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Kinetics and biofiltration of dimethyl sulfide emitted from P&P industry

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ABSTRACT

Anaerobic bio-treatment of waste air generated from various industries including pulp and paper (P&P) industry produce biogas containing reduced form of sulfur pollutants such as dimethyl sulfide (DMS) and hydrogen sulfide (H_2S). Some of the gaseous emissions containing DMS are also generated from several industrial wastes which are generally incinerated with high energy input. In the present investigation, a potential DMS degrading microorganism *Bacillus sphaericus* was isolated from garden soil near a P&P industry for biodegradation. Waste gas containing DMS has been treated in a hybrid biofilter system up to 70% removal efficiency, at an optimal load of 17.3 $g/m^3/h^1$ and an optimum effective bed contact time (EBCT) of 384 s. Growth kinetic for biodegradation was also evaluated through flask culture experiments. The values of the different biokinetic parameters for K_s, $\mu_{max,}$ degradation of substrate (K) and Y were obtained as 0.022 g/m^3, 0.0057 h^{-1} 0.013 h^{-1} and 0.0022, respectively. The relevance in the context of DMS biodegradation is discussed.

1. Introduction

DMS is an obnoxious sulfurous pollutant generated during the Kraft pulping, which is conventional energy from anaerobic treatment of waste water generated from industrial and domestic sectors. They are formed during kraft pulping by reaction of sulphides with methoxy groups of lignin via nucleophilic substitution reactions [1]. The major sources of TRS emissions include digester blow and relief gases, multiple-effect evaporator vent and condensates, the recovery furnace with direct-contact evaporators, smelt dissolving tank and slacker vents, brown-stock washers and seal tank vents, and the lime kiln exit vents. The biogas contains hydrogen sulfide along with DMS in traces and has significant environmental and health implications. The industries viz., pulp & paper, distillery, tanning, organic synthesis, dyeing of acetate textiles, and used as paint removers, dyes, pharmaceuticals, insecticides, fungicides, surface active agents, as a fuel additive, polymerization inhibitor, photographic developer, rocket propellant, domestic wastewater treatment plants, solid waste disposal sites of urban domestic origin etc operating anaerobic treatment plant generate biogas containing H_2S, methyl mercaptan (MM), DMS and dimethyl disulfide (DMDS) [2–5]. Further, DMS is also produced naturally by bacterial transformation of dimethyl sulfoxide (DMSO) waste that is disposed off into sewers, where it can cause environmental odor problems. In order to generate clean biogas, it is essential to clean by removing these sulfurous pollutants [2,4–6,26]. Giri et al., (2014) has been reported an overview of the bio-treatment processes for volatile sulfurous compounds (VSCs) with an emphasis on biofiltration in the pulp and paper industry and discussed up-to-date knowledge on the generation of sulfurous odorants and their microbial degradation processes in bio-treatment techniques [10,25,26]. The fundamental characteristics of such techniques are described with respect to the configuration and design of the bioreactor treatment facilities and the associated mechanisms of operation.

Giri et al., (2014) has reported that the Pulp and paper production has increased globally and will continue to increase in the near future. Approximately, 155 million tons of wood pulp is produced worldwide and is projected to increase near 260 million in the coming future. Although an increase in productivity is expected, the industry is also under constant pressure to reduce and/or suppress the emissions of associated pollutants into air [10]. In light

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of the usefulness of the biofiltration technique, the development of innovative combined bioreactors to replace a single bioreactor configuration is highly demanding to provide a universal solution to the treatment of volatile organic compounds (VOCs), VSCs, and related odor problems. To meet such a demand, a better knowledge covering the treatability of each individual substance should be obtained to establish proper treatment. The merits and demerits of these biofilters will be explained along with a discussion of their important operational parameters and future research and development (R&D) needs in this area.

Kinetic parameters of DMS degradation have been evaluated and discussed in the present investigation. The live vent gas containing DMS along with other traces of reduced sulfurous compounds (RSCs) have been treated by hybrid biofilter which was packed with wood chips and compost at a P&P industry. Biofilter was seeded with microorganism *Bacillus sphaericus*. The results on these aspects are presented and discussed in this paper.

