Effect of pH on nitrate and selenate reduction in flue gas desulfurization brine using the H\textsubscript{2}-based membrane biofilm reactor (MBfR)

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ABSTRACT

Increased tightening of air regulations is leading more electric utilities to install flue gas desulfurization (FGD) systems. These systems produce brine containing high concentrations of nitrate, nitrite, and selenate which must be removed before discharge. The H\textsubscript{2}-based membrane biofilm reactor (MBfR) was shown to consistently remove nitrate, nitrite, and selenate at high efficiencies. The maximum selenate removal flux reached 362 mg Se m\textsuperscript{-2}d\textsuperscript{-1} and was higher than that observed in earlier research, which shows continual improvement of the biofilm for selenate reduction. A low pH of 6.8 inhibited precipitation when treating actual FGD brine, yet did not inhibit removal. SO\textsubscript{4}\textsuperscript{2-} was not removed and therefore did not compete with nitrate, nitrite, and selenate reduction for the available H\textsubscript{2}.

Key words | nitrate, nitrite, selenate, flue gas desulfurization, membrane biofilm reactor (MBfR), hydrogen gas

INTRODUCTION

Although an essential element for human beings, selenium (Se) at high concentrations is toxic to life and is strictly regulated (U.S. Environmental Protection Agency 1999). Se can be released into the environment from two main sources. The first source is the mining, processing, and combustion of fossil fuels, particularly coal. The second source is the leaching of seleniferous soils during irrigation. The focus of this work is on the removal of Se from flue gas desulfurization (FGD) brine generated from coal combustion.

Se is found in coal at 1–10 ppm by weight (Finkelman 2009). While rain can leach Se from coal-mining operations, the more significant source is from coal combustion (Lemly 1997). During the combustion of coal, Se is vaporized and highly fractionated. Through electrostatic precipitation of the flue gas, Se is highly concentrated in the fly ash (~68%), and it also is co-removed with sulfur in forced oxidation, wet scrubber FGD systems used to control sulfur dioxide (SO\textsubscript{2}) emissions. Forced oxidation oxidizes various Se species into selenite (SeO\textsubscript{4}\textsuperscript{2-}), which is soluble in water. Since Se is relatively volatile in flue gas, a significant fraction of the Se from the coal may end up in the FGD brine (Chu 2006). Similarly, nitrogen species are oxidized to nitrate (NO\textsubscript{3}-) or nitrite (NO\textsubscript{2}--), are captured in FGD brine, and are often an order of magnitude higher in concentration than SeO\textsubscript{4}\textsuperscript{2-}. FGD brine typically contains total dissolved solids (TDS) of 15–35 g/L with high concentrations of calcium (Ca\textsuperscript{2+}) and magnesium (Mg\textsuperscript{2+}).

When an electron donor is available, NO\textsubscript{3}-, NO\textsubscript{2}--, and SeO\textsubscript{4}\textsuperscript{2-} can be microbially reduced in a dissimilatory manner and used as respiratory electron acceptors (Steinberg & Oremland 1993; Chung et al. 2006). The reduced products are N\textsubscript{2} gas that evolves from the brine and elemental Se (Se\textsubscript{0}), which can be separated from the brine as an insoluble solid. Electron donors could include organic compounds, such as acetate, or inorganic compounds, such as H\textsubscript{2} gas.

The H\textsubscript{2}-based membrane biofilm reactor (MBfR) contains bundles of bubble-less gas transfer membranes that deliver H\textsubscript{2} gas to a biofilm of microorganisms that grow on the membranes by oxidizing the H\textsubscript{2} and reducing soluble electron acceptors, including NO\textsubscript{3}-, NO\textsubscript{2}--, and SeO\textsubscript{4}\textsuperscript{2-}. This has been demonstrated for the bioreduction of NO\textsubscript{3}-- and ClO\textsubscript{4}-- in ion-exchange (IX) brine (Chung et al. 2007;
and NO$_3^-$ and SeO$_4^{2-}$ in FGD brine (Van Ginkel et al. 2008). Of particular relevance here is the study of Van Ginkel et al. (2008), who observed the simultaneous reduction of NO$_3^-$ and SeO$_4^{2-}$ in two MBfRs treating FGD brine, as long as H$_2$ was not limiting.

