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Long-term operation of a thermophilic biotrickling filter for removal of dimethyl sulfide

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Abstract

This study demonstrates the possibility of removal of dimethyl sulfide in a thermophilic biotrickling filter (BTF52) operated at 52 °C, using an enriched sludge inoculum. The efficiency and long-term performance of BTF52 were compared with a reactor operated in parallel at 22 °C (BTF22). After a start-up period of 17 and 25 days, maximum elimination capacity values of about 30 and 18 g m^{-3} h^{-1} were measured in BTF22 and BTF52, respectively. However, using tap water instead of deionized water as a matrix for the mineral medium caused a substantial improvement of maximum elimination capacity, increasing to 75 and 45 g m^{-3} h^{-1} in BTF22 and BTF52. $CaCO_3$ was found to be the crucial ingredient causing this performance increase. Also, the effect of variable operating conditions on the performance of both reactors was examined. At DMS loading rates of 6.5 g m^{-3} h^{-1}, the elimination capacities in both reactors recovered within 2 h after short-term (24 and 48 h) complete shut downs. Temperature changes to 21 and 59 °C decreased the removal efficiency of BTF52 by 90 and 30%, respectively. Finally, batch experiments showed that liquid-phase sulfate concentrations exceeding 2.2 g L^{-1}, decreased the removal rate by 50% at 52 °C.

Keywords: Thermophilic; Biotrickling filter; Dimethyl sulfide

1. Introduction

The emission of volatile organic sulfur compounds (VOSCs) such as dimethyl sulfide (DMS), dimethyl disulfide, methanethiol and carbon disulfide are found in processes where organic matter is heated or where anaerobic decay occurs. Treatment of these compounds takes special attention because they may cause odor nuisance due to their very low odor threshold value [1]. VOSCs are found in waste gases from different sources such as wastewater treatment, Kraft pulping, rendering and composting plants. Several treatment technologies exist including physical-chemical (scrubbing, adsorption, incineration, and masking) and biological technologies. Biological waste gas treatment technologies such as biofilters, biotrickling filters, bioscrubbers, and membrane bioreactors are advantageous because they are environmentally clean and cost-effective technologies. Several studies have proven the possibility of VOSCs removal in biofilters, biotrickling filters and membrane bioreactors at mesophilic temperatures (20–25 °C), usually with the application of inoculation [2]. However, some processes such as pulp and paper manufacturing, rendering and composting emit VOSCs at elevated temperatures (45–75 °C) resulting in decreased efficiencies of odor removing bioreactors [3]. The application of thermophilic microorganisms for the removal of VOSCs should be considered, since cooling down the gases to mesophilic temperatures is expensive [4,5]. Few studies have described successful thermophilic biofiltration of volatile compounds such as ethanol, hydrogen sulfide, methanol, α-pinene, and other organics [4–10]. Less biomass accumulation was observed in biotrickling filters operated at elevated temperatures, alleviating the problem of reactor clogging [4,7,8,10]. Furthermore, most of the studies reported that a higher elimination capacity (EC) can be obtained at elevated temperature [4,5,7,8,10]. Until now there has not been any study published about thermophilic biological treatment of VOSCs that we are aware of.

The aim of this study was to investigate the potential of biotrickling filters to remove DMS at elevated temperature (52 °C), to determine the long-term reactor stability and to compare its efficiency with that of a similar reactor operated at ambient conditions (22 °C). DMS was chosen as a target

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compound because it significantly contributes towards odorous emissions and its degradation rate is lower than methanethiol and dimethyl disulfide [3,11]. Biotrickling filters were chosen because of the better control of the reactor conditions compared with traditional biofilters and the absence of degradation, compaction and drying out of the filter-bed material at elevated temperatures.

2. Materials and methods

2.1. Inoculum enrichment and batch experiments

Highly activated nitrifying and denitrifying sludge (HANDS) from a membrane bioreactor treating landfill leachate (Avecom, Belgium) was used as inoculum. The inoculum details were previously described by Morgan-Sagastume et al. [12]. The enrichment consisted of sending DMS loaded air through 1 L of HANDS (15 g volatile suspended solids L^{-1}) in a bubbling flask at 22 and 52 °C for 45 days. DMS (Acros, 99+%, Geel, Belgium) was dosed in the air stream by using a capillary diffusion system, as described by Smet et al. [13]. The gas flow rate was set at 52 mL min^{-1} and the inlet concentration varied in the range of 29–100 ppmv. Higher temperature was maintained by placing the flask in a water bath (52 °C). Gas sampling ports were provided in the tubing before and after the bubbling flasks to measure DMS concentrations.

Batch experiments were performed at 22 and 52 °C, in order to determine the activity of inocula. Therefore, 10 mL of enriched sludge was placed in a 118 mL penicillin bottle, sealed with a mininert valve (Alltech Associates, Inc., Deerfield, IL) for gas analyses. 1 μL of liquid DMS was introduced in the liquid phase with a syringe. The decline of the pollutant concentration was followed in time by injecting 1 mL samples from the headspace in the gas chromatograph. To confirm the occurrence of biodegradation, the tests were repeated with autoclaved sludge at each temperature.

