Promoting the Biological Oxidation of Reduced Sulphur Compounds by pH Adjustment in a High Temperature Membrane Bioreactor Treating Kraft Pulp Mill Foul Condensate

PIERRE R. BÉRUBÉ*† AND ERIC R. HALL

Department of Civil Engineering and the Pulp and Paper Centre, The University of British Columbia, 2324 Main Mall, Vancouver, British Columbia V6T 1Z4

Over 99% of the reduced sulphur compounds (RSC) contained in a synthetic foul evaporator condensate were removed during treatment using a high temperature membrane bioreactor (MBR). At a neutral pH, the removal of the RSC was entirely due to stripping by the aeration system. It was possible to reduce the amount of RSC that was stripped to the atmosphere by promoting the biological oxidation of RSC through pH adjustment. A pH of less than approximately 4.5 was required to establish biological oxidation of RSC in the MBR. However, even at a pH of 3, which has been reported by others to be the optimal pH for the growth of thermophilic sulphur-oxidizing microorganisms, biological oxidation accounted for only approximately 50% of the RSC removed during treatment. The removal of the remaining 50% of the RSC removed during treatment was still due to stripping by the aeration system. The results further suggested that the long-term stability of a high temperature MBR operated at a low pH is questionable. In addition, the biological oxidation of methanol, which is considered to be the primary contaminant of concern contained in evaporator condensate, was significantly inhibited at a pH of less than approximately 4.5. Consequently, the simultaneous biological removal of methanol and RSC from foul evaporator condensate using a high temperature MBR was concluded to be impractical.

Key words: biological treatment, dimethyl disulphide, dimethyl sulphide, kraft evaporator condensate, high temperature membrane bioreactor, methanol, pH, reduced sulphur compounds

Introduction

Under typical current operating conditions, kraft pulp mills reuse a portion of the cleaner fraction of evaporator condensate as process water in brown stock washing and recausticizing. However, the foul fraction of evaporator condensate, hereafter referred to as condensate, is considered to be too contaminated to be reused directly. Directly reusing condensate could result in ambient air quality problems because of the subsequent
release of volatile and extremely odorous as well as hazardous contaminants contained in them (Venkatesh et al. 1997; Jain 1996). Of particular concern are the reduced sulphur compounds (RSC) present in condensate (hydrogen sulphide, methyl mercaptan, dimethyl sulphide-DMS and dimethyl disulphide-DMDS). These RSC are not only of concern because of their extremely foul odour, but also because of their direct toxicological effects on humans (Verschueren 1996; Tatum 1995).

There is increasing interest in treating condensate so that it can be reused as process water in a kraft pulp mill. Reusing treated condensate would reduce the contaminant load to an existing combined mill effluent treatment system, reduce the mill raw water requirements, and potentially reduce the impact of discharging treated wastewater to the environment. In addition, some legislation proposes a number of incentives for treating and reusing condensate as process water (Vice and Carroll 1998).

In a previous study, the removal of RSC from condensate using a high temperature membrane bioreactor, hereafter referred to as MBR, was investigated (Bérubé and Hall 2000a). As presented in Bérubé and Hall (1999, 2000b), an MBR was selected since it was thought to be more efficient and less costly than treatment using conventional competing technologies (i.e., steam stripping or conventional biological treatment) for the treatment of condensate for reuse. Results from this previous study indicated that over 99% of the RSC contained in condensate was removed during treatment using an MBR and that the removal was strictly due to abiotic mechanisms. Approximately 33% of the methyl mercaptan contained in the influent condensate was stripped from the MBR by the aeration system. The results suggested that the remaining 67% was abiotically oxidized during treatment. Approximately 3% of the hydrogen sulphide contained in the influent condensate was stripped from the MBR by the aeration system. The results suggested that the remaining 97% was abiotically oxidized during treatment. Over 99% of the DMS and DMDS contained in the influent condensate was removed from the MBR by stripping due to the aeration system.

These previous results indicated that approximately 39% of the RSC (as sulphur) contained in condensate is stripped to the atmosphere due to the aeration system during treatment using an MBR (Bérubé and Hall 2000a). Therefore, treating condensate for reuse using a high temperature MBR could potentially increase the emission of RSC to the atmosphere by up to 39%. This is of particular concern since the atmospheric concentration of RSC in some areas at many kraft pulp mills already periodically, and in some cases consistently, exceed ambient air quality standards (Jappinen et al. 1993; Kangas et al. 1984; ACGIH 1999).

