Removal of dimethyl sulfide in a thermophilic membrane bioreactor

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ABSTRACT

In this study, the removal of dimethylsulfide was investigated in a flat composite membrane bioreactor (MBR) at elevated temperature (52°C). A composite membrane with a 2 μm polydimethylsiloxane (PDMS) coating layer and porous polyvinylidene diflouride (PVDF) support layer was used. The effect of variable operating conditions such as empty bed retention time (EBRT), nutrient supply, mass loading rate, temperature on elimination capacity was investigated. A maximum elimination capacity (EC_{max}) of 54 g m^{-3} h^{-1} was obtained at mass loading rate of 64 g m^{-3} h^{-1}, removal efficiency (RE) 84%. The reactor was sensitive to temporary temperature decrease and recovery was slow compared with the biotrickling filter operated at thermophilic condition.

1 INTRODUCTION

Treatment of volatile organic sulfur compounds (VOSCs) such as methanethiol, dimethyl disulfide, dimethyl sulfide (DMS) and carbon disulfide takes special attention in waste gas treatment technologies because they cause odour nuisance due to their very low odor threshold value. The potential sources of VOSCs are waste water treatment plants, rendering and composting processes, Kraft and paper pulp industries (Smet *et al.*, 1998).

For VOSC removal, due to the chemical complexity of low concentrated waste gas streams and the high flow rates to be handled, biotechnological techniques and scrubbers are recommended. However, biological waste gas treatment technologies have attracted industrial attention because they do not produce secondary waste streams and have low investment cost. A number of studies have proven the effective VOSCs

removal in biofilters, biotrickling filters, and membrane bioreactor (De Bo *et al.*, 2003; Ruokojarvi *et al*., 2001; Sercu *et al*., 2005; Smet and Van Langenhove, 1998) at mesophilic conditions. But in practice, some processes such as pulp and paper manufacturing, rendering and composting emit VOSCs at elevated temperature (40-75°C) and cooling down the waste gas is necessary prior to the biotreatment (Chan, 2006). Cooling down the humid gas is expensive and also produces secondary waste stream. Therefore the treatment of these compounds at elevated temperature using thermophilic and thermotolerant microorganisms should be considered.

For the waste treatment at thermophilic condition, the challenge will arise related with the mass transfer limitation. With increasing temperature, Henry's coefficient will increase which will result in lower driving force for interphase mass transfer (Cox *et al*., 2001). In biofilters and biotrickling filters air flows through a packed bed of a carrier material on which microorganisms grow as biofilm. The biofilm is covered with a water layer, forming a barrier between the microorganisms and hydrophobic compounds in the air phase. Therefore for hydrophobic pollutants, mass transfer limitation is highly possible in biofilters and biotrickling filters at elevated temperature. According to Matteau and Ramsay (1999), the lower degradation rate at 60°C was due to the physical limitation rather than biological in toluene degrading biofilter. Dhamwichukorn *et al*. (2001) also suggested that high temperature affected ineffective mass transfer for α-pinene. But in a membrane bioreactor liquid phase and air phases are separated by a membrane thus allowing the transfer of hydrophobic compounds to the biofilm. Pollutants diffuse through the membrane and subsequently degraded in the biofilm. Therefore membrane bioreactors could be advantageous for treatment of waste gases at thermophilic conditions. Also in a membrane bioreactor it is easy to control operational parameters such as pH and nutrients.

Aim of this study was to investigate the possibility of removal of DMS at thermophilic condition (52°C) in a MBR using PDMS/PVDF composite membrane.

2 MATERIAL AND METHODS

Experimental setup

The schematic of the thermophilic MBR is shown in Figure 1. Flat membranes were clamped between two identical Perspex reactor halves. The effective membrane area was 40 cm^2, and the volume of each compartment was 8 mL. The commercially available composite membrane provided by GKSS Research Centre Geesthacht (Germany), consisted of a 2 μm PDMS layer coated on PVDF was used. Through one compartment mineral medium was recirculated by a Heidolph peristaltic pump (PD5006, Heidolph Instruments GmbH & Co., Schwabach, Germany). Through the other compartment the air was passed in countercurrent along the porous support

layer of the composite membrane. The membrane contactor was placed in a thermostat at 52°C to maintain the constant temperature. The temperature of the inlet gas and liquid entering the reactor was 52°C. Both gas and liquid phases were operated at atmospheric pressure. Dimethyl sulfide was continuously dosed to the inlet air stream using a dynamic vapor-generating system (Smet *et al*., 1993). The gas sampling ports were inserted before and after the reactor.