The MBfR provides an efficient and simple means to deliver H$_2$ to a contaminant-reducing biofilm. Directly supplying H$_2$ via membranes is becoming a proven technology and is more efficient than using an organic donor, since the biofilm uses only the stoichiometric amount of H$_2$ it needs to reduce the contaminants in the feed stream; this leads to reduced costs and precludes leakage of oxygen demand to the effluent. For these reasons, the MBfR is being researched and field tested for a range of bioreduction applications when the water can be routed through an *ex situ* bioreactor, as is the case with FGD brine.

The purpose of this paper is to compare MBfR bioreductions while treating FGD brine. In earlier MBfR research treating IX brine, Ca$^{2+}$ and Mg$^{2+}$ were shown to precipitate out and foul the membrane fibres, which blocks the transfer of H$_2$ to the biofilm and reduces contaminant removal fluxes (Van Ginkel et al. 2010a). FGD brines may pose more severe precipitation problems due to the high Ca$^{2+}$ and Mg$^{2+}$ concentrations and the high pH values obtained when denitrifying high concentrations of NO$_3^-$ or NO$_2^-$ (Rezania et al. 2006). Therefore, several TDS concentrations and compositions and pH were tested to observe the potential for precipitation.

**METHODOLOGY**

The inoculum used in this study was a microbial consortium obtained from all five IX brine-treating MBfRs described in Van Ginkel et al. (2008, 2010b) and Ahn et al. (2009). This consortium was split (100 mL each) between two 160 mL batch bottles and repeatedly spiked with NO$_3^-$, SeO$_4^{2-}$, and acetate under a H$_2$ headspace until the biomass concentration, measured as volatile suspended solids (VSS), reached approximately 3.0 g/L after six months. These batch cultures were then injected into two MBfRs (called ‘M1’ and ‘M2’) used to treat FGD brine.

The configuration and physical characteristics of the MBfRs are described in Chung et al. (2007) and shown in Figure 1. M1 contained 38 polyester fibres for a membrane surface area of 79 cm$^2$ and M2 contained 76 fibres for a membrane surface area of 156 cm$^2$. The fibres were potted, glued, placed inside a glass shell with a total MBfR liquid volume of 55 mL, and pressurized with H$_2$ gas at 30 psig. The ratio of the volumetric recirculation rate to the influent rate was 100:1 to provide completely mixed conditions. Both MBfRs had a heat jacket to control the temperature at 33 °C, which is the typical temperature of FGD brine.

M1 and M2 are a continuation of the same MBfRs operated for 331 days as described in Van Ginkel et al. (2008). During that period, the bacterial community of M2 was analysed via pyrosequencing and was dominated by NO$_3^-$ reducers, while a few SeO$_4^{2-}$ reducers were also detected (Van Ginkel et al. 2010b). Before starting the present study, the MBfRs were semi-continuously fed the 17 g/L TDS brine described in Table 1 for approximately two months. Then, both MBfRs were citric acid washed to dissolve any precipitates on the MBfR fibres. In brief, the MBfRs were drained of liquid, then 50 mL of 2% citric acid solution was injected into each MBfR and allowed to recirculate for ~10 min until the fibres became noticeably cleaner (i.e. absence of white deposits on the fibres). Then, brine was injected into each MBfR and fed at a fast flow rate until the effluent pH increased to 7.0. Acid washing has a small effect on bacterial activity as long as it is done quickly and the original medium is replaced quickly. The M1 and M2 in-reactor pHs were automatically set to 6.8 and 7.5, respectively, using acid feeds (HCl).

