A membrane bioreactor for the removal of dimethyl sulphide and toluene from waste air

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Abstract In biotrickling filters, mass transfer of hydrophobic compounds is the limiting factor. Biofilters are static systems, and so control and regulation of operational parameters such as pH and nutrient supply can be a problem. In membrane bioreactors, these drawbacks can be avoided. The hydrophobic membrane separates the waste air from the aqueous phase, thus avoiding mass-transfer limitation, while pH and nutrient supply can be directly controlled. In this contribution, an overview will be given of results obtained during a four-year project. First, the physical chemical characteristics (solubility, permeability, diffusivity) and microbial adhesion of different membranes were tested. This led to the selection of a composite membrane consisting of a porous polyvinylidenefluoride (PVDF) support layer coated with a thin (1 or 2.5 µm) dense polydimethylsiloxane (PDMS) top layer. This membrane was mounted into a module provided with four parallel rectangular channels for gas flow (in contact with the porous layer) and nutrient solution (in contact with the dense layer) respectively. After inoculation, a biofilm developed on the dense layer. Experiments were performed with dimethyl sulphide and toluene as target VOCs. Operational characteristics such as elimination capacity as a function of the volumetric load and residence time, effect of nutrient supply, long-term performance) were determined. Mass transfer was studied by measuring concentration profiles along the channels of the module in different conditions.

Keywords Dimethyl sulphide; membrane bioreactor; polydimethylsiloxane; polyvinylidenefluoride; toluene; VOC

Introduction
Biofilters (BF) and biotrickling filters (BTF) are the most frequently used biological techniques for treatment of waste air. In both techniques, air flows through a packed bed of carrier material on which micro-organisms grow as a biofilm. The biofilm is covered by a water layer, forming a barrier between the micro-organisms and hydrophobic compounds in the air phase. In a membrane bioreactor (MBR), the liquid and air phases can be separated by a membrane. Pollutants diffuse through the membrane and are subsequently degraded by the microorganisms in the biofilm. Because of the separation of the liquid and air phase, waste air containing hydrophobic compounds can be treated effectively. Oxygen is supplied from the air phase, while nutrients are present in the liquid phase. In a composite membrane bioreactor, the biofilm is formed at the dense side of the membrane. Both, the reduction of hydrophilic nature of the air/biofilm interface and the ease of control of operational parameters (pH, nutrient supply) are advantages of MBR over BF and BTF.

For membrane biofiltration of toluene, three types of reactor configurations have been used, i.e. hollow fibres (internal diameter (ID) < 0.5 mm), capillary (0.5 < ID < 10 mm) and flat membranes. Compared to a flat and capillary membrane configuration, hollow fibres have a very large specific gas–membrane contact area. Because of the large range in these specific membrane areas used in membrane bioreactor experiments, data on mass loading rate (LR) and elimination capacity (EC) should be compared per unit of available (specific) membrane area. Volumetric ECs suggest that a flat membrane configuration is inferior to hollow fibres. However, on the basis of the available membrane area, data are in the same
order of magnitude. Comparing tests performed with loading rates less than 1 g m\(^{-2}\) h, the highest volumetric EC (2520 g TOL m\(^{-3}\) h\(^{-1}\)) was gained by Ergas et al. (1999) while the highest EC per unit of membrane area (0.163 g TOL m\(^{-2}\) h\(^{-1}\)) was achieved by Parvatiyar et al. (1996). The research conducted by England and Fitch (2002) concerned another range of loading rates. Concerning the membrane materials, England and Fitch (2002) used dense membranes; Parvatiyar et al. (1996) used a hydrophilic porous membrane, while Hartmans et al. (1992), Ergas and McGrath (1997) and Ergas et al. (1999) used a hydrophobic porous membrane. Porous membranes have lower mass-transfer resistance than dense ones, but a disadvantage of these is biofouling (Attaway et al., 2002). Dimethyl sulphide has been studied as a target compound in BF (Cho et al., 1991; Zhang et al., 1991; Smet et al., 1996; Budwill and Coleman, 1999; Smet et al., 1999) and BTF (Tangi et al., 1989; Pol et al., 1994; Ruokojärvi et al., 2000) but not in MBR.