The inlet air flow was provided at 14, 19.2, 40, 50 and 60 ml min^{-1}, resulting in an EBRT of 36, 25, 12, 10 and 8 s. The air flow was controlled with a calibrated mass flow controller (Model 5850S, Brooks Instrument Division, Emerson Electric Co., Veenendaal, The Netherlands).

The reactor was inoculated by recirculating pre-enriched culture (TSS = 4 g L^{-1}) along the PDMS layer of the membrane. When the reactor liquid was clear and biofilm development on the membrane was observed, the microbial suspension was drained and replaced by fresh nutrient solution. The nutrient solution was placed in a water bath (53°C). Periodically, the nutrient solution was drained completely and replaced by a fresh nutrient solution. A mineral medium containing 3.0 g L^{-1} K_2HPO_4, 3.0 g L^{-1} KH_2PO_4, 3.0 g L^{-1} NH_4Cl, 0.5 g L^{-1} $MgSO_4.7H_2O$, and 0.01 g L^{-1} $FeSO_4.7H_2O$ was recirculated. The pH of the liquid media was controlled daily and readjusted to 7 with 1 M NaOH when it reached a value lower than 6.

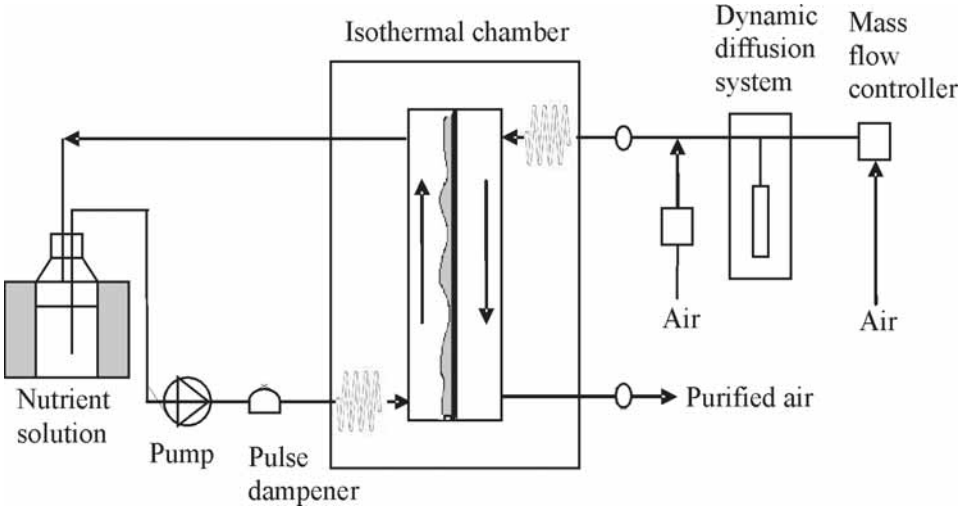

Figure 1. Schematic of flat membrane bioreactor.

Analytical methods

The concentration of DMS was determined by injection of 1 mL gas samples into a GC Agilent 4890D (Hewlett Packard Inc., Agilent Technologies Inc., USA) equipped with a flame ionization detector (FID), using a 15 m HP-5 column (internal diameter 0.53 mm; film thickness 1.5 μm) with helium as carrier gas. The pH of the recirculating liquid media was measured with an electronic pH sensor (Jenway Ltd., Essex, England 3310).

3 RESULTS AND DISCUSSION

The membrane bioreactor was operated for four months at 52°C. The reactor was started-up at inlet DMS concentration of 70 ± 10 g m^{-3} h^{-1} and EBRT of 10 s. As can be seen in Figure 2, the removal efficiency was low (< 20%) for the first 12 days. Therefore on day 13, the EBRT was increased to 25 s. As soon as the EBRT was increased, immediate improvement was observed and RE increased from 16 to 45%. When the loading rate was decreased stepwise down to 20 g m^{-3} h^{-1}, the RE stayed at 45% (EC ~10 g m^{-3} h^{-1}). When the EBRT was further increased to 36 s on day 19, no change was observed in RE. Instead the concentration of DMS in the head space in the bottle containing the liquid medium increased (results not shown). It showed that at high EBRT of 36 s, DMS was only transported to the liquid medium but not degraded. After increasing the EBRT back to 25 s, decreased RE of 30% was observed. This change could be caused by accumulation of DMS in liquid medium at high EBRT. On day 24, the microbial suspension was added to the MBR, and RE increased from 30 to 50% in 2 days and further to >90% in 9 days. Removal efficiencies exceeding 90% were obtained on day 33 at mass loading rate of 18 g m^{-3} h^{-1} and EBRT of 25 s. Shorter start-up period of 9 days was observed in a MBR inoculated with *Hyphomicrobium* VS for DMS at ambient temperature (De Bo *et al*., 2003). Similar start-up period of 25 days was observed in a thermophilic biotrickling filter treating DMS (Luvsanjamba *et al*., 2006).

