Treatment of waste gas containing low concentration of dimethyl sulphide in a high performance biotrickling filter

Balendu Shekher Giri, Asha Juwarkar, S N Mudliar & R A Pandey*
CSIR-National Environmental Engineering Research Institute, (CSIR-NEERI), Nehru Marg, Nagpur 440 020, India

Received 9 December 2012; revised 11 February 2013

A bench-scale biotrickling filter was operated in the laboratory for the treatment of dimethyl sulphide (DMS). The biotrickling filter was packed with pre-sterilized polyurethane foam and seeded with biomass developed from garden soil enriched with DMS. The biotrickling filter was operated for the generation of process parameters. The biotrickling filter could remove an average removal efficiency of 40.95 % at an effective bed contact time of 84 sec with an average loading rate of 0.56 mg/m$^3$/h. Evaluation of microbiological status of the biotrickling filter indicated the presence of other bacterial cultures viz. Paenibacillus polymyxa, and Bacillus megaterium, besides Bacillus sphaericus.

Keywords: Biotrickling filter, Dimethyl sulphide, Loading, Poly urethane foam, Removal efficiency

The emission of total reduced sulfur compounds (TRSC), such as hydrogen sulfide (H$_2$S), methanethiol (MT), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) is found in many industrial activities like waste water treatment, Kraft pulping, animal rendering, and composting$^{1-2}$. The main problem with these compounds is the combination of their bad smell and very low odor threshold (e.g., DMS 1.2 ppbv, MT 2.4 ppbv). Physical-chemical methods for treating gaseous emissions containing hydrogen sulfide and organic sulfur compounds have relatively high energy requirements and high chemical and disposal cost. Biological treatment methods have been proposed as a convenient alternative.

Bio-treatment for air pollution control started in the 1950s using soil beds. The technology has since matured and industrial applications of biofilters are numerous. More recently, research has focused on a variation of biofilters called biotrickling filter, or trickling biofilter. Biotrickling filters work in a similar manner to biofilters, except that an aqueous phase is trickled over the packing, and that the packing is usually made of some synthetic or inert material, like plastic rings, open pore foam, lava rock, etc. The trickling solution contains essential inorganic nutrients such as nitrogen, phosphorous, potassium, etc. and is usually recycled$^3$.

Biotrickling filters are more complex than biofilters but are usually more effective, especially for the treatment of compounds difficult to degrade or compounds that generate acidic by-products, such as H$_2$S$^{4-6}$. Biotrickling filters can also be built taller than biofilters which reduces the footprint. It is also easier to control the conditions because of the free liquid phase, so that difficult applications are better handled by a biotrickling filter than by a biofilter. These include but are not limited to the treatment of high concentrations of contaminants, treatment of hot gases and/or of acid producing contaminants, treatment of air streams containing grease or particles, etc. Biotrickling filters are more recent than biofilters, and have not yet been fully deployed in industrial applications, but the prospective future applications are promising.

In this research work the feasibility of treatment of waste gas containing DMS is evaluated using high performance biotrickling filter on bench scale seeded with the microorganisms having potential to degrade the DMS, and polyurethane foam was used as packing material.

Materials and Methods

Biotrickling filter (BTF) set up and operation—A schematic of the experimental setup is shown in Fig. 1. The biotrickling filter was constructed from a clear PVC pipe 70 cm long and 7 cm in
GIRI et al.: TREATMENT OF WASTE GAS IN A HIGH PERFORMANCE BIOTRICKLING FILTER

The biotrickling filter was packed with randomly dumped $4\times4\times4$ cm cubes of open pore polyurethane (PU) foam (EDT, Eckental, Germany). The PU foam packing was developed specifically for biotrickling filtration. It has a high specific surface area ($600 m^2 m^{-3}$) and a low density ($35 kg m^{-3}$), a relatively fine mesh (4–6 pores/cm), and a low compression strength (5–10 kPa). The PU foam bed had an initial porosity of about 0.97. The BTF consists of air compressor, rotameter, sample collection port, pump for recirculation of medium and a flask for recirculating media. Media from the circulating flask continuously trickle in to the BTF at constant flow rate. A dimensional detail of the BTF is given in Table 1.