In a composite membrane bioreactor, the porous layer is used as support, while the thin dense layer prevents microbial growth through the membrane. This type of membrane probably allows the combination of the advantages of both the dense (better interface) and the porous membranes (better mass transfer). The goal of this study was to investigate the biodegradation of gaseous toluene and dimethyl sulphide using a flat hydrophobic polymethylsiloxane (PDMS) composite membrane bioreactor, and to compare results with results from BF and BTF experiments.

**Methods**

**Membrane materials**

A commercially available composite membrane was kindly provided by GKSS Forschungszentrum Geesthacht (Germany). The hydrophobic dense top layer material was polydimethylsiloxane (PDMS), with a thickness of 1 or 2.5 µm. Polyvinylidene fluoride (PVDF, 210 µm) was used as a hydrophobic support layer material. The specific membrane area was 500 m\(^{-2}\) m\(^{-3}\); both the air- and MM-side had a membrane contact area of 40 cm\(^2\).

**Membrane biofiltration experiments**

Basically, the MBR consists of two parts of a Perspex reactor module. Each part had a compartment with four channels (20 cm \(\times\) 5 mm \(\times\) 2 mm). The membrane is clamped between both parts. Through one compartment (total volume 8 ml), the mineral medium was recirculated at the dense membrane side at a flow rate of 75 ml min\(^{-1}\) by a peristaltic pump (Masterflex, Cole Parmer). Through the other compartment, contaminated air passed along the porous membrane side countercurrently with the liquid stream. Gas flow rates between 20 and 240 ml min\(^{-1}\) were selected, corresponding with gas residence times between 24 and 2 s. The module was placed in an isothermal chamber at 30°C. A full description of the experimental setup can be found in De Bo et al. (2003).

**Microbiological procedures**

*Inocula and media.* *Pseudomonas putida* TVA8 was chosen as the inoculum because of its high capacity to metabolise toluene and for its good properties of adhesion at the PDMS membrane. The microorganisms were grown in Luria-Bertani (LB) medium for 24 hours, at 28°C. The microorganisms were separated from the LB medium by centrifuging for 4 minutes at 5,000 rpm (Sigma 4-10, B. Braun) and washing twice with mineral medium (MM). The microbial suspension was then brought into an impinger filled with MM. Toluene loaded air (20 ml min\(^{-1}\); 1 g TOL m\(^{-3}\)) bubbled through the suspension until 99% of the toluene was removed from the air stream. The MM used for toluene experiments consisted of 3 g L\(^{-1}\) K\(_2\)HPO\(_4\), 3 g L\(^{-1}\) KH\(_2\)PO\(_4\), 3 g L\(^{-1}\) NH\(_4\)Cl, 5 g L\(^{-1}\) KNO\(_3\), 0.5 g L\(^{-1}\) H. Van Langenhove et al.
MgSO$_4$.7H$_2$O, 0.01 g L$^{-1}$ FeSO$_4$.7H$_2$O. The pH was set at 7.0 Later NH$_4$Cl was replaced with 5.72 g KNO$_3$ L$^{-1}$, resulting in a total concentration of 10.72 g L$^{-1}$ KNO$_3$.

Two different inocula were selected: a pure *Hyphomicrobium* VS culture and a mixed suspension of *Hyphomicrobium* VS, ammonium-oxidizing bacteria and nitrite-oxidizing bacteria. *Hyphomicrobium* VS was enriched from activated sewage sludge and isolated by Pol et al. (1994). *Hyphomicrobium* VS was grown on a mineral salts medium containing 3 g K$_2$HPO$_4$, 3 g KH$_2$PO$_4$, 3 g NH$_4$Cl, 0.5 g MgSO$_4$.7H$_2$O and 0.01 g FeSO$_4$.7H$_2$O per litre of distilled water (pH = 7). Methanol (2% v/v) was added as the sole carbon and energy source. The bacteria were incubated at 28°C and 140 rpm, during seven days. Before each experiment, the cultures were centrifuged at 3,500 rpm for five minutes (Sigma 4-10, B. Braun), washed three times in 160 mM physiological solution (8.5 g NaCl, 0.5 g KH$_2$PO$_4$ and 0.5 g K$_2$HPO$_4$ per litre of distilled water; pH 6.8) and re-suspended in the different solutions to a final cell concentration of 10$^7$–10$^8$ cells cm$^{-3}$.