The operation of the MBfRs was divided into several phases (Table 1). During Phase 1, the same 17 g/L TDS brine noted above was fed continuously to both M1 and M2. During Phases 2 and 3 for M1, the influent TDS was...
increased to 22 g/L and 30 g/L, respectively, by adding Ca$^{2+}$ and Mg$^{2+}$ chlorides in order to prepare the M1 biofilm for the treatment of actual FGD brine, which contains 33 g/L TDS and Ca$^{2+}$ and Mg$^{2+}$ concentrations of 3.4 and 2.8 g/L, respectively. Phase 4 is the treatment of the actual FGD brine by M1, which is not shown in Table 1. For M2, Phases 2 and 3 represent decreases in the influent NO$_3^-$ concentration. During these phases, the influent flowrate was changed as noted below. Due to the low buffering capacity of the actual FGD brine, 1 g/L MES (2-(N morpholino) ethanesulfonic acid) buffer was added to the actual brine and the 22 and 30 g/L TDS synthetic brines. Also note that influent phosphate concentrations were lower in the M1 brine compared to the M2 brine. All anions (selenate, nitrate, nitrite, and sulfate) were measured as described in Van Ginkel et al. (2010a).

### RESULTS

**Performance of M1 during Phases 1–3, the treatment of synthetic FGD brine**

After the acid wash, M1 was restarted on synthetic FGD brine containing 500 mgN/L and 38 mg Se/L at a hydraulic loading rate of 0.016 mL/min (Phase 1, Table 1). Influent and effluent NO$_3^-$ and SeO$_4^{2-}$ concentrations are shown in Figure 2.

The NO$_3^-$ and SeO$_4^{2-}$ removal fluxes reached their maximum of 1,500 mg N m$^{-2}$d$^{-1}$ and 110 mg Se m$^{-2}$d$^{-1}$ after 40 days for >98% removal for both anions (Figure 3). The NO$_3^-$ and SeO$_4^{2-}$ removal flux is defined according to Equation (1).

\[
J = (S' - S)Q/A
\]

where S' and S are the influent and effluent NO$_3^-$ or SeO$_4^{2-}$ concentrations (g/L), Q is the volumetric flow rate through the main membrane module (L/h), and A is the membrane surface area (m$^2$). The flux of the rate-limiting substrate is a fundamental kinetic parameter for a biofilm process, as it describes substrate utilization and mass transport. In addition, normalizing the removal rate [(S' - S)Q] to the membrane surface area (A) makes it possible to compare directly the performance of MBfRs according to the amount of membrane surface area, which is of practical and economic importance.

On about day 60, the acid pumps to control the pH at 6.8 were over-active and decreased the pH to ∼4.8. The low pH seemed to affect SeO$_4^{2-}$ reduction less than NO$_3^-$ reduction (Figures 2 and 3). The fluxes recovered to their maximum values by day 83. During Phases 2 and 3, the influent NO$_3^-$ and SeO$_4^{2-}$ concentrations were decreased to 50 mgN/L and 10 mg Se/L (Table 1). The NO$_3^-$ and SeO$_4^{2-}$ removal fluxes were reduced accordingly with >99% removal for both NO$_3^-$ and SeO$_4^{2-}$ (Figure 3). The higher TDS during Phases 2 and 3 did not seem to decrease removal. SO$_4^{2-}$ was not removed during these phases.

### Table 1  Media composition of the synthetic FGD brines (g/L)

<table>
<thead>
<tr>
<th>Phase</th>
<th>M1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Days of operation</td>
<td>0–83</td>
<td>83–113</td>
</tr>
<tr>
<td>NaNO$_3$ (mgN/L)</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>Na$_2$SeO$_4$ (mg Se/L)</td>
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<td>10</td>
</tr>
<tr>
<td>NaCl</td>
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<td>4.0</td>
</tr>
<tr>
<td>CaCl$_2$</td>
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<td>3.0</td>
</tr>
<tr>
<td>MgCl$_2$</td>
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<td>7.9</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
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<td>0.1</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
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<td>0.5</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
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<td>5.8</td>
</tr>
<tr>
<td>KH$_2$PO$_4$</td>
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<td>0.8</td>
</tr>
<tr>
<td>K$_2$HPO$_4$</td>
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<td>0.0</td>
</tr>
<tr>
<td>TDS</td>
<td>17</td>
<td>22</td>
</tr>
</tbody>
</table>

**Figure 2** | Influent and effluent NO$_3^-$ and SeO$_4^{2-}$ concentrations for M1 during Phases 1–3.

**Figure 3** | NO$_3^-$ and SeO$_4^{2-}$ removal fluxes for M1 during Phases 1–3.
Performance of M1 during Phase 4, the treatment of actual FGD brine