Potential microorganisms degrading DMS

**Biomass seeded to the biotrickling filter**—The seeded biomass used for this study was developed from garden soil using DMS for enrichment. These microorganisms were identified morphologically and biochemically as per Bergey's manual, FAME-GC and using molecular tools and techniques. The isolated cultures were stored at 4 °C in oxygen-free vials no longer than 4 months before use. The Genome Bio Technologies Pvt Ltd, Pune, India, maintains the strain. Cultures were grown in a nutrient broth medium under shaking condition prior to harvesting of biomass, re-suspended in fresh nutrient medium, and seeded in the packing medium during the startup of the biotrickling filter.

**Characterization of isolated cultures for DMS degradation by FAME-GC**—The lipid/fatty acid content was expressed using the ratio of total lipid/fatty acid concentration to biomass concentration. The total lipids were measured as FAME following the direct trans-esterification method using a gas chromatograph with FID detector (PerkinElmer, USA). The sample (5–8 µL) was evaporated in a split-less injector at 2,600 °C. GC conditions were set as follows: column, Supelco column SP-2560 (100 m×0.25 mm I.D., 0.20 µm); injection temp, 2,600 °C; column, 1,400 °C; FID detector temp, 2,600 °C; carrier gas, helium; and standard Supelco 37 Component FAME Mix on SP-2560 Column supplied by Sigma (Germany).

DNA isolation, purification, and Tm calculation for isolated DMS-degrading culture—DNA isolation was done using the conventional CTAB method, and extracted DNA was made RNA free by enzymatic treatment. The RNase was then removed by organic extraction prior to the work. For determining the melting temperature, the DNA was dissolved in a 1× saline sodium citrate buffer at a final concentration of 20 µg/mL. The DNA solution was then subjected to an incremental increase in temperature using a temperature-regulated water bath, and the range of the temperature (25–85 °C) corresponding to the hyper-chromatic shift was determined. The midpoint was identified and noted as the melting temperature.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Parameters</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Height of the packed bed</td>
<td>70 cm</td>
</tr>
<tr>
<td>2</td>
<td>Diameter column</td>
<td>7 cm</td>
</tr>
<tr>
<td>3</td>
<td>Flow rate of waste air lpm</td>
<td>2.5 lpm (0.15 m³/h)</td>
</tr>
<tr>
<td>4</td>
<td>Volume (m³)</td>
<td>0.00269 (3.5 L)</td>
</tr>
<tr>
<td>5</td>
<td>Packed Material (Polyurethane Foam)</td>
<td>250 mg 4×4×4 cm³</td>
</tr>
<tr>
<td>6</td>
<td>Recycle liquid volume</td>
<td>4 L</td>
</tr>
<tr>
<td>7</td>
<td>Medium feed rate</td>
<td>120 mL/h</td>
</tr>
<tr>
<td>8</td>
<td>Medium composition (g/L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂HPO₄</td>
<td>0.615</td>
</tr>
<tr>
<td></td>
<td>KH₂PO₄</td>
<td>0.385</td>
</tr>
<tr>
<td></td>
<td>NH₄NO₃</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>MgCl₂</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>FeCl₃</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>7±0.2 (8.0)</td>
</tr>
<tr>
<td>9</td>
<td>Effective bed residence time (sec)</td>
<td>84</td>
</tr>
<tr>
<td>10</td>
<td>Operating temperature (°C)</td>
<td>35±5 °C</td>
</tr>
<tr>
<td>11</td>
<td>Substrate loading (mg/m²/h)</td>
<td>9.7-65.12</td>
</tr>
<tr>
<td>12</td>
<td>Inlet concentration (mg/m³)</td>
<td>0.28-1.9</td>
</tr>
<tr>
<td>13</td>
<td>Outlet concentration (mg/m³)</td>
<td>00-1.09</td>
</tr>
<tr>
<td>14</td>
<td>Removal efficiency (%)</td>
<td>13-100</td>
</tr>
</tbody>
</table>