The mixed inoculum type was obtained by adding 50 cm$^3$ of an active association of nitrifying bacteria (code name ABIL) to 250 cm$^3$ *Hyphomicrobium* suspension. Details about the nitrifying culture are reported by Grommen et al. (2002). Both inoculum suspensions were adapted to DMS in 350 cm$^3$ glass fermentors by bubbling DMS-loaded air through the suspension (20 cm$^3$ min$^{-1}$; ± 1.0 g DMS m$^{-3}$).

**Analytical methods**

Gas-phase toluene concentrations were measured using a gas chromatograph (Varian 3700), equipped with a flame ionization detector (FID) and a 30-m long DB-1 column (J&W Scientific) with an inner diameter of 530 µm and a film thickness of 5 µm. The column temperature was 120°C; the injector and detector temperature were 220 and 250°C, respectively. Helium was used as a carrier gas at a flow rate of 4.2 ml min$^{-1}$; the air and hydrogen flow rate were 300 and 32 ml min$^{-1}$, respectively. Dimethyl sulphide was measured with an Agilent 6890 Series gas chromatograph. Gas samples were taken in triplicate with a 1 ml Vici gas syringe. The residual standard deviation on the measurements was less than 10%. Nitrate and nitrite were analysed using a Dionex DX-600 series ion chromatograph equipped with a conductivity detector. Operational parameters were as follows: column: AS9-HC, eluent: 9 mM Na$_2$CO$_3$, flow: 1 ml min$^{-1}$, sample loop: 200 µl. Ammonium concentrations were determined according to Kjeldahl’s method. The pH was measured with a Jenway 3310 apparatus, equipped with a Hanna Instruments electrode. Sulphate concentrations in nutrient solutions were measured by means of the turbidimetric method (Greenberg, 1981). After the liquid sample was filtered to remove colouring agents and suspended solids, sulphate ions were precipitated with barium chloride in acetic acid medium. The absorbance of the suspension of BaSO$_4$ crystals was measured with a spectrophotometer (Spectronic® 21 Milton Roy) at 420 nm. Conductivity was measured with a digital conductometer of Hanna Instruments.

**Results and discussion**

**Characterization of the membrane properties**

Because the PDMS polymer determines the selective character and sorption in porous layers can be considered as negligible (Reij et al., 1998), the transport mechanism through the PDMS polymer was investigated extensively. Permeability, diffusivity and solubility coefficients were determined experimentally for oxygen, carbon dioxide, ethylene (ET), dimethyl sulphide (DMS), toluene (TOL) and trichloroethylene (TCE). Details of these experiments can be found in De Bo et al. (2003) and De Bo et al. (2002). A summary of the results is given in Table 1. All coefficients were found to be concentration independent for concentrations lower than 53 g VOC m$^{-3}$. Dimethyl sulphide, toluene and trichloroethylene were determined to be highly permeable compounds, while ethylene, carbon dioxide and...
oxygen could be classified as less-permeable compounds. The transport mechanism through the selected composite membrane was studied as well. The porous PVDF support layer dominated the overall membrane resistance of highly permeable compounds. As a consequence, the thickness of the thin PDMS films (1 or 2.5 µm) did not influence the compound’s transfer. When less-permeable compounds were considered, it was observed that the top layer thickness played a role as well. During transport of VOC mixtures, the transfer rate of the individual compounds was not affected by the presence of other organic compounds. Furthermore, the presence of water vapor in the air did not change the compound’s partition coefficient between air and PDMS. These results indicate that, for biological waste gas treatment of mixtures, only biological interfering effects are expected.

### Toluene degradation in the MBR

**Inoculation and reactor start-up.** The inoculum was re-circulated along the dense side of the membrane, while toluene was supplied from the air phase from the other side of the membrane (τ = 24 s; C\textsubscript{in} = 0.22 g TOL m\textsuperscript{-3}). After 24 h of operation, 83% removal efficiency was observed and a biofilm became visible on the membrane. After three days, more than 95% toluene removal was obtained. The short acclimatisation period observed was attributed to the pre-acclimatisation of the microorganisms prior to inoculation of the reactor. The microbial suspension was then replaced by fresh MM, and thus all non-adhering cells were removed. During the next 14 days, a decrease in reactor performance to less than 50% removal efficiency was observed. Simultaneously, the pH of the liquid phase decreased to 6.0 and nitrite concentrations up to 0.18 g NO\textsubscript{2}-N L\textsuperscript{-1} were found. Replacing the liquid phase with a fresh mineral medium resulted in an immediate recovery of the reactor performance. After six days, pH and performance declined and nitrite concentration increased again to the status before renewing the liquid phase. If, later on, only the pH was corrected without renewing the liquid phase, no improvement was observed. It is likely that a combination of both effects, together with other effects like oxygen depletion due to nitrifying activity, caused the drop in reactor performance. Replacing ammonia by nitrate solved the problem.

