Removal of odorant dimethyl disulfide under alkaline and neutral conditions in biotrickling filters
L. Arellano-García, A. González-Sánchez, H. Van Langenhove, A. Kumar and S. Revah

ABSTRACT
The aim of this paper was to evaluate the performance of biotrickling filters (BTFs) for treating low concentrations of dimethyl disulfide (DMDS), using different bacterial consortia adapted to consume reduced sulfur compounds under alkaline (pH ≈ 10) or neutral (pH ≈ 7) conditions. Solubility experiments indicated that the partition of DMDS in neutral and alkaline mineral media was similar to the value with distilled water. Respirometric assays showed that oxygen consumption was around ten times faster in the neutrophilic as compared with the alkaliphilic consortium. Batch experiments demonstrated that sulfate was the main product of the DMDS degradation. Two laboratory-scale BTFs were implemented for the continuous treatment of DMDS in both neutral and alkaline conditions. Elimination capacities of up to 17 and 24 gDMDS m⁻³ h⁻¹ were achieved for the alkaliphilic and neutrophilic reactors with 100% removal efficiency after an initial adaptation and biomass build-up.

INTRODUCTION
Nowadays, the level of the atmospheric pollution due to anthropogenic activities has increased, provoking short and long lasting effects in the environment. Pollution associated with the generation of foul odors is a regular problem presented in big cities (i.e. Mexico City); where emission are related to activities such as transportation, treatment and disposal of huge amounts of produced organic waste (De la Rosa et al. 2006). This problem is specially accentuated when the dispersion of the gaseous contaminants is poor.

Some relevant malodorous gases include methanethiol (MT), ethanethiol (ET), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) which are grouped as volatile organic sulfur compounds (VOSCs) and are normally produced along with hydrogen sulfide (H₂S) in processes such as landfiling (Kim et al. 2005), composting (Smet et al. 1998) and wastewater treatment plants (WWTPs) (Dimitriou-Christidis & Wilner 2009). The emission of VOSCs from these treatment facilities may cause complaints by local neighbors due to the sensory irritation.

Biotechnological processes for the removal of foul smelling compounds such as H₂S, carbon disulfide (CS₂) and methylated sulfides has been widely reported, but not acceptable removal efficiencies (RE) and elimination capacities (EC) have been kept for long periods, mainly attributed to the inherent slow interfacial mass transfer rates of the malodorous gases to the degrading microorganisms. To overcome this restriction, the gas absorption with a chemical acid-base reaction was promoted before the biological degradation (González-Sánchez et al. 2008; Arellano-García et al. 2010). These authors reported the alkaline biofiltration of H₂S, CS₂ and ET, with successful results in the case of H₂S but not for the other sulfur compounds. The low ECs and REs for CS₂ and ET were attributed to the small degradation activity of the inoculated alkaliphilic sulfide-oxidizing bacterial consortium (ASBC). In this regard, it would be possible to reach higher VOSCs removal rates by increasing the biomass concentration as well as its adaptation in one biotrickling filter (BTF).
The aim of this work was to demonstrate the feasibility of removing DMDS under alkaline pH condition in BTFs with a high microbial concentration. Some key features of the process were evaluated separately such as the DMDS induced respiration activity of the applied bacterial consortium, and the partition coefficient of DMDS in both neutral and alkaline aqueous solutions. Results will be compared with a similar system which was operated under neutral pH conditions.

**METHODS**

**Solubility assessment**

The experiments for determining the solubility of DMDS followed the procedure described by Iliuta & Larachi (2005). In this case the DMDS gas–liquid equilibrium was determined in both neutral and alkaline medium at 30 °C. The partition coefficients (m) were expressed as a concentration quotient

\[ m = \frac{(\text{DMDS}_\text{gas}) \times (\text{DMDS}_\text{liquid})}{C_0} \]

**Microorganisms**

An ASBC adapted to pH 8–10 (González-Sánchez & Revah 2007; Granada et al. 2009) was grown in an alkaline medium at pH 10.0 previously reported by Arellano-García et al. (2010). Also a neutrophilic sulfide-oxidizing bacterial consortium (NSBC) adapted to grow at pH 7 was utilized; it was obtained from WWTP activated sludge. The NSBC was cultured with the mineral medium reported by Ruokojärvi et al. (2000).

**Adaptation to DMDS consumption**

The ASBC and NSBC were adapted for four months to DMDS consumption in 500 mL sealed flasks, containing 150 mL of culture at 100 rpm and 30 °C. A volume of 75 mL of fresh medium with DMDS was interchanged every two weeks, reaching an initial concentration of 0.3 mM DMDS in the liquid.

**Respirometry**

The respirometric method described by Arellano-García et al. (2010) was used to evaluate the aerobic microbial activity of the DMDS degrading consortiums during its adaptation process as well as its performance on the respective operating BTF. In this study the DMDS aqueous concentrations ranged from 0.05 to 2.0 mM. The experiments were done by triplicate and the oxygen consumption rates were corrected by endogenous respiration and chemical oxidation.