When the reactor reached the steady state, EC_{max} was determined in a thermophilic MBR (Figure 3). From day 68, the mass loading rate was increased stepwise up to 70 g m^{-3} h^{-1} at EBRT of 25 s. EC_{max} of 54 g m^{-3} h^{-1} was observed in MBR at mass loading rate of 64 g m^{-3} h^{-1} (RE 84%). De Bo *et al*. (2003) reported EC_{max} of 100 g m^{-3} h^{-1} (EBRT = 24 s) for DMS in a MBR inoculated with *Hyphomicrobium* VS using PDMS/PVDF membrane. The lower EC obtained in this study compared with the latter was most probably due to the lower DMS degrading capacity of the biofilm established in thermophilic MBR. But compared with thermophilic biotrickling filter removing DMS (EC_{max} = 45 g m^{-3} h^{-1}), somewhat higher EC of 54 g m^{-3} h^{-1} was obtained in MBR (Luvsanjamba *et al*., 2006). Also shorter EBRT of 25 s was required to obtain

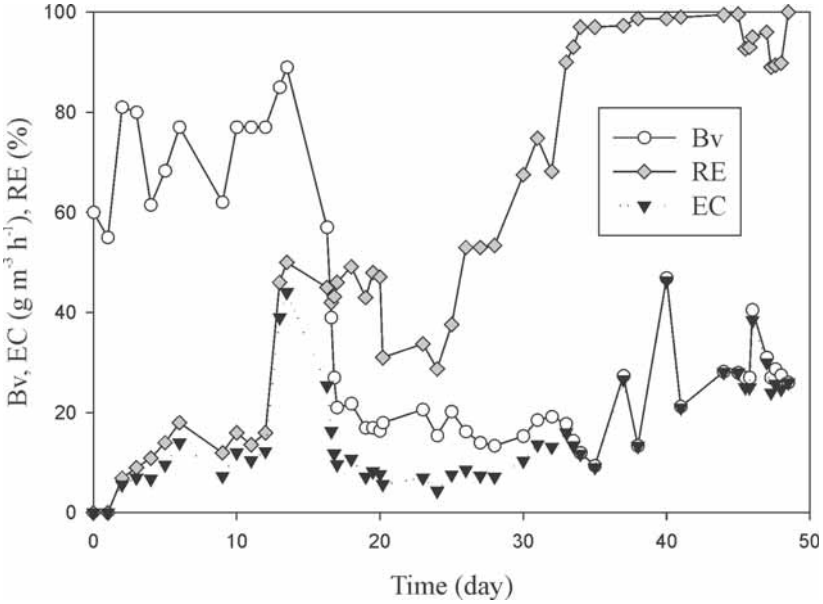

Figure 2. Start-up period of the MBR at 52°C. The dashed line indicates the change in EBRT from 10 to 25s.

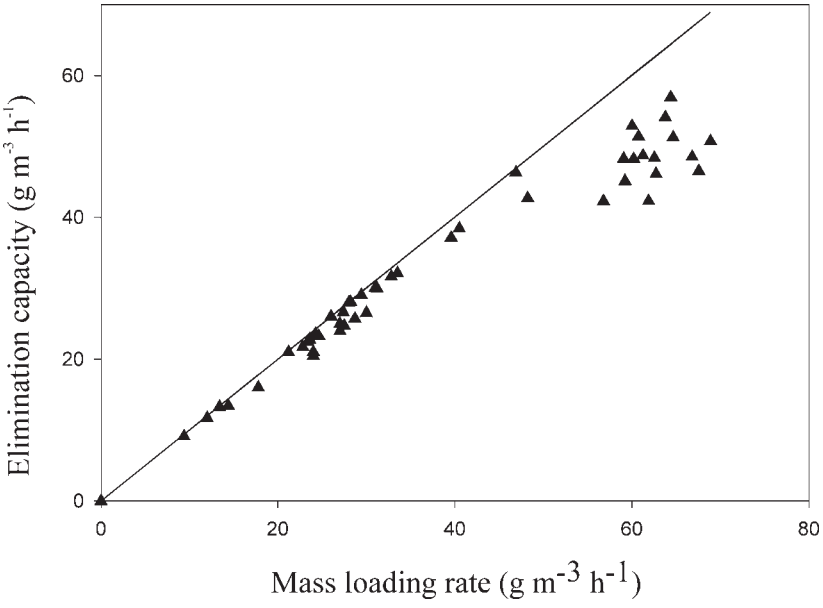

Figure 3. Elimination capacity for DMS as a function of loading rate in a thermophilic MBR.

this EC compared with the thermophilic biotrickling filter (EBRT = 200 s). This difference could be attributed to enhanced mass transfer rate in the MBR compared with a biotrickling filter.