**Influence of loading rate and gas residence time on the reactor performance.** During an experiment lasting for 115 days, the inlet concentrations were changed stepwise between 0.21 and 3.18 g TOL m\textsuperscript{−3}. The gas residence time was switched for each setting of C\textsubscript{in} between 24 s and 8 s. Consequently, the mass loading rate was increased stepwise from 0.77 to 11.6 kg TOL m\textsuperscript{−3} d\textsuperscript{−1}. After changing the concentration and/or the gas residence time, removal efficiency and elimination capacity were stable within 24 hours. Each setting was kept constant for a few days to be sure that reactor performance was stable over time. A summary of the results obtained during this experiment is given in Table 2.

After the experiments, the MBR was operated without supervision at a gas residence time of 24 s and at a loading rate of ±3.6 kg TOL m\textsuperscript{−3} d\textsuperscript{−1} during a four month period. No

<table>
<thead>
<tr>
<th>Component A</th>
<th>P (10\textsuperscript{10} m\textsuperscript{2} s\textsuperscript{−1})</th>
<th>S (g m\textsuperscript{−3} pdms/g m\textsuperscript{−3} air)</th>
<th>D\textsubscript{m} (10\textsuperscript{10} m\textsuperscript{2} s\textsuperscript{−1})</th>
<th>α\textsubscript{A/N\textsubscript{2}} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2}</td>
<td>6.91</td>
<td>–</td>
<td>–</td>
<td>2.1</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>36.3</td>
<td>1.43</td>
<td>25.4</td>
<td>11</td>
</tr>
<tr>
<td>ET</td>
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<td>2.53</td>
<td>11.4</td>
<td>8.6</td>
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<tr>
<td>DMS</td>
<td>561</td>
<td>92.8</td>
<td>6.05</td>
<td>167</td>
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<tr>
<td>TCE</td>
<td>1433</td>
<td>360</td>
<td>3.98</td>
<td>427</td>
</tr>
<tr>
<td>TOL</td>
<td>2105</td>
<td>902</td>
<td>2.33</td>
<td>627</td>
</tr>
</tbody>
</table>

\(P\): permeability, \(S\): solubility, \(D\textsubscript{m}\): membrane diffusivity, \(\alpha\textsubscript{A/N\textsubscript{2}}\): selectivity with nitrogen as reference.
measurements were carried out, and the mineral solution was never renewed. In order to evaluate the long-term performance, the effect of the loading rate and gas residence time was investigated within the same range as applied in the previous period. The same reactor performance was measured for all settings, as illustrated in Figure 1. Despite ageing of the biofilm, the reactor was still optimally active. All eight conditions were measured in a 20-day period, which illustrates the rapid response in reactor performance.

The toluene experiments demonstrate the long-term stability and good reactor performance of a composite membrane bioreactor for treatment of toluene-contaminated air. Toluene membrane biofiltration was performed at $C_{in}$ and $\tau$ varying between 0.20 and 3.2 g TOL m$^{-3}$, and 2 and 24 s, respectively. During reactor start-up, unstable bioreactor performance, together with a pH drop (to 6.0) and presence of nitrite in the liquid phase (up to 0.18 g NO$_2$–N L$^{-1}$) were observed. Neither the separate effect of a pH drop nor the presence of nitrite alone could explain the observed 50% fall in reactor performance. Unstable