**DMDS consumption in batch cultures**

DMDS consumption rates were evaluated with the adapted ASBC and NSBC cultures in 125 mL glass bottles capped with Mininert® valves. The flasks contained 25 mL of the respective mineral medium and 5 mL of a concentrated cell suspension, attaining a final biomass concentration of around 0.4 gprotein L⁻¹. DMDS from a stock solution was injected into the bottles to have an initial liquid concentration close to 0.3 mM. The cultures were stirred in an orbital shaker at 100 rpm and 30 °C and the headspace was periodically analyzed by gas chromatography (GC) until DMDS was not detected. The sulfate and biomass concentrations were measured at the beginning and at the end of the experiments.

**Biotrickling filters**

Two bench-scale BTFs were used for the removal of gaseous DMDS under neutral and alkaline pH at 30 ± 2 °C. The BTF operated under neutral conditions had a 5 cm ID, with 70 cm height and 1 L packed with open-pore polyurethane foam (EDT, Eckenhaid-Eckental, Germany), which had 600 m⁻¹ specific area, 35 kg m⁻³ density, and 0.97 of porosity. The alkaline BTF, previously described by Arellano-García et al. (2010), had a volume of 4.7 L and was packed with the same material. In the latter, biomass accumulation was fostered by feeding a thiosulfate (Na₂S₂O₃) solution according to Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Stages during the operation of neutral and alkaline BTFs</th>
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<tr>
<td><strong>Neutral BTF</strong></td>
<td>Length/Feeding characteristics</td>
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<tr>
<td>Period</td>
<td>Days 12–29 (not shown)/Dissolved DMDS, 0.3 mM</td>
</tr>
<tr>
<td>Adaptation</td>
<td>Days 30–160/Gaseous DMDS, EBRT 1 min</td>
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<tr>
<td><strong>Alkaline BTF</strong></td>
<td>Length/Feeding characteristics</td>
</tr>
<tr>
<td>Period</td>
<td>45 days (not shown)/250 gΝa₂S₂O₃ m⁻³ h⁻¹ (dissolved)</td>
</tr>
<tr>
<td>Fast biomass growth</td>
<td>Days 1–25/Gaseous DMDS, EBRT 2 min</td>
</tr>
<tr>
<td>Adaptation</td>
<td>Days 26–160/Gaseous DMDS, EBRT 1 min</td>
</tr>
</tbody>
</table>
A schematic diagram of the experimental systems is shown in Figure 1. The air and the liquid flowed counter-currently through the fixed bed of the BTFs. Centrifugal pumps were used to recirculate the mineral medium with rates of 0.70 and 0.84 L min⁻¹ for the neutral and alkaline BTFs, respectively. The pH was controlled by the automatic addition of 1.0 N NaOH solution. Gaseous DMDS was fed to the BTFs by bubbling air, with a controlled flow, and mixing it downstream with clean air. The DMDS feeding concentrations for both BTFs ranged from 10 to 180 ppmv. The gas empty bed residence times (EBRTs) are specified in Table 1.

**Analytical techniques**

Gaseous DMDS was analyzed using a FPD-GC (HP 5890 USA, equipped with a Varian CP-PORABOND Q column 25 m × 0.32 mm × 5 mm, USA). Biomass concentration was quantified as protein using the Lowry method (BIORAD DC protein assay, California, USA). Sulfate was evaluated according to Standard Methods (1998). The parameters for evaluating the performance of the BTFs were: loading rate \( L \) (g DMDS m⁻³ h⁻¹), elimination capacity \( EC \) (gDMDS m⁻³ h⁻¹), and removal efficiency \( RE \) (%), and were calculated as: \( L = (C_{in}/V) \times Q \); \( EC = [(C_{in} - C_{out})/V] \times Q \); \( RE = [(C_{in} - C_{out})/C_{in}] \times 100 \). \( C_{in} \) (gDMDS m⁻³) is the inlet concentration, \( C_{out} \) (gDMDS m⁻³) is the outlet concentration, \( Q \) (m³ h⁻¹) is the gas flow rate, and \( V \) (m³) is the packed bed volume.

**RESULTS AND DISCUSSION**

**Partition coefficient**

DMDS partition coefficients of 0.066 and 0.061 were obtained in neutral and alkaline mineral mediums, respectively. The maximum DMDS liquid concentration reached was 2.0 mM. Compared with the results a value of 0.054 was reported by Iliuta & Larachi (2005) for DMDS in distilled water under similar conditions. Therefore it is concluded that the salinity in both media did not affect significantly the solubility of the DMDS. Besides, the non-polar character of the DMDS molecule did not allow interactions with the predominant OH⁻ ions at pH 10.0, as it was reported for H₂S by González-Sánchez et al. (2008).