Fig. 1—Schematic diagram of air phase biotrickling for the treatment of simulated waste gas containing DMS
Molecular characterization of isolated culture for DMS degradation—Native DNA molecules usually denature within a very small increment of temperature. In fact, thermal denaturation of DNA is often designated as melting. DNA specimens from different cell types have characteristically different melting points, defined as Tm, the temperature at the midpoint of the melting curve. Tm increases in a linear fashion with the content of G–C base pairs, which have three hydrogen bonds and are more stable than A–T base pairs. The higher the content of G–C base pairs, the more stable the structure and the more thermal energy required to disrupt it. Careful determination of the melting point of the DNA specimen, under fixed condition of pH and ionic strength, can give remarkably good estimate of its base composition.

The formula for percent G + C calculation is:

\[
\% (G + C) = 2.44 \left( Tm - K \right)
\]

where, K is a constant depending on the solvent (68 °C).

Potential microorganism used in this study was isolated from sediments of a stream containing sewage in a pulp and paper industry by the conventional enrichment technique, which was further identified by fatty acid methyl esterification (FAME) and molecular characterization as *B. sphaericus*.

Chemicals and basal medium—All the chemicals used for analysis were of analytical grade. The chemicals/solvents used for gas chromatographic analysis were of chromatographic grade. The odorant compound – DMS used in the investigation was in liquid form and was procured from M/s. Sigma Aldrich Co., Germany. The basal medium for the growth of microorganisms degrading DMS includes (g/L) di-potassium hydrogen phosphate 1.55, sodium di-hydrogen phosphate 0.85, ammonium chloride 2.0, magnesium chloride (hexahydrate) 0.075, yeast extract 0.1 and 1.0 m/L of trace elements. The trace elements constitute (g/L) di-sodium ethylene diamine teta acetic acid 50.0, zinc sulphate (heptahydrate) 2.2, calcium chloride (dihydrate) 7.34, manganous chloride (tetrahydrate) 2.5, cobaltous chloride (hexahydrate) 0.5, ammonium molybdate (tetrahydrate) 0.5, ferrous sulphate (heptahydrate) 5.0, cupric sulphate (pent hydrate) 0.2, and sodium hydroxide 11.0. The basal agar medium was supplemented with yeast extract (0.1% w/v) for the evaluation of total count of the microorganisms of the biotrickling filter unit, while for the specific count, the medium yeast extract was replaced with DMS.

Experimental protocol—The nutrient basal medium adjusted to pH 7.0 was used for bacterial culture in the biotrickling filter and also for maintenance of moisture in the packing medium. Air was blown with the aid of a blower through waste gas-generating unit containing DMS and operated at fixed flow rate at fixed temperature and pressure. This resulted in generation of the waste gas containing DMS, and the same after appropriate dilution with air was introduced from the bottom of the biotrickling filter. The nutrient medium was trickled from the top of the biotrickling filter to maintain proper moisture content in the biotrickling filter in order to sustain the growth of microorganisms on the packed poly urethane foam. The samples of the waste gas from the inlet and outlet of the biotrickling filter were collected and analyzed for DMS concentration. The samples of poly urethane foam packed in biotrickling filter were collected, mixed, and analyzed for microbial status by adopting standard methods.

