO₂⁻ concentrations (g N/L), \( Q \) is the volumetric flow rate through the main membrane module (L/d), and \( A \) is the membrane surface area (m²). The loading rate equals the removal flux with \( S = 0 \).

Figure 1 shows the NO₃⁻ removal fluxes up to day 647. The NO₃⁻ removal flux increased linearly with the NO₃⁻ loading rate with >90% removal for TDS of 2.9 to 20 g/L. The NO₃⁻ removal flux declined for high loading when the TDS was 30 g/L. This fall off in performance is likely due to the high NaCl concentration, which slowed bacterial metabolism, or lack of time needed for acclimation to higher NaCl. In addition, membrane fouling could have decreased the NO₃⁻ removal flux.

Figure 2 shows H₂-normalized NO₃⁻ loading rates and removal fluxes until day 647. During the period of 180–210 days, the in-reactor pH averaged ~8.5, and Ca²⁺ and Mg²⁺ were removed from an influent concentration of ~20 mg/L to an effluent concentration of ~2 mg/L, or removals of ~18 mg/L for each cation. As it appeared likely that membrane fouling was occurring, on day 310 the influent pH was decreased to 7.0, making the in-reactor pH 7.5 ± 0.3 until day 403. Ca²⁺ and Mg²⁺ were removed from an influent concentration of ~20 mg/L to an effluent concentration of ~16 mg/L, or removals of ~4 mg/L for each cation. On day 403, the TDS was increased to 20 g/L, and NO₃⁻ removal slightly decreased (Table 1, Figure 2). On day 440, the TDS was increased to 30 g/L, and this caused a steep decline in NO₃⁻ removal. However, after a citric acid wash on day 547 (and also a lower NO₃⁻ loading rate), NO₃⁻ removals increased to 98%. The pH was 7.9 ± 0.2 in this period. As the H₂ pressure was increased over time, the H₂-normalized flux decreased over time. As IX spent brine is regenerated in batches, periodic acid cleanings or pressurizing the fibers with CO₂ seems to be a viable means to acidify precipitates to maintain high NO₃⁻ removal fluxes.

In preparation for high NO₃⁻ loading rates at 30 g/L TDS, M1 was again citric acid washed on day 647. The NO₃⁻ removal fluxes for the high-loading period (days 647–650) are shown in Figure 3(a), and fluxes normalized to H₂ pressure are in Figure 3(b). Although percent removals were only 8 to 17% (Figure 3(b)), the removal fluxes (up to 6,200 mg/m²d, Figure 3(a)) were up to five and 200 times higher than fluxes observed at 30 g/L TDS in Van Ginkel et al. (2008) and 40 g/L TDS in Chung et al. (2007). In Chung et al. (2007), the operating pH was not mentioned, while, in Van Ginkel et al. (2008), the pH was uncontrolled and was >9 at times which likely caused membrane fouling. This shows that high NO₃⁻ removal fluxes can be achieved at TDS concentrations of 30 g/L as long acclimation occurs and membranes are not fouled. However, the high fluxes did not give high removal efficiency. Figure 3(b) suggests that the H₂ pressure was at least partly the limiting factor, as the H₂-normalized loading was about 10 times greater than the loading allowing close to 100% removal (Figure 2). Furthermore, the H₂ flux at this condition (~2.1 g H₂/m²d) was nearly equal to the maximum flux achievable by the MHF 200TL membranes at the applied pressure of 30 psig (Tang et al. 2011).
Effect of K\(^{+}\) in generating NaCl tolerance

In order to test the possibility that K\(^{+}\) can maintain high water activity in high sodium environments, K\(^{+}\) was removed from the 7.5 and 20 g/L brines. No effect could be observed when feeding the 7.5 g/L IX brine (data not shown). However, Figure 4 shows that the NO\(_{3}^{-}\) removal flux declined about 10 days after K\(^{+}\) was removed when feeding the 20 g/L brine. While trace amounts of K\(^{+}\) from medium chemicals appears to be sufficient to maintain high water activity for NaCl of 7.5 g/L (Oren 2010), 20 g/L NaCl presented a need for K\(^{+}\) as a compatible solute to promote osmotic tolerance (Ventosa et al. 1998; Sleator & Hill 2001; Oren 2008).

CONCLUSIONS

When regenerating IX brine, the H\(_{2}\)-based MBfR could achieve NO\(_{3}^{-}\) removal efficiencies of 98% with NaCl concentration as high as 30 g/L, as long as the H\(_{2}\) pressure was adequate, mineral fouling was eliminated, and potassium was present. The main fouling mechanisms was precipitation of Ca\(^{2+}\) and Mg\(^{2+}\) solids, but fouling could be relieved by citric-acid washing, which allowed continuous operation for 650 days. K\(^{+}\) was necessary to create osmotic tolerance at a TDS of 20 g/L, but not 7.5 g/L. At 30 psig H\(_{2}\) and high nitrate loading rates of 15 to 80 g/m\(^{2}\) d, NO\(_{3}^{-}\) removal fluxes ranged from 2.5 to \(\sim\) 6 g/m\(^{2}\) d, which are the highest fluxes observed when treating 30 g/L IX brine. However, the percentage removal was low for the highest loadings, and the H\(_{2}\) pressure may have been limiting in this case.

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REFERENCES