**DMDS induced respiration activity**

The oxygen consumption rates as a function of the aqueous DMDS concentration are depicted in Figure 2. The corresponding theoretical gaseous DMDS concentrations in equilibrium with the aqueous DMDS concentrations are presented on the upper x-axis scale. The maximum oxygen consumption rates obtained with biomass at the end of the adaptation period were \( 3.0 \times 10^{-3} \) and \( 3.0 \times 10^{-4} \) gO₂ gprot⁻¹ min⁻¹, for the NSBC and ASBC, respectively. DMDS concentrations above 0.5 mM seemed to inhibit the activity of both groups of microorganisms; nevertheless that liquid DMDS concentrations would correspond to...
650 ppmv on the gas phase, which is rarely found according to Bordado & Gomes (2001), who reported a maximum DMDS concentration of 296 ppmv emitted from a Kraft pulp mill operation. Meanwhile Dimitriou-Christidis & Wilner (2003) reported that DMDS emissions from other facilities like WWTP reached concentrations below 0.1 g m⁻³ (aprox. 25 ppmv at 1 atm).

**DMDS consumption in batch cultures**

From these experiments (data not shown) it was determined that the NSBC was able to degrade the dosed DMDS in half the time than that taken for the ASBC (50 and 110 h respectively). When doubling the DMDS concentration (0.6 mM) in another NSBC culture, the degradation time was 70 h. All the cultures showed complete oxidation of the DMDS sulfur to sulfate (yield above 0.98) while the biomass remained constant at 0.4 gprot L⁻¹ during the experiments.

**Biotrickling filters performance**

Figure 3 shows the performance of the alkaline and neutral BTFs during their operation for 170 days. On the first 54 days the alkaline BTF reached a maximum RE of 80% for loads close to 9.5 gDMDS m⁻³ h⁻¹. A sudden load increase on day 55 led to a RE below 60%. Afterwards a progressive load increment, starting on day 60, allowed the BTF adaptation up to an EC of 17 gDMDS m⁻³ h⁻¹ with 100% of RE, on day 82. An accidental NaOH overdose to the alkaline BTF on day 85 provoked an efficiency reduction which recovered after 28 days. Performance after day 110 showed REs close to 100% for loads over 10 gDMDS m⁻³ h⁻¹. Sulfate concentrations of 10 g L⁻¹ did not affect the alkaline BTF elimination capacity.

The biomass concentration around day 160 was close to 3 gprot L⁻¹ bed in the alkaline BTF and around 2 gprot L⁻¹ bed for the neutrophilic BTF. These values were higher than the 1.59 gprot L⁻¹ bed obtained by González-Sánchez et al. (2008). Considering that initial DMDS oxidation requires two oxygen molecules (Lomans et al. 2002) the maximum
theoretical volumetric elimination capacities can be calculated based on the specific oxygen consumption rates. Maximum estimated EC values of around 80 gDMDS m$^{-3}$ h$^{-1}$ for the alkaline BTF and 525 gDMDS m$^{-3}$ h$^{-1}$ for the neutrophilic BTF show, from Figures 3 and 4(a), higher loads might be treated. Nevertheless, as the respirometry values are obtained with biomass in suspension with fresh medium, lower maximum ECs in the BTFs should be expected considering actual mass transfer limitations, the possibility that not all of the attached biomass is active or inhibition by intermediates or end products.

The neutrophilic BTF attained complete removal of the gaseous DMDS after a short adaptation period. In spite of this, a load step increase led to RE reductions on days 55, 71 and 96. Thereafter, a gradual increase of the load allowed the neutral BTF adaptation and REs close to 100% were reached from day 120 with loads over 16.5 gDMDS m$^{-3}$ h$^{-1}$. In contrast to the alkaline BTF, the effectiveness of the neutral BTF was clearly diminished by sulfate concentrations around 10 g L$^{-1}$.

Between days 140–170 loading rates as high as 15 and 24 gDMDS m$^{-3}$ h$^{-1}$ were treated with 100% of RE in the alkaline and neutral BTFs respectively. In comparison recent studies described ECs as high as 53 and 32 gDMDS m$^{-3}$ h$^{-1}$ with a RE of 94%, for BTFs inoculated with neutrophilic bacteria (Ramírez et al. 2011; Wan et al. 2011), nonetheless in both reported cases the operation time was more than 400 days and the EBRTs were 76 and 110 s, respectively. The differences between the ECs may be a consequence of the biomass specific activity as well as its concentration inside the BTFs which were not reported in these studies.

From the gaseous DMDS removal data, the theoretical production of sulfate was calculated assuming complete oxidation of its sulfur moiety, as suggested by the batch culture results. The estimated integrated sulfate production is compared with the experimental values in Figure 5. While the experimental values correlated with the estimated sulfate produced calculated from the spent NaOH required to maintain the pH (not shown), there was a relative offset (<10%) with respect to the theoretical value. This offset, which became apparent with the increased loads, may be related to the oxidation of other sulfide species found as impurities in the inlet gas.
CONCLUSIONS

Biofiltration was shown to sustain continuous removal of low concentration (odors) of DMDS using an alkaliphilic biomass. Although this biomass was shown to have intrinsic oxidation rates which were an order of magnitude smaller to those obtained with the neutrophilic consortium, high concentrations in the reactor and resistance to the increasing sulfate concentrations compensated the kinetic handicap. This result complements those obtained with other odorous compounds as H2S showing the interest in developing alkaline biofiltration to treat mixed inorganic and organic sulfides in low concentrations. With all the accumulated information it is plausible to design an efficient treatment system to clean problematic malodorous gaseous streams.

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REFERENCES


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