Also, six more batch tests were performed at 52 °C to examine the effect of sulfate concentrations on microbial activity. The test was performed in the same way as described above. Liquid medium containing 2 mL mineral medium and 8 mL tap water (TW) was placed in a penicillin bottle. 0.5 mL of enriched microbial suspension was added to each bottle. A Na_2SO_4 solution (50 g L^{-1}) was added to the bottles to obtain sulfate concentrations of 0.3, 0.8, 1.3, 1.6, 1.9 and 2.2 g L^{-1}. 1 μL of liquid DMS was introduced in the liquid phase with a syringe. The bottles were placed in water bath (52 °C) and the suspension was stirred using magnetic stirrers. To confirm biodegradation, the tests were repeated with the same medium without addition of the bacterial suspension.

2.2. Biotrickling filter experiments

Two biotrickling filter systems were set up in parallel and operated at two temperatures: ambient temperature (control, BTF22) and 52 °C (thermophilic, BTF52). The temperature of BTF22 was not controlled and was equal to the laboratory temperature (~22 °C). The bioreactors were constructed of Plexiglas (internal diameter: 0.044 m; height 0.67 m). The thermophilic bioreactor was constructed with a double wall (internal diameter of the outer wall: 0.074 m) which enables recycling of heated water to maintain a high temperature in the whole reactor. The water recycled was heated in a thermostatic bath (53 °C). The inlet air stream passed through head space (16 cm) before reaching the filter bed to minimize the heat loss in the filter bed. The actual temperature of the filter bed was 49–51.5 °C. The temperature loss of the reactor was minimized due to continuous recirculation of water in the outer wall of the reactor. The temperature of the gas leaving the reactor was around 49 °C. The bioreactors were packed with 1 L of high density polyethylene KMB carrier rings (Kaldnes Miljøteknologi AS, Tønsberg, Norway). KMB rings are wheel shaped with longitudinal fins at the outside (diameter: 10 mm, height: 7 mm, free volume: 75.6%, specific surface area: 333 m^2 m^{-3}).

Both biotrickling reactors were operated with gas and liquid flowing co-currently (down-flow mode). Dry air was supplied by a diaphragm pump (KNF Neuberger, Aartselaar, Belgium). The inlet air flow was set at 1, 0.6 and 0.3 L min^{-1} during different experimental periods, resulting in an empty bed residence time (EBRT) of 60, 100 and 200 s. The air flow was controlled with flowmeters (Sho-Rate 1355; Brooks Instrument Division, Emerson Electric Co., Veenendaal, The Netherlands). DMS was dosed in the air stream using the capillary diffusion system, as described in the enrichment experiment. Gas sampling ports were provided in the tubing before and after the biotrickling filters.

The reactors were inoculated by pouring 1 L of enriched HANDS over the packing material. 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} $MgSO_4{\cdot}7H_2O$, and 0.01 g L^{-1} $FeSO_4{\cdot}7H_2O$ was diluted five times with deionized water (DW) and recirculated over the biotrickling filters at 118 mL min^{-1} using peristaltic liquid pumps (PD5006, Heidolph Instruments GmbH & Co., Schwabach, Germany and Masterflex model-7518-00, Cole Parmer, USA). During the final phase of the experiment, NH_4Cl was replaced by KNO_3 (5.7 g L^{-1}) to prevent acidification caused by nitrification (see Section 3). The pH of the liquid media was checked daily and readjusted to 7 with 1 M NaOH when it reached a value below 6. The recirculating liquid medium was changed every 2–7 days.

1 mL of vitamin solution (pH 7.0) containing 10.0 mg L^{-1} thiamine-HCl·$2H_2O$ (vitamin B_1); 20.0 mg L^{-1} nicotinic acid (vitamin B_3); 20.0 mg L^{-1} pyridoxine-HCl (vitamin B_6), 10.0 mg L^{-1} *p*-aminobenzoic acid (vitamin B_X); 20.0 mg L^{-1} riboflavin (vitamin B_2); 20.0 mg L^{-1} Ca-pantothenate (vitamin B_5); 1.0 mg L^{-1} biotin (vitamin B_8); and 1.0 mg L^{-1} vitamin B_{12} was added to the recirculating medium to examine the effect of vitamin on degradation activity. Also 1 and 10 mL of trace elements solution (pH 6.0) containing 50.0 g L^{-1} Na_2EDTA; 11.0 g L^{-1} $ZnSO_4{\cdot}7H_2O$; 7.34 g L^{-1} $CaCl_2{\cdot}2H_2O$; 2.5 g L^{-1} $MnCl_2{\cdot}4H_2O$; 0.5 g L^{-1} $CoCl_2{\cdot}6H_2O$; 0.5 g L^{-1} $(NH_4)_6Mo_7O_{24}$ H_2O; 5.0 g L^{-1} $FeSO_4{\cdot}7H_2O$; 0.2 g L^{-1} $CuSO_4{\cdot}5H_2O$; and 11.0 g L^{-1} NaOH was tested in the recirculating medium.