Further, the collected solid poly urethane foam samples from the biotrickling filter were monitored for pH and moisture content. Continuous operation of the biotrickling filter was carried out for evaluation of different parameters viz. Start-up time of the biotrickling filter, effective bed contact time (EBCT), DMS loading at optimal EBCT, requirement of moisture content for the packing medium for treatment of DMS. The biotrickling filter was operated for more than 100 days on bench scale on a continuous feed basis. Varying the flow rate of waste gas with constant input of DMS in waste gas varied the EBCT. Changing the input DMS concentration in the waste gas at optimal EBCT varied the DMS loading. During the moisture assessment requirement for the packing medium of the biotrickling filter, manipulating the irrigation rate of the biotrickling filter varied the moisture content of the system.

Results and Discussion

Start up of biotrickling filter during treatment of simulated waste gas containing DMS—At the initial stage of start-up, the biotrickling filter was fed with simulated waste gas containing DMS with an average input concentration range of 0.94 mg/m³, (1 ppm=2.54 mg/m³ at 25 °C) seeded with specific microorganisms. At the initial stages of operation of
the biotrickling filter with addition of microorganism, there was no significant decrease in the DMS concentration (0.79–0.43 mg/m$^3$) in the outlet of the biotrickling filter up to 15 days. This may be attributed to the minimal adsorption of DMS on the packing medium of the biotrickling filter since the DMS is volatile organic sulphur constituent. During 15–50 days of the operation, there was decrease of DMS concentration (0.88–0.33 mg/m$^3$) in the outlet of the biotrickling filter with an increase of removal efficiencies of 64.2% (Figs 2 and 3). Hence, the start-up time for the biotrickling filter was found to be 35 days.

Many different sorts of packing materials have been tested in biotrickling filters. Important requirements to the packing include a large specific area, high porosity, high chemical stability and structural strength, low weight, suitable surface for bacterial attachment and growth, and low cost.

A commonly used packing material is lava rock. This material has the advantage of providing a large specific surface, a porous structure that facilitates colonization by microorganisms and a low price. Disadvantages are the low porosity (~50%) and the heavy weight which requires special construction of the reactor. Another disadvantage recently observed in the laboratory is that lava rock is not chemically inert. A substantial weight loss was observed over several months at a low pH. This might be of importance for biotrickling filter applications with a low pH, e.g., odour treatment and H$_2$S removal at wastewater purification plants as discussed above.

Random-dump plastic packings such as Pall rings have been used in many laboratory studies and large-scale reactors. These packings are easy to handle, however, experiments indicate that startup is relatively long presumably because poor biofilm establishment on the surface$^{16,17}$. Also, the relatively low specific surface area is a disadvantage for achieving a high elimination capacity. On the other hand, the use of plastic packing may be disadvantageous because of its stability, low cost and high porosity$^{18}$. Structured packings made from stainless steel or plastic combine a high porosity and large specific surface. Good performance has been observed with these type of packings, but they are more expensive.

Activated carbon-based packings have adsorbing properties that are not encountered in other materials. It is often assumed that adsorption is beneficial especially when the pollutant concentration in the waste gas is fluctuating ("peak-dampening"). However, activated carbon particles in biotrickling filters will be covered by a biofilm, which will decrease the absorptive capacity of the carbon. A better option would be using a separate activated carbon unit preceding the biotrickling filter.

A relatively new packing used in biotrickling filters is open-pore polyurethane foam products. Published data on the performance are scarce, but some major European vendors offer these products, often for biotrickling filters designed for H$_2$S removal. Our own experiences in the laboratory (unpublished) indicated improved performance with polyurethane foam cubes over other types of packing, especially at high gas flow rates with low H$_2$S concentrations. Due to the open structure and high porosity, the pressure drop over the packing remained low at a relatively high gas velocity. The large specific surface area proved beneficial with respect to mass transfer limitation observed at low H$_2$S concentration.
Performance of biotrickling filter during treatment of simulated waste gas containing DMS—The optimum EBCT for the biotrickling filter was 84 sec. Bench scale biotrickling filter/high performance bioreactor packed with poly urethane foam seeded with potential culture (*Bacillus sphaericus*) degrading DMS could efficiently remove from simulated waste gas containing DMS at laboratory scale with removal efficiency in the range of 13-99% at an EBCT of 84 sec with loading rate in the range of 9.7-65.12 mg/m$^3$/h in 100 days continuous operation of biotrickling filter.