The amount of RSC that is released to the atmosphere during treatment in an MBR can be reduced if the RSC can be rapidly oxidized to non-volatile compounds before having the opportunity to be stripped by the aeration system. The present study investigated the possibility of enhancing the oxidation of RSC during treatment in an MBR by promoting the growth of microorganisms capable of oxidizing RSC, while maintaining a relatively high rate of biological methanol removal. Methanol is consid-
ered to be the primary contaminant of concern contained in condensate (Vice and Carroll 1998). Although sulphur-oxidizing microorganisms capable of growth at a high temperature can grow at a neutral pH, their growth is optimal at a much lower pH (Brock 1978). To promote the growth of thermophilic sulphur-oxidizing microorganisms, the operating pH in the MBR was reduced.

**Materials and Methods**

The bench scale MBR used (Fig. 1) consisted of a Plexiglas reactor with an 8-L working volume, a ceramic tubular membrane ultrafiltration system (Membralox 1T1-70 bench scale filtration unit: 7 mm ID, 0.0055 m² surface area, 500 angstrom pore size) and a progressive cavity pump (Moyno Model SP 33304).

The MBR was fed semi-continuously by adding a mixture of synthetic condensate and nutrients, once every 3 hours. The synthetic condensate contained methanol, DMS and DMDS, in tap water, at concentrations similar to those observed in the condensate from a local kraft

Fig. 1. Schematic of bench scale MBR system.
pulp mill (Western Pulp Limited Partnership, Squamish, B.C., Canada) as presented in Table 1. The synthetic condensate did not contain hydrogen sulphide or methyl mercaptan due to the difficulty of solubilizing these RSC to specific concentrations in water. DMS and DMDS were used as surrogates for all RSC contained in condensate. The nutrient solution contained NH₄NO₃, KH₂PO₄, MgSO₄·7H₂O, CaCl₂·7H₂O, FeCl₃·6H₂O, MnCl₂·4H₂O, Na₂B₄O₇·10H₂O, ZnSO₄·7H₂O, CoCl₂·6H₂O and Na₂MoO₄·2H₂O, as required to provide non-limiting nutrient concentrations in the MBR (Bérubé 2000). The hydraulic detention time and the sludge detention time were set to 12 hours and 20 days, respectively. The operating temperature for the MBR was maintained at 55 ± 2°C. An operating temperature of 55°C was selected since it corresponds to the lowest expected temperature for condensate (Sebbas 1987; Blackwell et al. 1979). Mill-scale operation of an MBR at a lower temperature is believed to require cooling of condensate before treatment and would reduce the recoverable heat content of the treated condensate. The pH was initially maintained above 6 (approximately 6.5) using a pH meter/controller that added sodium hydroxide to the MBR as required. The aeration rate through a fine bubble diffuser was approximately 1.6 L/minute. This produced non-limiting dissolved oxygen conditions in the MBR (Bérubé 2000).

During start-up, the MBR was inoculated with sludge from a lab-scale activated sludge system treating combined kraft pulp mill effluent at 45°C (Pulp and Paper Centre, The University of British Columbia, Vancouver, Canada), sludge from a full-scale activated sludge system treating kraft pulp mill effluent (Western Pulp Limited Partnership, Squamish, B.C., Canada), sludge from a pilot-scale municipal activated sludge system (The University of British Columbia — Civil Engineering Pilot Plant), and water and soil samples collected from Harrison Hot Springs (Harrison, Canada). Approximately 500 mL of inoculum from

### Table 1. Characteristics of foul evaporator condensate

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Typical valuesa for industry</th>
<th>Western pulp b</th>
<th>Synthetic condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>180–1200</td>
<td>595 ± 65</td>
<td>500</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>1–240</td>
<td>67 ± 20</td>
<td></td>
</tr>
<tr>
<td>Methyl mercaptan</td>
<td>1–410</td>
<td>60 ± 27</td>
<td></td>
</tr>
<tr>
<td>DMS</td>
<td>1–15</td>
<td>39 ± 20</td>
<td>37</td>
</tr>
<tr>
<td>DMDS</td>
<td>1–50</td>
<td>22 ± 11</td>
<td>25</td>
</tr>
</tbody>
</table>

a Adapted from Blackwell et al. 1979.
b Based on grab samples collected weekly over a 4-month period.
± corresponds to 90% confidence interval of measurements made during monitoring period.
each location was added directly to the MBR at approximately the same time. This was repeated approximately one week following the initial inoculation. Initial steady-state conditions were reached approximately 6 weeks following the initial inoculation. Steady-state conditions were assumed to have been reached when the concentration of mixed liquor volatile suspended solids (MLVSS) and the rate of RSC removal in the MBR were constant.