On day 133, M1 was fed actual FGD brine. The nitrogen and SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} concentrations averaged 56 mg N/L and 11 mg Se/L with ~60% of the nitrogen as NO\textsubscript{2}\textsuperscript{\textsuperscript{-}} and ~40% as NO\textsubscript{3}\textsuperscript{-} (Figure 4). During days 139 to 153, a new batch of actual brine was fed with an influent SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} concentration of 2 mg Se/L, and this led to the low flux shown in Figure 5. SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} was then spiked on day 153, and the SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} removal flux returned back to the previous value with >99% removal (Figure 4). Nitrogen removal was nearly >97% during this period, except for a H\textsubscript{2} leak which occurred on day 173. After the leak was fixed and the H\textsubscript{2} pressure restored, the SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} removal flux returned to the previous value. In contrast to the low pH problem on day 60, the H\textsubscript{2} pressure problem on day 173 seemed to affect SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} reduction more than nitrogen reduction, which may mean NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} are preferred electron acceptors compared to SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}}. On day 193, the flow rate was increased from 0.016 to 0.037 mL/min. This higher flow rate and a slightly higher influent nitrogen concentration led to a tripling of the nitrogen removal flux from to 140 to 420 mg N m\textsuperscript{-2}d\textsuperscript{-1} (Figure 5). The SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} removal also tripled.

After a period of batch operation, the M1 flow rate was increased to 0.06 mL/min. Influent and effluent nitrogen and SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} concentrations are shown in Figure 6. During this period, the influent SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} concentration was increased from 16 mg Se/L (day 265), to 22 mg Se/L (day 275), to 32 mg Se/L (day 335). The nitrogen removal flux was maintained at ~600 mg N m\textsuperscript{-2}d\textsuperscript{-1} for 80 days, except for two periods of low-pH problems on days 306 and 335 (Figure 7). Nitrogen removal was >98% during this period. Except for the pH excursions, the SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} removal flux increased according to the increase in the influent SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} concentration, with a maximum SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} removal flux of 362 mg Se m\textsuperscript{-2}d\textsuperscript{-1}, which is the highest flux observed to date using a 33 g/L TDS FGD brine (Van Ginkel et al. 2010a). SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} removal was >95% during the entire period. This time, it appears that SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} reduction was more sensitive to these pH changes than nitrogen reduction. SO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} was not removed; however, Ca\textsuperscript{2\textsuperscript{+}} and Mg\textsuperscript{2\textsuperscript{+}} removals were both 4% (n = 46 for both).

During Phase 1 of M2, except for the higher pH of 7.5, M2 was operated identically to M1; however, the NO\textsubscript{3}\textsuperscript{-} removal flux was four times lower than M1, averaging 400 mg N m\textsuperscript{-2}d\textsuperscript{-1}, and SeO\textsubscript{4}\textsuperscript{2\textsuperscript{-}} reduction was highly erratic (data not shown). NO\textsubscript{3}\textsuperscript{-} removal averaged 40%. The NO\textsubscript{3}\textsuperscript{-} removal flux for M2 continued to decline, averaging ~300 mg N m\textsuperscript{-2}d\textsuperscript{-1} for about 30 days by the end of Phase 1. During Phase 2, the influent NO\textsubscript{3}\textsuperscript{-} concentration was decreased to 250 mgN/L and the NO\textsubscript{3}\textsuperscript{-} removal flux decreased gradually from 250 to 150 mg N m\textsuperscript{-2}d\textsuperscript{-1}. After a doubling of the flow rate, the NO\textsubscript{3}\textsuperscript{-} removal flux increased to 250 mg N m\textsuperscript{-2}d\textsuperscript{-1}, but then decreased back to 150 mg N m\textsuperscript{-2}d\textsuperscript{-1} (data not shown). On day 260 of Phase 3, M2 was citric acid washed to remove precipitates from the membranes, and the influent NO\textsubscript{3}\textsuperscript{-} concentration was decreased to 100 mgN/L and the in-reactor pH was set to 7.0 – both in order to lessen the potential for precipitation.
As shown in Figure 8, the NO$_3^-$ removal flux increased to $\sim$500 mg N m$^{-2}$d$^{-1}$; however the flux was highly unstable and decreased thereafter. The SeO$_4^{2-}$ removal flux followed a similar pattern. Ca$^{2+}$ and Mg$^{2+}$ removals were 20% (n = 21) and 21% (n = 19), respectively (data not shown).

