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Review

Review of biotreatment techniques for volatile sulfur compounds with an emphasis on dimethyl sulfide

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ABSTRACT

Emissions of volatile sulfur compounds (VSCs) including hydrogen sulfide (H_2S), methanethiol (MT), dimethylsulfide (DMS), and dimethyldisulfide (DMDS), referred to collectively as reduced sulfur compounds (RSCs), occur from a host of anthropogenic sources including the pulp and paper industries, refineries, petrochemicals, sewage treatment plants, etc. This article is organized to provide an overview of the biotreatment processes for VSCs with an emphasis on biofiltration in the pulp and paper industry. To this end, we discuss up-to-date knowledge on the generation of sulfurous odorants and their microbial degradation processes in biotreatment techniques. 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. Finally, we add our perspectives on future research and development needs in this research area.

Contents

Abbreviations: BFs, biofilter; BTFs, biotrickling filter; BSBR, bioscrubber bioreactor; CAS, chemical abstracts service; CO_2, carbon dioxide; CSIR, Council of Scientific and Industrial Research; GC-FID, gas chromatography–flame ionization detector; DMS, dimethyl sulfide; DMDS, dimethyl disulfide; DEDS, diethyl disulfide; DMSO, dimethyl sulfoxide; EBCT, effective bed contact time; EC, elimination capacity; FEBR, foamed emulsion bioreactor; H_2O, di-hydrogen oxide (water); H_2S, hydrogen sulfide; HAPs, hazardous air pollutants; MBR, membrane bioreactor; MT, methane thiol; MDL, minimum detection limit; MW, molecular weight; NEERI, National Environmental Engineering Research Institute; Ppm, parts per million; Ppb, parts per billion; RE, removal efficiency; R&D, research and development; RDB, rotating drum bioreactor; 16S-rRNA, 16S-r ribonucleic acid; RRB, rotating rope bioreactor; RSCs, reduced sulfur compounds; TCE, trichloro ethane; VOCs, volatile organic compounds; VSCs, volatile sulfur compounds.

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1. Introduction

Volatile organic compounds (VOCs) and volatile sulfur compounds (VSCs) are produced and released from different industries including pulp and paper (P&P), refineries, distilleries, and waste water treatment plants [1–3]. Many of them are known to have the potential to pose human health hazards and nuisances with odor phenomena [4]. The demand for good breathable air has been intensifying with rapid industrial developments and associated air quality deterioration. Moreover, the trend of stringent environmental regulations has forced polluting industries around the world to comply with such guidelines through the adoption of effective pollution treatment measures. As one of the feasible options to control VOCs, VSCs, and odor, biological waste air treatment techniques have gained a great deal of popularity in light of the many associated advantages, e.g., cost-effectiveness and environment-friendliness relative to common traditional methods such as incineration or adsorption methods [5,6].

There are several types of bioreactors that perform waste-air treatment. The selection of a particular bioreactor is dependent upon such key parameters as loading capacity and properties of target pollutants. As such, for the selection of bioreactors, the factors determining the efficiency of the treatment processes for pollution abatement are the key components to consider [7]. For the proper application of the biotreatment technique, one needs knowledge of the design, configuration, and operational parameters of bioreactor which govern the efficiency of the treatment processes. This article aims to provide an overview of the various bioreactors used for the control of VSCs, with an emphasis on dimethylsulfide (DMS). In most cases, DMS is a major constituent (65–70%) of the P&P waste gas, followed by dimethyldisulfide (DMDS) (30–35%), while less than 5% is constituted by hydrogen sulfide (H_2S) and methanethiol (MT) [6].

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 [4,6]. 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.

In light 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 VOCs, VSCs, and the related odor problems. To meet such a demand, a better knowledge covering the treatability of each individual substance should be obtained to establish the proper treatment. The merits and demerits of these bioreactors will be explained along with a discussion of their important operational parameters and future research and development (R&D) needs in this area.

2. Sources of VSCs emissions from waste treatment

In this review, four VSCs compounds generated from the P&P industry, H_2S, MT, DMS, DMDS, are DMSO are dealt as the main targets of treatment. Each of those compounds contains one or two sulfur atoms exerting toxic effects above certain concentration levels. Consequently, environmental authorities are imposing regulatory guidelines to control VSCs emissions, and accordingly, the P&P industry has been implementing more advanced abatement strategies to protect facility workers and the neighboring environment [6,8,84].

One of the most critical pieces of information for selecting the best treatment option is the physical and chemical properties of the target compounds (Table 1). In terms of volatility, most VSCs generally have low boiling points which facilitate their emissions during industrial processes. For instance, about 5 ppm of DMS is known to be released from the recovery boiler flue gases when processing 1 ton of pulp in the P&P industry [6]. DMS has also been identified as a major odorant constituent generated from distillery and wastewater treatment plants, along with H_2S [9,10]. The odor threshold for H_2S, MT, DMS, and DMDS vapor is approximately 0.5–20, 0.0014–18, 0.12–2.5 and 0.10–15.5 ppb, respectively [11]. Moreover, these compounds can pose human health threats, causing headaches, skin and respiratory irritation, and vomiting.

DMS and other VSCs are also generated as by-products in the wood-pulping industry. For example, DMS can occur in significant amounts in liquors of the so-called Kraft process as a by-product of the Swern oxidation of alcohols to aldehydes. Schematic illustration of the gaseous emissions from the Kraft process (flow sheet) is given in Fig. 1. The major sources of VSC emissions include digester blow and relief gases, and slacker vents, brown-stock washers and seal tank vents, and the lime kiln exit vents [8,11]. Among such units, the highest concentration of DMS in the range of 100–60,000 ppm was observed in the digesters at onsite wastewater treatment facilities [9]. The emission concentrations of different VSCs generated in the P&P industries are presented in Table 1.

The generation of VSCs in P&P operation units has been attributed to the presence of sulfur containing proteins (e.g., amino acids like cysteine and methionine in the biomass) and other process input chemicals. The VSC concentrations were reported to decrease from 3 kg ton^{-1} of pulp in 1960 to less than 0.5 kg ton^{-1} of pulp in the early 2000s [6]. It was reported that the mean concentrations of MT, DMS, and DMDS were monitored as 4.4 (2.236), 576.2 (226.86) and 274.9 (71.35) mg m^{-3} (or ppm), respectively, from a source unit of a P&P mill in Northern Sweden [11]. These concentrations in ambient air inside some P&P facilities in Korea are much higher than those measured in the range H_2S (0.07–17.4); MT (0.02–4.28); DMS (0.003–1.68); CS_2 (0.004–6.39); and DMDS (0.005-0.305) ppb [8].

3. Microbiology of bioreactors

The utility of diverse bioreactors including biofilter (BFs), biotrickling filters (BTFs), bioscrubbers, and membrane bioreactor (MBRs) has been investigated over several decades [12,13]. Some recent studies have also proposed and developed other alternative technologies such as photo-bioreactors and activated sludge bioreactors [7,14].

In general, the efficiencies of biotreatment systems can be improved by identifying and inoculating some specific