2.3. 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 (250 °C), using a 15 m HP-5 column (internal diameter 0.53 mm; film thickness 1.5 μm, column temperature of 35 °C) with helium as carrier gas (flow rate 4–5 mL min^{-1}). The gas injector temperature was 220 °C. The pH of the recirculating liquid media was measured with an electronic pH sensor (Jenway Ltd., Essex, England).

Analysis of the NH_4^+-N and ($NO_2^- + NO_3^-$)-N content of the recirculating liquid medium was performed by steam distillation [14].

3. Results

3.1. Enrichment and batch test of inoculum

Before starting up the reactors, HANDS (pH 8.2) was enriched by sending DMS loaded gas through the bubbling flasks at 22 and 52 °C. A DMS removal efficiency (RE) exceeding 95% was observed after 4 weeks at 22 °C. Although an average RE of 10% was observed at 52 °C, DMS degradation was not constant in this condition and dropped to zero from time to time.

Therefore batch experiments were performed to confirm biodegradation of DMS by enriched HANDS at 22 and 52 °C. At 22 °C, DMS concentrations decreased below the detection limit (0.1 ppmv) within 20 h, after a lag phase of 50 h. At 52 °C, the same DMS concentration decrease was obtained in 70 h after a lag phase of 70 h. In the control bottles containing autoclaved sludge, the concentrations of the compounds remained constant. This confirmed that the batch experimental set up was air tight and that no abiotic degradation occurred at 22 and 52 °C. As the biodegradation of DMS at 52 °C was proven in a batch system, the two biotrickling filters were inoculated with enriched inocula.

3.2. Removal of DMS in biotrickling filters at 22 and 52 °C

Two BTFs were operated at 22 and 52 °C in parallel for 9 months. The biotrickling filtration experiment was divided into five periods depending on the purpose of the experiment (Table 1).

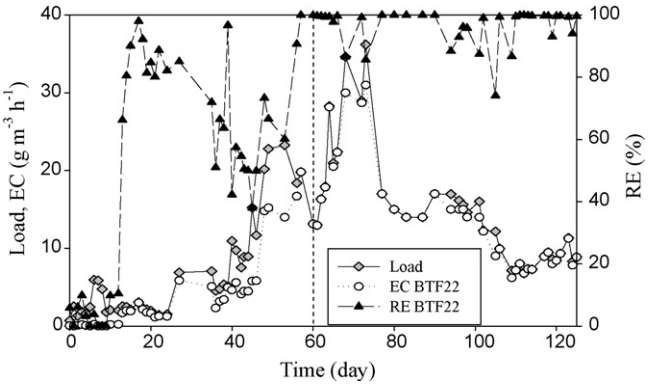

Fig. 1. Mass loading rate, elimination capacity and removal efficiency in BTF22 from day 0 to 125. The dashed line indicates the change of EBRT from 100 to 200 s.

3.2.1. Start-up of the biotrickling filters

Period 1 included the acclimation period of the biotrickling filters at 22 and 52 °C. Different start-up periods were observed in BTF22 and BTF52 in spite of using enriched inocula from the same source. A RE exceeding 98% was observed on day 17 in BTF22 at a mass loading rate of 2.3 ± 0.6 g m^{-3} h^{-1} and EBRT of 100 s (Fig. 1). For BTF52 it took 25 days to reach a RE exceeding 80% (Fig. 2), at the same loading rate.

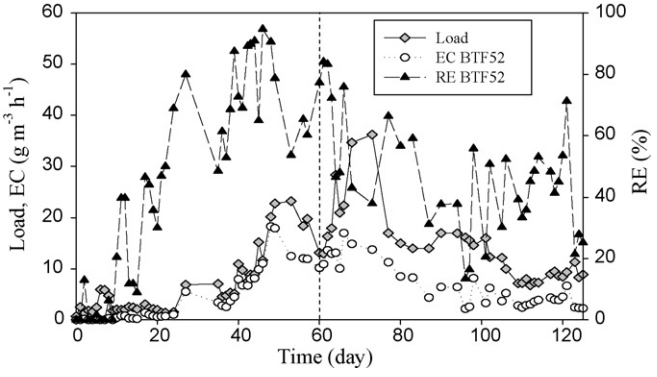

Fig. 2. Mass loading rate, elimination capacity and removal efficiency in BTF52 from day 0 to 125. The dashed line indicates the change of EBRT from 100 to 200 s.