The operating pH was varied during the study. The operating pHs investigated were 6, 4 and 3. The pH was controlled using a pH meter/controller that added hydrochloric acid or potassium hydroxide to the MBR as required. Between each experimental run, the operating pH was decreased at a rate of one unit over one feed cycle (3 hours). Following a reduction in the operating pH from 6 to 4, steady state conditions were re-established within approximately 2 weeks. When the pH was reduced from 4 to 3, pseudo steady-state conditions appeared to have been reached within 3 weeks. However, as discussed below, the long-term stability of an MBR at such a low pH was questionable. After each change in the operating pH, the MBR was re-inoculated with 100 mL of activated sludge from the Western Pulp Limited Partnership bleached kraft pulp mill. This was done to re-introduce microorganisms that might not have been able to grow under the previous growth conditions.

The RSC removal kinetics were determined by monitoring the concentrations of DMS and DMDS in the MBR over time. Samples were collected from the recycling line of the MBR and analyzed for DMS and DMDS at 5, 20, 35, 50 and 65 minutes following the start of selected batch feed cycles. The analytical method used to measure the concentration of RSC in the collected samples is presented in Bérubé et al. (1999). The RSC removal kinetics in the MBR were monitored for at least one sludge age, following the acclimatization period, at each operating pH investigated. Methanol removal kinetics were also monitored by measuring the methanol concentration in the MBR over time as described above for the RSC. This was done to investigate the feasibility of simultaneous biological removal of methanol and RSC using a high temperature MBR. The analytical method used to measure the concentration of methanol in the collected samples is presented in Bérubé and Hall (1999). The MLVSS concentration in the MBR was measured according to standard methods (APHA et al. 1995)

Stripping of RSC from the MBR due to the aeration system was investigated at the end of the study. Stripping of these contaminants was investigated by monitoring the changes in the concentrations of DMS and DMDS in the MBR when it was filled with tap water, synthetic condensate and nutrients, and then aerated. Stripping of the RSC from the MBR was monitored for each of the operating pHs investigated. Biological growth during the clean-water stripping tests was prevented by adding sodium azide to a concentration of 1% (w/v) in the MBR.

The kinetic parameters were estimated by fitting the equations, presented below, to the measured data using linear regression with logarithmic transform (Sigma Plot™).
Results

RSC Removal

To promote the growth of thermophilic sulphur-oxidizing microorganisms, the operating pH in the MBR was reduced from a relatively neutral pH to a pH of 3. A pH of 3 has been reported by others to be optimal for the growth of thermophilic sulphur-oxidizing microorganisms (Brock 1978). As illustrated in Fig. 2, the concentrations of DMS and DMDS in the MBR decreased at a faster rate when the operating pH was reduced. This indicates that these RSC were removed from the MBR more rapidly as the pH was decreased. The observed increase in the rate of DMS and DMDS removal at a lower pH was attributed to the enhanced biological oxidation of RSC at a lower pH since the abiotic rates of DMS and DMDS removal were not significantly different for all operating pHs investigated. The abiotic rates of DMS and DMDS removal were determined based on clean-water stripping tests (Fig. 3).

The removal of volatile compounds by a mixed microbial culture in an aerobic biological treatment system can be modeled using a Monod-type relationship as presented in equation 1 (Bailey and Ollis 1986):

\[
R_{T-RSC} = \frac{dC_{RSC}}{dt} = U_{RSC} \left( \frac{C_{RSC}}{C_{RSC} + K_{sRSC}} \right) \left( \frac{K_{iRSC}}{K_{iRSC} + C_{RSC}} \right) \left( 1 + C_{RSC}K_{STRIP-RSC} \right)
\]

where \( R_{T-RSC} \) is the total rate of RSC removal (mg/L • minute), \( C_{RSC} \) is the concentration of RSC in the biological treatment system (mg/L), \( U_{RSC} \) is the specific RSC utilization coefficient (/minute), \( K_{sRSC} \) is the half saturation concentration (mg/L), \( K_{iRSC} \) is the half inhibition concentration.