<table>
<thead>
<tr>
<th>$\tau$ (s)</th>
<th>$C_{in}$ (g TOL m$^{-3}$)</th>
<th>LR (kg TOL m$^{-3}$ d$^{-1}$)</th>
<th>$n$ (–)</th>
<th>$\eta$ (%)</th>
<th>$\eta$$_{max}$ (%)</th>
</tr>
</thead>
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<tr>
<td>24</td>
<td>0.21</td>
<td>0.77</td>
<td>10</td>
<td>90</td>
<td>99</td>
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<tr>
<td></td>
<td>0.66</td>
<td>2.4</td>
<td>5</td>
<td>91</td>
<td>94</td>
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<tr>
<td></td>
<td>1.07</td>
<td>3.9</td>
<td>12</td>
<td>88</td>
<td>97</td>
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<td></td>
<td>2.15</td>
<td>7.8</td>
<td>3</td>
<td>78</td>
<td>78</td>
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<tr>
<td></td>
<td>3.18</td>
<td>11.5</td>
<td>10</td>
<td>74</td>
<td>84</td>
</tr>
<tr>
<td>8</td>
<td>0.23</td>
<td>2.5</td>
<td>8</td>
<td>65</td>
<td>72</td>
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<tr>
<td></td>
<td>0.64</td>
<td>6.9</td>
<td>5</td>
<td>47</td>
<td>52</td>
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<tr>
<td></td>
<td>1.07</td>
<td>11.6</td>
<td>13</td>
<td>41</td>
<td>55</td>
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</tbody>
</table>

$\tau$: gas residence time, $C_{in}$: toluene inlet concentration, LR: loading rate, $n$: number of data points, $\eta$: average efficiency, $\eta$$_{max}$: maximum efficiency

Figure 1: Average elimination capacity for TOL as a function of LR for MBR1, operated at $\tau = 24$ s (circles) and $\tau = 8$ s (triangles) during the first and second period of the experiment. The straight line represents 100% removal efficiency, while the dotted lines are best fits of data from period II. The error bars show the RSD on the measured ECs ($n = 3$–13).
reactor performance was restored by substituting ammonium in the liquid phase with nitrate. This way, nitrifying activity was ruled out. At \( \tau = 24 \) s, more than 90% could be eliminated for LRs up to 2.4 kg TOL m\(^{-3}\) d\(^{-1}\). An EC\(_{\text{max}}\) of 9.5 kg TOL m\(^{-3}\) d\(^{-1}\) was obtained (\( \eta = 84\% \)). Per unit of membrane area, \( EC_{m, \text{max}} \) amounts to 19.0 g TOL m\(^{-2}\) d\(^{-1}\), being five times higher than results obtained with other membrane bioreactors in the same range of loading rates (Table 3). Only England and Fitch (2002) reported higher elimination capacity, but at loading rates that were more than 100 times larger than the loadings applied in this study. Reactor performance was clearly affected by the gas residence time and inlet concentration. For \( \tau = 8 \) s, removal efficiencies between 40 and 65% were achieved. Lowering gas residence times at a constant LR clearly resulted in lower reactor performance (\( \eta = 53\% \) at \( \tau = 2 \) s). Moreover, at \( \tau = 2 \) s, lowering LR could not increase the removal efficiency, indicating that at this low gas residence time, reactor performance was limited by mass transfer.

### Dimethyl sulphide degradation in the MBR

**Optimal parameters for Hyphomicrobium VS DMS degradation.** In order to maintain optimal activity during MBR tests, the influence of pH and SO\(_4^–\), NO\(_2^–\) and NO\(_3^–\) concentrations on the DMS degradation activity of Hyphomicrobium VS in suspension was investigated. A maximum specific DMS degradation rate of 160 mg DMS g VS\(^{-1}\) d\(^{-1}\) was observed between pH 6.0 and 7.0. At pH 8.5 and below 4.0, the degradation activity was decreased to 60% of its maximum value, while, at pH 2.4, the relative activity was decreased to below 20%. Consequently, during the membrane biofiltration of dimethyl sulphide, the pH was re-adjusted to 7.0 whenever the measured value was lower than 6.0. No inhibiting effect on the degradation activity was observed for sulphate concentrations up to 8 g SO\(_4^–\)-S L\(^{-1}\). The microbial activity was not influenced by the presence of nitrite in concentrations lower than 0.070 g NO\(_2^–\)-N L\(^{-1}\), which was the highest level determined in the mobile liquid phase during the bioreactor tests. Replacing ammonium as a nitrogen source by nitrate did not affect the degradation activity of Hyphomicrobium VS.