Table 1
Experimental periods of biotrickling filtration of DMS in BTF22 and BTF52

Experimental period	Day	Mass loading rate (g m^{-3} h^{-1})	EBRT (s)	Purpose of the experiment
Period 1	1–25	2–8	100	Start-up of the reactors
Period 2	26–127	9–36	100, 200	Performance of the biotrickling filters, determination of ECs_{max}
Period 3	128–162	7–16	200	Adjustment of recirculation medium
Period 4	163–176	20–100	200	Operation of biotrickling filters with a liquid medium based on tap water
Period 5	177–270	7–25	60–200	Reactor stability under varying conditions, long-term performance of the biotrickling filters

3.2.2. Performances of the biotrickling filters, determination of ECs_{max}

In period 2, the maximum elimination capacities (EC_{max}) in both reactors were determined. When the loading rate was increased stepwise, the RE of BTF52 reached 90% for the first time on day 41 (at a loading rate of 9 g m^{-3} h^{-1}). From day 60, the EBRT was increased from 100 to 200 s in both reactors, to check if the removal efficiency would improve at longer EBRT. The removal efficiency increased slightly from 60 to 80% in BTF52 even when higher loading rate was applied. Therefore, the EBRT was kept at 200 s for further experimental periods for both BTFs. The RE of BTF22 was 99% at EBRT of 100 s. ECs_{max} of 30 and 18 g m^{-3} h^{-1} were measured at 22 and 52 °C, respectively (RE of 83 and 79%). Because the maximum EC in BTF52 was 18 g m^{-3} h^{-1}, the loading rate was decreased back to 17 g m^{-3} h^{-1} (at EBRT = 200 s) on day 77 in both reactors. Fig. 2 indicates that the EC did not reach the previously obtained value (>10 g m^{-3} h^{-1}) and dropped to 6 g m^{-3} h^{-1} in BTF52. Therefore, the loading rate was further decreased to 7 g m^{-3} h^{-1} on day 109, still no improvement in RE was observed and EC decreased to an average of 4 g m^{-3} h^{-1} (RE 50%). In contrast to BTF52, the RE in BTF22 stayed mostly 99% (Fig. 1).

3.2.3. Effect of composition of liquid medium on the EC of the biotrickling filters

In period 3, recirculating liquid media with different composition (TW, vitamins and trace elements) were applied to enhance the biofilm activity in BTF52. On day 128, TW was used instead of DW in the mineral medium in BTF52. Immediately, the RE increased from 56% to more than 90% (EC ≅ 10 g m^{-3} h^{-1}) (Fig. 3). When DW was added again in the liquid medium on day 129, the RE dropped back to 34%. When the liquid medium was based again on TW (day 132), an immediate improvement in RE (enhancement from 42 to 99%) was observed. According to the report of quality control laboratory of the drinking water supplier (TMVW Water Company, Ghent, Belgium) the tap water contained the Ca^{2+} and Mg^{2+} ions at concentrations of 100.9 ± 31 and 12.0 ± 3.9 mg L^{-1}, respectively. To identify the crucial element causing the increases in RE, mineral media containing $CaCl_2$ and $CaCO_3$ were tested. After adding 0.4 g L^{-1} $CaCl_2$ to the liquid medium (200 mL mineral medium and 800 mL DW) on day 138, the RE decreased from 99 to 89% in 3 h and to 40% next day. Subsequent addition of 0.4 g of $CaCO_3$ to the liquid medium on day 139 caused the RE to increase to 99% and the removal remained stable for 4 more days afterwards. Thereafter, additional vitamins and trace metals were tested in the medium. On day 143, 1 mL of vitamin solution was added to the fresh medium containing mineral medium and DW, leading to an increase in RE from 87 to 96%. On day 157, the same amount of vitamin solution was added again to confirm the vitamin effect and the RE increased from 55 to 77%. On day 158, 1 mL of trace element solution was added to the fresh recirculating medium containing mineral medium and DW. However no significant change was observed in RE of DMS in BTF52 and the RE stayed at 70%. Subsequent addition of 10 mL of trace element solution also did not affect the RE of the reactor. After replacing the medium with liquid medium containing 200 mL mineral medium and 800 mL TW on day 163, the RE reached 99% within 1 day. During these experiments, recirculating medium based on TW was used in BTF22, in which the RE stayed 99%. Therefore, the liquid medium prepared with tap water was kept for the rest of the experimental period in both BTFs.

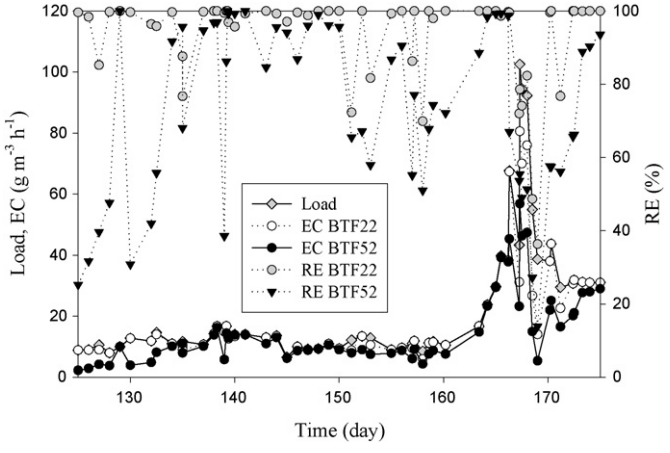

Fig. 3. Mass loading rate, EC and RE in BTF22 and BTF52 from day 124 to 175.