After determining the maximum EC in the thermophilic MBR, effect of variable operating conditions such as mass loading rate, EBRT, temperature, and nutrient supply on reactor performance was investigated.

Firstly the mass loading rate was increased from 20 to 60 g m^{-3} h^{-1}. At the same EBRT of 25 s, RE decreased from > 95% to 70 - 80%. When longer EBRT of 36 s was tested at the loading rate of 60 g m^{-3} h^{-1}, the RE increased from 80 to 88%. However this RE did not remain constant and decreased to 80% next days. The concentration of DMS in the head space of the liquid bottle increased, proving that DMS was accumulated instead of being degraded. Thereafter the EBRT was decreased from 25 to 12 and 8 s at a constant mass loading rate of 60 ±3 g m^{-3} h^{-1}. As indicated in Figure 4, the RE decreased from 76 to 56 and 40%, respectively. It shows that the reactor performance is greatly influenced by EBRT.

Thirdly the effect of temperature decrease to mesophilic range on EC was investigated. The temperature of the isothermal chamber was kept at 25°C for 3 days. The EC dropped from 26 g m^{-3} h^{-1} (RE = 100%) to 15 g m^{-3} h^{-1} (RE = 51%). It took 11 days to reach the RE 95% at loading rate of 25 g m^{-3} h^{-1} when the temperature was set back to 52°C. In contrast, it took only 2 hours in a DMS degrading thermophilic biotrickling filter inoculated with activated sludge (Luvsanjamba *et al*., 2006).

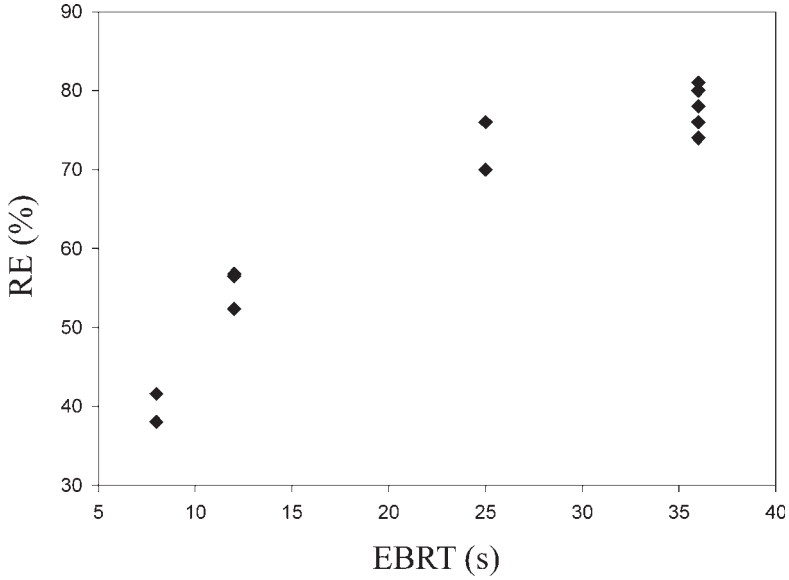

Figure 4. Effect of the EBRT on removal efficiency of the MBR.

Different nutrient supplies such as vitamin, trace elements and tap water were tested in a recirculating liquid medium to examine the effect of medium composition on EC of the reactor. However no significant effect was observed on the elimination capacity.

From the third month of an operation the elimination capacity of the reactor decreased to 30 g m^{-3} h^{-1} (RE = 50% at an EBRT of 25 s). The decreased EC could be influenced by ageing of the biofilm as well as formation of thick biofilm layer on the membrane lowering the transportation of the pollutant.

4 CONCLUSIONS

This study demonstrated the possibility of removal of DMS in membrane bioreactor at thermophilic condition. Higher elimination capacity (54 g m^{-3} h^{-1}) was obtained in MBR in comparison with biotrickling filter operated at 52°C (45 g m^{-3} h^{-1}). The optimum EBRT was found to be 25 s. Since the declined performance of was observed after an operation of three months, the long-term efficiency of thermophilic MBR should be further investigated.

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