2. Material and methods

2.1. Chemicals and culture 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 0.615, potassium di-hydrogen phosphate 0.385, ammonium nitrate 1.5, magnesium chloride (hexahydrate) 0.2, yeast extract 0.1 and 1.0 ml/L of trace elements. The trace elements constitute (g/L) di-sodium ethylene di-amine tetra acetic acid 50.0, zinc sulphate (heptahydrate) 2.2, calcium chloride (dihydrate) 7.34, manganous chloride (tetra hydrate) 2.5, cobaltous chloride (hexahydrate) 0.5, ammonium molybdate (tetra hydrate) 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 biofilter unit, while for the specific count; the medium yeast extract was replaced with DMS.

2.2. Analytical equipments and measurement protocols

DMS concentration was determined by using a Clarus 500, Gas Chromatography System (Perkin–Elmer, USA) and Restek, 800—356—1688 Packed Column, RT Sulfur 2 m having Flame Photometer Detector (FPD). Nitrogen was used as the carrier gas at 20 ml/min. The temperatures of the injectors and detectors were 250 and 300 °C, respectively. The programmed temperature of the column was maintained at 60 °C for 2 min and then increased to 200 °C at a rate of 10 °C min^{-1} [6–10]. A Shimadzu spectrophotometer, Japan was used for the determination of culture growth at 600 nm and spectrophotometric analysis of DMS at OD_{520} nm at pH 7.0 ± 0.5 [11] and the product of DMS biodegradation viz. sulfate was monitored as per standard methods [1,31]. A control dynamics pH meter (Eutech, Instruments pH 510, pH/mV/°C meter) was used for monitoring the different liquids samples. An automatic model incubator was maintained at a temperature 30 ± 2 °C and used for growing the bacterial strain and also for plating studies. The Emenvee rotary shaker was used for shake flask experiments. Glass wares were dried in a hot air oven made by Bio-techniques India ISO 9001 2000.

2.3. Bench-scale biofilter unit

The schematic of the bench-scale biofiltration unit is presented in Fig. 1. The laboratory-scale biofilter was made up of PVC material. The biofilter unit consisted of a blower, an odor-generating unit, a rotameter (1–10 L/min), a biofilter, a temperature indicator, and a manometer for pressure reading as well as sample collection ports. A leachate collection unit with water seal was also provided at the bottom of the biofilter. The biofilter was filled with packing material consisting of compost (% w/w carbon 38, nitrogen 1.3, phosphorous 0.02, potassium 0.71, calcium 1.62, magnesium0.14, and sodium 0.01; other metal elements mg/kg: copper 44, manganese 360, and zinc 70) and wood chips in alternate layers. No additional carbon source (e.g., methanol) was added to the biofilter [31].

2.4. Hybrid bioreactor system

The schematic of a hybrid bioreactor system is made up with two laboratory scale biofilter in series combination. The biofilter reactor (discussed above) connected to another biofilter was constructed of PVC column, 55 cm high with the working volume of 12 L. The packing materials were wood chips and compost (cow dung) 1:3 mixtures. The waste gas containing DMS enters into the bottom of the second biofilter and the treated waste gas from first biofilter was let into the second biofilter through a rotametre as inlet. The outlet gas from second biofilter was monitored as a final treated waste air containing DMS at P&P industry.

2.5. Potential microorganisms degrading DMS

Potential microorganism used in this study was isolated from sediments of a streamcontaining sewagein 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*.

2.6. Experimental protocol

The nutrient basal medium adjusted to pH 7.0 was used for bacterial culture in the biofilter 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 fix flow rate, 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 biofilter. The nutrient medium was sprinkled from the top of the biofilter to maintain proper moisture content in the biofilter in order to sustain the growth of microorganisms on the packed compost. The samples of the waste gas from the inlet and outlet of the biofilter were collected and analyzed for DMS concentration. The samples of compost packed in biofilter were collected, mixed, and analyzed for microbial status by adopting standard methods. Further, the collected solid compost samples from the biofilter were monitored for pH and moisture content. Continuous operation of the biofilter was carried out for evaluation of different parameters viz. startup time of the biofilter, EBCT, DMS loading at optimal EBCT, requirement of moisture content for the packing medium for treatment of DMS. The biofilter was operated for more than 140 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 biofilter, manipulating the irrigation rate of the biofilter varied the moisture content of the system. The compost samples of known weight from the four sampling ports at different heights were collected and mixed together. The mixed