3.2.4. Performances of biotrickling filters with a liquid medium based on tap water

In period 4, after observing an increased removal rate during application of tap water in the medium, the new maximum elimination capacity was determined in both reactors. The latter increased the EC to 68 and 45 g m^{-3} h^{-1} in BTF22 and BTF52, respectively, at a loading rate of 68 g m^{-3} h^{-1} (Fig. 3). Upon further increase of the loading rate to 92–102 g m^{-3} h^{-1}, the EC increased further in BTF22 to 70–81 g m^{-3} h^{-1}, but the EC in BTF52 remained around 45 g m^{-3} h^{-1}, with a transient peak at 57 g m^{-3} h^{-1}. However, afterwards, even when the loading rate decreased to 40 g m^{-3} h^{-1} and recirculating liquid media were refreshed, the EC decreased to 14 and 5.4 g m^{-3} h^{-1} in BTF22 and BTF52, respectively. It took 6 days for BTF52 to reach a RE of 90% at the loading rate of 30 g m^{-3} h^{-1} after this peak in DMS loading. In contrast to BTF52, it took only 2 days for BTF22, to reach a RE of 99% (loading rate 40 g m^{-3} h^{-1}). During the recovery period, the liquid medium was refreshed every one to 2 days to maintain the optimum pH and nutrient balance. Batch tests were performed to examine if accumulation of sulfate could have caused a decreased DMS removal (Fig. 4). At sulfate concentrations of 0.3–1.6 g L^{-1}, no difference was observed in the removal rate. The degradation slowed down at a sulfate concentration of 1.9 g L^{-1} and the rate was half of the rates in the other batches at sulfate concentration of 2.2 g L^{-1}. This was consistent with the concentration calculated after the peak loading (1.86 g SO_4^{2-} would have been formed at an EC of 47 g m^{-3} h^{-1} for 24 h). In the bottle where no bacterial suspension was added, the DMS concentration stayed constant proving that no abiotic degradation occurred during the tests. Optimal pH ranges of 5.0–7.0 and 5.0–6.4 were deter-

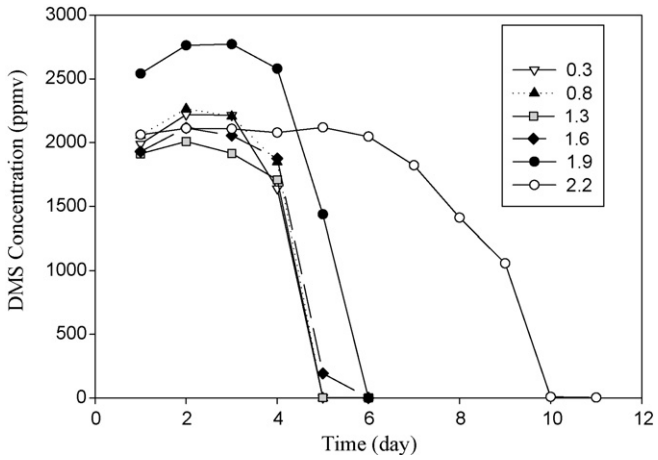

Fig. 4. Effect of sulfate concentration of liquid medium on removal of DMS at 52 °C. The sulfate concentration indicated is in g L^{-1}.

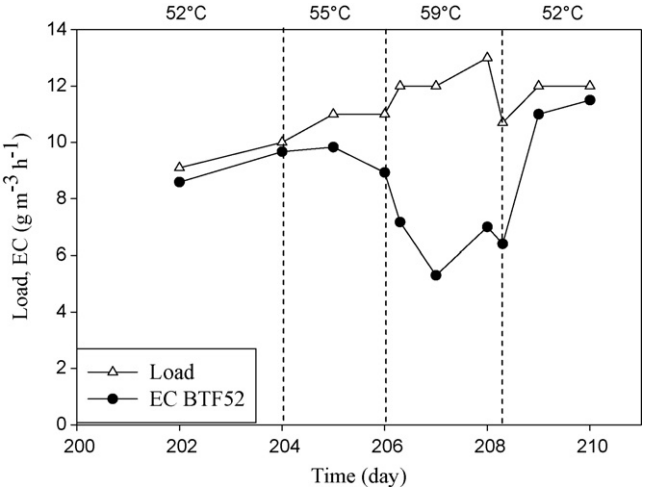

Fig. 6. Effect of heating on elimination capacity of DMS in BTF52. The dashed lines indicate the change of temperature.

mined in BTF22 and BTF52 (Fig. 5) by plotting all pH data versus RE. The pH values were obtained at mass loading rate of 20–40 g m^{-3} h^{-1} when the liquid medium consisting of 200 mL mineral medium and 800 mL TW was recirculated in the reactor. The RE efficiency recovery to 90% after correcting the pH of the medium proved that the decreased RE was only due to the pH decrease.