**DMS degradation by nitrifying bacteria.** Since the specificity of the ammonium mono-oxygenase enzyme is rather low, DMS oxidation can be performed by nitrifying microorganisms. Since MBR are open systems, the possible contribution of nitrifying microorganisms towards DMS oxidation was investigated in suspension. For these experiments a mixed inoculum of ammonium oxidizing and nitrite oxidizing bacteria (ABIL) was used. Experiments were performed in batch cultures, and DMS progress curves were recorded by analysing the headspace. Curves were fitted to a first-order degradation equation. As a reference, an experiment with inactivated ABIL (addition of allyl thiourea, ATU) was performed. Overall results are presented in Table 4.

### Table 3  Literature data of toluene degradation in MBR

<table>
<thead>
<tr>
<th>Reference</th>
<th>Type</th>
<th>MP</th>
<th>( \Phi ) (m(^2) m(^{-3}))</th>
<th>LR(_{\text{m}}) (g m(^{-2}) d(^{-1}))</th>
<th>h (%)</th>
<th>EC(_{m, \text{max}}) (g m(^{-2}) d(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ergas and McGrath (1997)</td>
<td>HF</td>
<td>PE</td>
<td>10256</td>
<td>1.63</td>
<td>97</td>
<td>1.58</td>
</tr>
<tr>
<td>Hartmans et al. (1992)</td>
<td>F</td>
<td>PP</td>
<td>500</td>
<td>8.11</td>
<td>35</td>
<td>2.83</td>
</tr>
<tr>
<td>Ergas et al. (1999)</td>
<td>HF</td>
<td>PP</td>
<td>20000</td>
<td>8.28</td>
<td>35</td>
<td>3.02</td>
</tr>
<tr>
<td>Parvatiyar et al. (1996)</td>
<td>C</td>
<td>PSf</td>
<td>2622</td>
<td>4.66</td>
<td>84</td>
<td>3.91</td>
</tr>
<tr>
<td>Reiser et al. (1994)</td>
<td>C</td>
<td>PDMS</td>
<td>n.r.</td>
<td>84</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>England and Fitch (2002)</td>
<td>T</td>
<td>PDMS</td>
<td>558</td>
<td>720</td>
<td>20</td>
<td>144</td>
</tr>
</tbody>
</table>

A maximum degradation activity of 11.2 mg DMS g VS\(^{-1}\) d\(^{-1}\) was observed for the microbial community comprising *Hyphomicrobium* VS and ABIL. As calculated from the regression curves, it took about 49 hours to consume all added substrate in the system. The addition of ATU as a selective inhibitor of the nitrifiers (Völsch et al., 1990) resulted in a lower degradation activity (7.00 mg DMS g VS\(^{-1}\) d\(^{-1}\)) and an increase of time to reach full substrate depletion to 90 h. The contribution of nitrifying bacteria to dimethyl sulphide removal was confirmed in the experiments with only ABIL. A relatively small degradation activity (1.34 mg DMS g VS\(^{-1}\) d\(^{-1}\)) and consequently a long depletion time of 155 h, was determined with a three times higher biomass content in the system. In a separate control experiment with ATU, the inactivated nitrifying bacteria did not degrade DMS. From these tests it can be concluded that the presence of an association of nitrifying bacteria in parallel with *Hyphomicrobium* VS positively influenced the DMS-degradation capacity. However, nitrite and acid should be further removed in order to avoid decreasing the activity of *Hyphomicrobium* VS.

### Influence of loading rate and gas residence time on the reactor performance

In a MBR reactor with 2.5 \(\mu\)m PDMS/PVDF, the EC was monitored over 100 days under different LRs (see Figure 2). After nine days of operation at \(\tau = 8\) s, complete degradation of DMS was observed for a mass loading rate of 0.14 kg DMS m\(^{-3}\) d\(^{-1}\). The loading rate was increased up to 3.6 kg DMS m\(^{-3}\) d\(^{-1}\) by increasing the inlet concentration. After 54 days, the MBR was operated at 24 s gas residence time (31 days) and 4 s gas residence (15 days), whereby stepwise increases of \(C_{\text{in}}\) were applied until an average LR of 4.0 kg DMS m\(^{-3}\) d\(^{-1}\) was reached. At a LR of about 2.6 kg DMS m\(^{-3}\) d\(^{-1}\), ECs of 1.8 (\(\tau = 4\) s), 2.0 (\(\tau = 8\) s) and 2.4 kg DMS m\(^{-3}\) d\(^{-1}\) (\(\tau = 24\) s) were observed. The maximum EC observed with MBR was 3.2 kg DMS m\(^{-3}\) d\(^{-1}\) (\(\eta = 89\%\)).