Fig. 2. Concentrations of DMS and DMDS in MBR during typical batch cycles at different operating pHs. ● and solid line: pH = 6; ■ and long dashed line: pH = 4; ▲ and short dashed line: pH = 3; lines: equation 3b fitted to concentrations of DMS and DMDS.
According to equation 1, the rate of RSC removal is a function of the concentration of RSC remaining in the MBR. As illustrated in Fig. 2, the rate of DMS and DMDS removal did vary as a function of the concentration of these RSC in the MBR decreased. In fact, the rate of removal of DMS and DMDS followed a first-order relationship. The first-order removal rates for DMS and DMDS indicated that the concentrations of RSC were not inhibiting the uptake of RSC by the mixed microbial culture in the range of concentrations examined (initial concentrations of DMS and DMDS in the MBR at the start of the batch feed cycles were approximately 9.5 and 3.5 mg/L, respectively). In addition, the first-order removal rates for DMS and DMDS indicated that the concentrations of these RSC were limiting the uptake of RSC by the mixed microbial culture in the range of concentrations examined. These observations are consistent with results obtained by Kargi and Robinson (1982). When investigating the biological oxidation of dibenzothiophene, a RSC, by a pure culture of thermophilic sulphur-oxidizing microorganisms, they observed a relatively high half inhibition concentration of 480 mg/L and a half saturation concentration of 666 mg/L.

For limiting and non-inhibiting conditions, equation 1 can be simplified to a first-order relationship as presented in equations 2a and 2b.

\[
R_{T-RSC} = \frac{dC_{RSC}}{dt} = C_{RSC} \left( K_{B-RSC} + K_{STRI P-RSC} \right)
\]  
(2a)

\[
R_{T-RSC} = \frac{dC_{RSC}}{dt} = C_{RSC} K_{T-RSC}
\]  
(2b)
where $K_{B-RSC}$ is the first-order coefficient for the biological removal of RSC (/minute) and $K_{T-RSC}$ is the first-order coefficient for the total removal of RSC (i.e., sum of $K_{B-RSC}$ and $K_{STRIP-RSC}$) (/minute).

For the batch fed MBR used, equations 2a and 2b can be solved analytically as presented in equations 3a and 3b.

\begin{align*}
C_{t-RSC} &= C_{0-RSC} e^{(K_{B-RSC} + K_{STRIP-RSC})t} \quad (3a) \\
C_{t-RSC} &= C_{0-RSC} e^{(K_{T-RSC})t} \quad (3b)
\end{align*}

where $C_{t-RSC}$ is the concentration of RSC in the MBR at time $t$ following the start of a batch feed cycle (mg/L), $C_{0-RSC}$ is the concentration of RSC in the MBR at the start of a batch feed cycle (mg/L) and $t$ is the elapsed time since the start of a batch feed cycle (minutes).

The total first-order coefficients for the removal DMS and DMDS removal were estimated by fitting equation 3b to the concentrations of DMS and DMDS in the MBR measured during selected batch feed cycles for different operating pHs as illustrated in Fig. 2. The first-order coefficients for the stripping of DMS and DMDS were estimated by fitting equation 3a to the concentrations of DMS and DMDS in the MBR measured during the clean-water stripping tests as illustrated in Fig. 3. For the abiotic stripping tests, the first-order coefficient for the biological removal of RSC ($K_{B-RSC}$) was assumed to be zero. The first-order coefficients for the stripping of DMS and DMDS were estimated to be $0.022 \pm 0.0024$ and $0.019 \pm 0.0060$ /minute, respectively, for all pHs investigated. The first-order coefficients for the biological removal of RSC were calculated based on the difference between the total first-order coefficients for the removal of RSC and the first-order coefficients for the stripping of RSC measured for the different operating pHs. The first-order coefficients for the biological removal of DMS and DMDS increased from essentially zero, at a pH of 6, to $0.019 \pm 0.0042$ /minute and $0.016 \pm 0.00026$ /minute, at a pH of 4, and to $0.020 \pm 0.0017$ /minute and $0.027 \pm 0.0021$ /minute, respectively, when the pH was lowered to 3 as presented in Fig. 4. This is in agreement with Brock (1978) who reported that the growth of thermophilic sulphur-oxidizing bacteria increases as the pH decreases and is optimal at a pH of approximately 3.