3.2.5. *Performances of biotrickling filters under varying operational conditions*

In period 5, the effect of different operational conditions, such as different EBRTs, temperature changes and shut downs, on the performance of the bioreactors was examined. Also long-term operation of BTF52 was compared with that of BTF22. The EBRT was kept at 200 s except during the experiment with different EBRTs.

Firstly, on day 190, removal of DMS was tested at different EBRTs in BTF22 and BTF52 at constant loading rate of 20 g m^{-3} h^{-1}. When the EBRT was decreased from 200 to 100 and 60 s at inlet DMS concentrations of 1.12, 0.56 and 0.34 g m^{-3}, the RE dropped from 90 to 80 and 60%, respectively. The removal rate in BTF22 was not affected significantly (93–100%) when the EBRT was decreased.

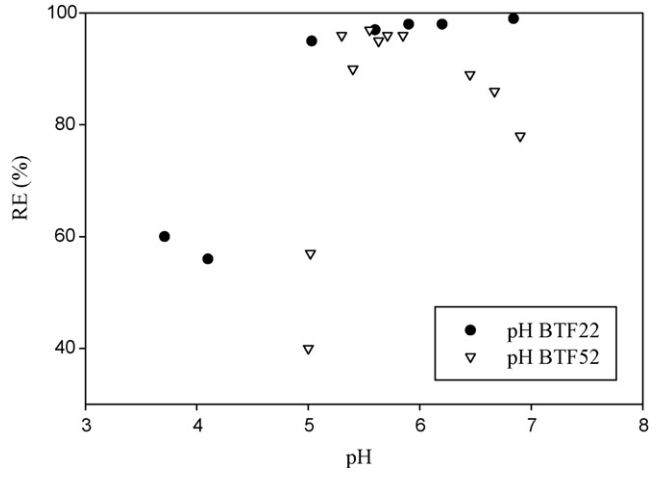

Fig. 5. Effect of pH on RE of BTF22 and BTF52.

Secondly, the stability of the thermophilic bioreactor to temperature changes was examined. When the temperature of the BTF52 was decreased to 21 °C, the RE decreased from 95 to 10% (loading rate 7.5 g m^{-3} h^{-1}). After keeping BTF52 at 21 °C for 24 h, the temperature was set back to 52 °C. The RE recovered back to 95% within 3 h. Thereafter, the BTF52 was subjected to higher temperatures (Fig. 6). When the temperature was increased to 55 °C (loading rate 11 g m^{-3} h^{-1}), the EC did not change much and stayed at 9.4 ± 0.5 g m^{-3} h^{-1} (RE 80–89%). After keeping the reactor temperature at 55 °C for 2 days the temperature was further increased to 59 °C, leading to a decrease in EC from 8.9 g m^{-3} h^{-1} (RE 80%) to 7 g m^{-3} h^{-1} (RE 47%). When the temperature was set back to 52 °C the RE reached to 90% in 1 day.

Thirdly, short-term shutdowns were tested in both reactors. On day 240, the DMS supply was switched off for 24 h while air was still passing through the reactor. After resuming the DMS supply (loading rate 6.5 g m^{-3} h^{-1}), the RE recovered back to >95% in BTF52 within 6 h. In BTF22, the recovery was slower (6 h to reach the RE 50%) than in BTF52, however this slow recovery could be influenced also by nitrification (see Section 4). Next, the DMS and air supply, liquid recycle and heating was shut down for 24 h. The RE recovered back to >98% within 2 h after switching on both reactors. Afterwards, the complete shut down was repeated for 48 h. Still, the EC recovered back completely in both reactors within 2 h.

3.2.6. *Long-term stability of the biotrickling filters*

From the 7th month of operation, the removal of DMS in BTF22 decreased from 99 to 30% (loading rate 6 g m^{-3} h^{-1}). The pH of the recirculating medium of BTF22 decreased from 6.7 to 3.5 in course of 1 day. As pH was adjusted to >6 or the liquid was replaced by fresh medium, the RE increased from 30 to 86% immediately. This indicated that the low RE was caused by pH drop in BTF22. Because nitrification was suspected to cause the pH decrease, NO_3^-, NO_2^- and

NH_4^+ concentrations were determined in the fresh medium and the medium recirculated for 24 h in BTF22 without dosing DMS. The concentration of ammonium decreased from 200 to 140 mg L^{-1} (−3.3 mmol L^{-1}) in BTF22 and the concentration of nitrate increased from 0 to 200 mg L^{-1} (+3.2 mmol L^{-1}), indicating stoichiometric production of nitrate from ammonium. When NH_4Cl was replaced by KNO_3 in the recirculating liquid medium, the RE recovered back to >90% in 1 day and pH changed from 6.7 to 6.2 at loading rate of 6 g m^{-3} h^{-1} (RE 97%) after 24 h of operation in BTF22. In BTF52, however, the concentration of ammonia and nitrate did not change.