The changes of pH could be correlated to the DMS degradation. A pH change with 0.5 units took about 42 days for a LR of 0.13 kg DMS m\(^{-3}\) d\(^{-1}\) and 14 days for a LR of 1.0 kg DMS m\(^{-3}\) d\(^{-1}\). Only when the waste air contained relatively high DMS concentrations (1.12 g DMS.m\(^{-3}\)), small liquid concentrations in influent (0.37 g.m\(^{-3}\)) and effluent samples (0.56 g.m\(^{-3}\)) (\(n = 3\)) were found. It was calculated that 16% of the supplied DMS mass was not transported through the membrane; thus 84% was transferred and was available for microbial degradation. Only 4% accumulated in the nutrient solution while 2% was degraded by suspended cells. A summary of the reactor performance is given in Table 5.

Comparison of a membrane bioreactor with other waste gas biotreatment types such as biofilters and biotrickling filters can be performed by expressing the elimination capacities on reactor bed volume instead of gas volume throughput. For biofilters and biotrickling filters, maximum elimination capacities of 1.68 kg DMS m\(^{-3}\) d\(^{-1}\) (Smet et al., 1999) and

<table>
<thead>
<tr>
<th>(S_0) (g DMS m(^{-3}))</th>
<th>(v) (mg DMS m(^{-3})h(^{-1}))</th>
<th>95% confidence interval of (v)</th>
<th>(R^2) (n)</th>
<th>Biomass (mg VS)</th>
<th>(A_{\text{m}}) (mg DMS g VS(^{-1}) d(^{-1}))</th>
<th>(t) when (S = 0) g m(^{-3}) (h)(^{a})</th>
</tr>
</thead>
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<tr>
<td>0.88</td>
<td>17.9</td>
<td>17.0; 18.8</td>
<td>0.999 (6)</td>
<td>0.55</td>
<td>11.2</td>
<td>49</td>
</tr>
<tr>
<td>1.03</td>
<td>11.5</td>
<td>10.1; 12.9</td>
<td>0.996 (5)</td>
<td>0.55</td>
<td>7.00</td>
<td>90</td>
</tr>
<tr>
<td>0.80</td>
<td>5.2</td>
<td>4.1; 6.3</td>
<td>0.962 (7)</td>
<td>1.60</td>
<td>1.34</td>
<td>155</td>
</tr>
</tbody>
</table>

\(S_0\): initial substrate concentration, \(v\): degradation rate, \(R\): regression coefficient, \(A_{\text{m}}\): degradation rate per unit biomass, \(a\): calculated from the regression curve

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**Table 4** Results of the batch biodegradation experiments. The progress curves were fitted to: \(S = S_0 - vt\)

1.86 kg DMS m\(^{-3}\) d\(^{-1}\) (Ruokojärvi et al., 2000), respectively, were reported. In this study, the maximum EC was 2.41 kg DMS m\(^{-3}\) d\(^{-1}\).

**Conclusions**

A membrane bioreactor with a porous membrane (PDMS/PVDF) was investigated for removal of toluene and dimethyl sulphide from waste air during long-term experiments. In both sets of experiments the bioreactor was inoculated with specific organisms. Since a bioreactor is an open system, the development of a mixed flora cannot be prevented. If ammonia is used as a nutrient, nitrifying micro-organisms will develop in the bioreactor. In the case of toluene degradation, the bioreactor performance was decreased due to the presence of nitrifiers. Substituting nitrate for ammonia solved the problem; dimethyl sulphide degradation was enhanced by the presence of nitrifiers as long as pH and the presence of degradation product (nitrite, sulphate etc.) was controlled. In the case of toluene degradation, a maximum elimination capacity of 19.0 g TOL m\(_R\)^{-2} d\(^{-1}\) was measured, which is the highest degradation reported in the literature for similar loading rates to those used in the experiments. For dimethyl sulphide degradation now MBR results are reported in the literature.
literature. Compared to the results of the biofilter and biotrickling filter experiments the MBR performance was a little higher (2.4 compared to 1.86 kg DMS m$^{-3}$ d$^{-1}$).

References