The effect of pH on biological substrate removal can typically be modeled using the relationship presented in equation 4 (Bailey and Ollis 1986):

\begin{equation}
K_{pH} = \frac{K_{0pH}}{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}} \quad (4)
\end{equation}

where $K_{pH}$ is the biological removal coefficient at a given pH (/minute), $K_{0pH}$ is the maximum biological removal coefficient at the optimal pH (/minute), $[H^+]$ is the concentration of hydrogen ions at a given pH (mg/L), and $K_1$ and $K_2$ are dissociation constants (mg/L).

Equation 4 was successfully fitted to the estimated first-order coefficients for the biological removal of RSC as presented in Fig. 4. As illus-
Biological methanol, DMS and DMDS removal coefficients vs. operating pH.

- **●**: methanol; **▼**: DMS; **▲**: DMDS; solid line: equation 4 fitted to the first-order coefficients for the biological removal of DMDS measured at different pHs; long dashed line: equation 4 fitted to the first-order coefficients for the biological removal of DMS measured at different pHs; short dashed line: equation 4 fitted to the zero-order coefficient for the biological removal of methanol measured at different pHs.

The increase in the rates of biological oxidation of DMS and DMDS resulted in a reduction in the amount of RSC that was stripped to the atmosphere due to the aeration system during treatment using a high temperature MBR. The amounts of DMS and DMDS contained in the condensate that were stripped to the atmosphere were reduced from over 99% at a neutral pH, to approximately 55% at a pH of 4, and to approximately 53% and 42% for DMS and DMDS, respectively, when the pH was further lowered to 3.

**Methanol Removal**

The biological removal of methanol was significantly inhibited when the pH was lowered as illustrated in Fig. 4. The estimated zero-order coefficient...
ficients for the biological removal of methanol was reduced from 1.38 ± 0.24 mg/L•minute at a neutral pH, to 0.4 ± 0.034 mg/L•minute at a pH of 4. As presented in Bérubé and Hall (1999), methanol removal followed a zero-order relationship. At a pH of 3, there was essentially no biological removal of methanol occurring in the MBR. As previously mentioned, methanol is considered to be the primary contaminant of concern contained in the foul fraction of evaporator condensate (Vice and Carroll 1998). Equation 4 was successfully fitted to the estimated zero-order coefficients for the biological removal of methanol, respectively. As illustrated in Fig. 4, the biological removal of methanol was significantly inhibited at a pH below approximately 4.5. The reduction in the zero-order biological methanol removal coefficient at a lower pH is likely due to the instability of formate dehydrogenase, an enzyme involved in the biological oxidation of methanol, at a pH below 6 as reported by Izumi et al. (1989). However, further research would be required to confirm this hypothesis.

Discussion

The results from the present study indicate that it is possible to decrease the amount of RSC that is stripped to the atmosphere due to the aeration system during treatment using an MBR by promoting the growth of thermophilic sulphur-oxidizing microorganisms through pH adjustment. However, even under the optimal conditions for the growth of thermophilic sulphur-oxidizing microorganisms, stripping of RSC is still significant. At a pH of 3, which has been reported to be optimal for the growth of thermophilic sulphur-oxidizing microorganisms, approximately 53% and 42% of the DMS and DMDS, respectively, contained in the condensate were stripped to the atmosphere. Consequently, treating condensate for reuse using an MBR could increase the atmospheric concentrations of these compounds, producing conditions where ambient air quality standards are more frequently of even consistently exceeded. Also, the stability of an MBR operated at a low pH is questionable. As illustrated in Fig. 5, after approximately 4 weeks of operation at a pH of 3, the total first-order coefficients for the removal of DMS and DMDS declined sharply. After 5 weeks of operation at a pH of 3, there was no observable biological removal of RSC. In addition, the biological removal of methanol is significantly inhibited in the pH range required for the growth of thermophilic sulphur-oxidizing microorganisms.

For the above reasons, the simultaneous biological removal of methanol and RSC from condensate using an MBR is not considered to be feasible. As an alternative to promoting the biological oxidation of the RSC by pH adjustment, the off-gas from an MBR treating condensate could be collected and burned in a designated catalytic incinerator. The off-gas could also be hard piped to an existing power or recovery boiler for incineration. The incinerator would thermally oxidize all of the RSC that are stripped from the MBR during treatment of condensate and, therefore, prevent any increase in the ambient air concentration of these compounds.
Fig. 5. Effect of pH on total first-order coefficient for the removal of RCS during monitoring period. ▼: DMS; ▲: DMDS; dashed line: operating pH; clear symbols: first-order coefficients for the stripping of RSC; stars indicate where both ▼ and ▲ coincide.

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References