During the entire operation of the two reactors, biomass washout and foaming occurred in BTF22, although this did not have significant effect on the EC. Neither biomass washout nor foaming was visually observed in BTF52.

4. Discussion

In this study, we demonstrated that an enriched inoculum can be used to remove DMS from waste gas at thermophilic conditions (52 °C). In addition, we compared the DMS removal in two biotrickling filters, one at 52 °C and one at 22 °C, during varying operational conditions. Maximum elimination capacities of 30 and 18 g m^{-3} h^{-1} were initially found in BTF22 and BTF52, respectively. These values were lower than the ones found before (57–77 g m^{-3} h^{-1}) under mesophilic conditions [2,15,16]. In comparison to the biotrickling filter operated at ambient temperature, the thermophilic reactor did not perform well with respect to DMS elimination capacity and removal efficiency. In some studies, thermophilic bioreactors exhibited higher ECs in comparison to their mesophilic counterparts [5,7–9]. According to the authors, higher ECs for methanol, toluene and isobutyraldehyde were explained by higher degrading activity of thermophilic microorganisms. Also lack of excessive biomass accumulation at thermophilic conditions resulted in better reactor performance. In contrast, some studies proved the occurrence of mass transfer limitation at thermophilic conditions resulting in a decreased EC. Dhamwichukorn et al. [5] observed a mass transfer limitation for α-pinene in a thermophilic biofilter operated at 55 °C. When the EBRT was decreased from 18.24 to 6.08 min, the removal efficiency of α-pinene decreased from 97 to 26%. But in the same system, no evidence of mass transfer limitation was observed for methanol. Strauss et al. [17] also reported occurrence of mass transfer limitation caused by high temperature for toluene in a biofilter. Mesophilic toluene removal efficiencies reached values of >95% at EBRT >0.48 min, while the same removal efficiencies were achieved only at 1.3 min under thermophilic conditions. The effect of temperature on the removal of VOCs in biotrickling filters is therefore compound-specific, and dependent on the relative importance of biodegradability versus mass transfer limitation at higher temperatures. As temperature rises from 25 to 50 °C, the Henry's coefficient of DMS in water increases from 0.085 to 0.190 [18]. A higher Henry's coefficient will result in lower driving force for interphase mass transfer and lower pollutant availability to the biofilm [4]. DMS already has a relatively high Henry's coefficient, so mass transfer will influence the degradation process more significantly than for other compounds, having lower Henry's coefficients. In addition, the RE exceeding 95% could be obtained only at EBRT of 200 s in the thermophilic reactor while the same RE was possible at EBRT of 60 s in the mesophilic reactor at mass loading rate of 20 g m^{-3} h^{-1}. All this indicates that the DMS mass transfer rate was lower in BTF52 in comparison to the mesophilic reactor. In addition, lower DMS degradation rates were observed for the enriched culture at 52 °C in batch tests, so the microbial community active at 52 °C has a lower DMS degrading activity compared with the one at mesophilic conditions. Therefore, the lower EC for DMS at 52 °C compared with the one obtained at 22 °C was influenced by both lower mass transfer and biodegradation rates.

While a relatively low EC_{max} (30 and 18 g m^{-3} h^{-1}) was obtained in both biotrickling filters initially, EC_{max} was further enhanced (to 75 g m^{-3} h^{-1} for BTF22 and 45 g m^{-3} h^{-1} for BTF52) by using tap water instead of deionized water to formulate the recycling medium. However, the reported EC_{max} values, while using tap water, were not sustained for a long time, probably due to the sulfate accumulation in the liquid medium as was shown by separate batch tests. The enhancement in EC caused by the tap water can be explained by the presence of $CaCO_3$, as addition of the latter to deionized water also increased the EC in BTF52. Increasing only the pH of the liquid medium or the calcium (as $CaCl_2$) concentration did not have the same effect. Possibly the liquid medium was not buffered enough to be able to influence the pH of the biofilm itself after pH adjustment. Therefore, the effect of $CaCO_3$ could be related with its pH buffering properties, as it is known that DMS biotrickling filtration is sensitive to low pH [1,15,16]. Warton and Mattheissen [19], for example, similarly observed enhanced biodegradation of the pesticide metam-sodium by adding calcium carbonate to sand. The authors explained this effect by the interdependence of pH and calcium concentration in enhancing biodegradation. Besides $CaCO_3$, the addition of a vitamin solution also stimulated DMS biodegradation in the thermophilic biotrickling filter. Besides optimizing the composition of the liquid medium in biotrickling filters, it is also important to maintain these optimal conditions during reactor operation. In this study, to avoid pH decreases and accumulation of metabolites, the liquid medium was renewed every 2–7 days. Generally, it is found that a pH >5 should be maintained for optimum DMS removal in both reactors. This is similar as found in previous studies investigating DMS removal in biotrickling filters [15]. After applying the highest DMS loading rates to the reactors, it was suspected that sulfate accumulation caused lower DMS elimination capacities in both reactors. Furthermore, after renewing the media, still a slow recovery occurred, especially in BTF52. Previous studies indicated that sulfate concentrations of 16 g SO_4^{2-} L^{-1} can decrease DMS biodegradation in a mesophilic bioreactor [20]. Batch tests in this study showed that sulfate concentrations exceeding 2.2 g L^{-1} decreased the DMS removal rate for the BTF52 inoculum. So, the thermophilic inoculum appears more sensitive to sulfate accumulation than previously described inocula. As pH and sulfate concentrations in the reactors were adjusted back within the optimal range, recovery was not imme-