The polyurethane foam has good water percolation capacity, neutral pH, and soluble nutrients. The use of polyurethane foam as a packing material media in the biotrickling filter has also been cited in the literature for bio-treatment$^{4,8}$. The microbial growth observed is show in Fig. 4.

Fig. 4—Packing material from biotrickling filter: (a) poly urethane foam cubes before inoculation and (b) after 100 days of operation; packing from reactor: The foam cubes are 4 × 4 × 4 cm, while the HD Q-PAC is 7 cm in diameter.

The microorganisms in the biotrickling filter utilize DMS as a source of carbon and energy. They also need mineral nutrients, viz. nitrogen, phosphorous, potassium, sulphur, calcium, magnesium, sodium, iron and many others. In the present investigation also, the biotrickling filter took only 35 days for acclimatization after bio-augmentation with pre-grown DMS degrading microorganisms. Lesson and Smith$^{12}$ came to a similar conclusion, suggesting that inoculation of microorganisms having the potential for degradation of a particular constituent will speed up the enrichment. Those microorganisms, which can degrade the DMS, could grow rapidly in packed bed of the biotrickling filter. According to Munkhtsetseg$^{13}$ DMS degradation in a thermophilic biotrickling filter was found to be 84% at 52 °C with an average loading of 64 g/m$^3$/h (0.128 g/m$^2$/h) with 24 sec EBCT and an average loading of 54 g/m$^3$/h (0.108 g/m$^2$/h) with 90% removal efficiency at 21 °C. Chan$^{14}$ found that removal efficiency of 83% was observed in a flasks experiment with a loading of 152.4 mg/m$^3$ in 45 days.

Arellano-García$^{15}$ reported that gaseous DMS was eliminated in a biotrickling filter with *Thiobacillus thioparus* grown in polyurethane foam cubes as carrier material. The temperature, pH and empty bed residence time of the gas were maintained at 30 °C, 7.0 and 40 sec, respectively. In the first 45 days, DMS loads of around 2.0 gm$^{-3}$h$^{-1}$ were fed to the BTF to adapt *T. thioparus* to DMS consumption, attaining close to 100% removal efficiency (RE) on day 46, and the maximum elimination capacity (EC) was 4.0 gm$^{-3}$h$^{-1}$ with a RE of 77%. The overall performance was enhanced by adding a nitrogen-enriched (9x) medium but was negatively affected by high superficial liquid velocity (8.18 m h$^{-1}$) and high pH (>7.5). Sulphate concentrations (up to 10 gL$^{-1}$) showed no effect. The system supported shock loads up to 58 gm$^{-3}$h$^{-1}$ with increased elimination. With nitrogen-enriched medium and a pH of 7.0 it was possible to increase the EC of DMS up to a maximum of around 23 gm$^{-3}$h$^{-1}$ with 65% RE.

**Conclusion**

Bench scale biotrickling filter/high performance bioreactor packed with poly urethane foam seeded with potential culture (*Bacillus sphaericus*) degrading DMS could efficiently remove DMS from simulated waste gas containing DMS at laboratory scale with
removal efficiency of 13-100% at an EBCT of 84 sec with loading rate in the range of 9.7-65.12 mg/m³/h. The biotrickling filter took only 35 days for acclimatization after bio-augmentation with pre-grown DMS degrading microorganisms.

Acknowledgment
BSG is thankful to Dr. Satish R. Wate, Director, CSIR-NEERI, for permission to publish this article and CSIR, New Delhi and the Department of Biotechnology, Ministry of Science, and the Govt. of India for financial assistance.

References