## DISCUSSION

The results show that NO$_3^-$, NO$_2^-$, and SeO$_4^{2-}$ can be simultaneously removed at high removal efficiencies. SO$_4^{2-}$ was not removed, likely due to the high TDS, and therefore did not compete for the available H$_2$ (Steinberg & Oremland 1990). The highest NO$_3^-$ removal flux of $\sim$1,500 mg Nm$^{-2}$d$^{-1}$ was similar to the flux of $\sim$1,600 mg Nm$^{-2}$d$^{-1}$ in Van Ginkel et al. (2004a). However, the SeO$_4^{2-}$ removal flux reached $\sim$362 mg Se m$^{-2}$d$^{-1}$, which is four times higher than the SeO$_4^{2-}$ removal flux observed earlier at a similar TDS of 33 g/L. The higher SeO$_4^{2-}$ removal flux is likely due to the lower pH of 6.8. Even though the bulk liquid pH was set to 6.8, which is outside the normal range for denitrification, the biofilm pH is likely much higher due to denitrification and SeO$_4^{2-}$ reduction inside the biofilm. Thus, the lower bulk liquid pH helped to mitigate against excessive pH inside the biofilm and more biofilm was active in the reductions. An additional reason could be that concentration of SeO$_4^{2-}$ reducers increased.

In the earlier studies, NO$_3^-$ reducers dominated the bacterial community and SeO$_4^{2-}$ reduction was attributed to secondary utilization with NO$_3^-$ as the main electron acceptor. Since M1 was operated for nearly two years with both NO$_3^-$ and SeO$_4^{2-}$, it is possible that bacterial species that prefer SeO$_4^{2-}$ as the electron acceptor increased.

The pH value of 6.8 also appeared to prevent Ca$^{2+}$ and Mg$^{2+}$ precipitation in M1, while a pH of 7.0 to 7.5 likely led to membrane fouling in M2. Even though Ca$^{2+}$ and Mg$^{2+}$ concentrations were much higher in M1, Ca$^{2+}$ and Mg$^{2+}$ removals were higher in M2, likely due to the higher pH.

At the effluent Ca$^{2+}$ and Mg$^{2+}$ concentrations of 250 and 700 mg/L, respectively, the Langlier Indices (LI) were 1.2 and 2.05 for CaCO$_3$ and MgCO$_3$, respectively (Snoeyink & Jenkins 1980). This assumes a biofilm pH of 8.0. These LI values indicate precipitating conditions, and operating M2 under these conditions likely led to fouling of the membranes. Furthermore, in this study and the previous study, M1 was fed actual brine, while M2 was fed synthetic brine with a strong phosphate buffer, which likely fouled the membranes (e.g. Ca$_3$(PO$_4$)$_2$) more than the actual brine. These results stress that the hardness (Ca$^{2+}$ and Mg$^{2+}$), pH, nitrogen, SeO$_4^{2-}$, PO$_4^{3-}$, or all five should be kept low enough to avoid serious precipitation. Ideally, Ca$^{2+}$ and Mg$^{2+}$ are precipitated out before soluble nitrogen and SeO$_4^{2-}$ are removed in the MBR.

## CONCLUSIONS

Nitrogen (NO$_3^-$ and NO$_2^-$) and SeO$_4^{2-}$ were consistently removed at high efficiencies, and the SeO$_4^{2-}$ removal flux was higher than that observed earlier, which shows continual improvement of the biofilm for SeO$_4^{2-}$ reduction. A low pH of 6.8 inhibited precipitation when treating actual FGD brine without a phosphate buffer and did not decrease contaminant removal. SO$_4^{2-}$ was not removed and therefore did not compete with nitrogen and SeO$_4^{2-}$ reduction for the available H$_2$.

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