diate. It indicates a longer-lasting effect on the DMS degrading microbial communities after the peak loading.

After assessing the effects of medium composition on the performance of the thermophilic reactor, the effect of temperature changes (including periodical shutdowns) on removal efficiency was also investigated. Increasing the temperature to 55 and 59 °C decreased the DMS removal efficiency, and in addition, a relatively long recovery period of 1 day was needed, after returning the temperature to 52 °C. Also Cox et al. [4] reported that ethanol elimination remained constant when the temperature was increased from 53 up to 62 °C but decreased significantly at temperatures above 62 °C. Similarly, Kong et al. [7] found that raising the temperature from 60 to 65 °C stopped the removal of α-pinene in a biotrickling filter. Lowering the reactor operating temperature to 21 °C for 24 h temperature had a greater effect on the DMS removal efficiency (decreased to 10%), but the recovery afterwards at 52 °C was faster (<3 h). After short-term complete shutdowns, without DMS loading or temperature control, a similar recovery period was needed when resuming the operation at BTF52. The recovery of the BTF22 after shutdown was also similar, indicating that the thermophilic microbial community in BTF52 is not more sensitive to shutdowns than its mesophilic counterpart, even when thermophilic temperatures were not maintained during the shutdown. Hence, after accidental or deliberate short-term shutdowns of a similar thermophilic reactor, no long start-up periods are required. However, it is advised to control the temperature during reactor operation near the enrichment temperature of the inoculum (i.e. 52 °C), to guarantee optimal DMS removal. The observation that there is a low but significant (RE 10%) degradation of DMS in BTF52 at 21 °C, shows that there are still some mesophilic DMS degrading bacteria present. Similarly, Cox et al. [4] observed mesophilic, thermotolerant and thermophilic microorganisms in a biotrickling filter at 53 °C, although thermophilic microorganisms were dominating.

Long-term performance of the two reactors was investigated by running the reactors for 9 months. After 7 months of reactor operation, there was evidence for the occurrence of nitrification in BTF22. The pH decrease in BTF22 was faster than expected based on the load of DMS that was removed in that experiment. Moreover, additional measurements indicated stoichiometric conversion of ammonia to nitrate in the liquid medium. A faster pH decrease is not desirable because it will increase the chemical and/or water use needed to keep the pH of the liquid in the optimum range for DMS removal. In addition, nitrifying bacteria will compete for oxygen, nutrients and space, which can reduce the DMS degradation even more. Although nitrifiers can also contribute to DMS degradation [21], their contribution to decreasing the pH will remain problematic. Reduction of nitrification and subsequent pH decrease was accomplished by replacing ammonium by nitrate in the liquid medium in BTF22. In contrast, no proof for the occurrence of nitrification was found in BTF52. This is probably related with suppressed growth of ammonium oxidizers, since their optimal temperature is 22–30 °C [22]. Hence, these results illustrate that operating biotrickling filters at thermophilic conditions can be advantageous, because it suppresses the growth of competing microorganisms, originating from the environment.

5. Conclusion

Our study proves the feasibility of DMS removal in a biotrickling filter from waste gases at temperatures up to 55 °C by using an enriched sludge inoculum. However, compared with a reactor operated at ambient temperatures, a longer EBRT was required (200 s compared with 60 s) to obtain efficient removal (RE > 90%) of DMS in BTF52, at loading rates of $>20\,g\,m^{-3}\,h^{-1}$. The thermophilic bioreactor showed a lower DMS elimination capacity but the performance of the reactor was stable in the long-term. The sulfate concentration of the liquid medium exceeding $2.2\,g\,L^{-1}$ decreased the DMS removal rate in batch. Finally, we showed that the use of tap water or the addition of calcium carbonate to the liquid medium enhanced the removal of DMS in both bioreactors.

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