Research Article

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Treatment performance of volatile organic sulfide compounds by the immobilized microorganisms of B350 group in a biotrickling filter

Shungang Wan,[a,b] Guiying Li[a]* and Taicheng An[a]*

Abstract

BACKGROUND: In this work, the feasibility of biodegradation and the removal performance of sole and mixed odorous vapors, such as dimethyl disulfide (DMDS), methyl phenyl sulfide (MPS), and ethanethiol (EtSH) in an EtSH-acclimated biotrickling filter seeded with commercially available B350 microorganisms, were investigated.

RESULTS: Removal efficiencies (REs) for DMDS as a sole substrate were evaluated under different inlet concentrations and empty bed residence times (EBRT), 100% RE was achieved at concentration below 0.4 g m^{-3} at EBRT 110 s. In addition, 100% RE was obtained for binary EtSH and DMDS (3 : 2) at the same EBRT. According to the Michaelis–Menten type kinetic equation, the maximum removal rates (V_{max}) were calculated as 28.7 and 13.9 g m^{-3} h^{-1} for DMDS and MPS as sole substrate, respectively, while V_{max} was 22.1 and 10.1 g m^{-3} h^{-1} for DMDS and MPS in the presence of EtSH and EtSH-DMDS mixture, respectively. After 5 and 20 days starvation, the re-acclimation times were only 2 and 8 days, respectively, for the binary system. An EtSH : DMDS : MPS (3 : 2 : 1) ternary mixture was removed efficiently by the rebooted system after starvation.

CONCLUSION: The proposed system can be applied to cost-effectively decompose a mixture of volatile organic sulfide compounds at pilot scale.

Keywords: biotrickling filter; ethanethiol; dimethyl disulfide; methyl phenyl sulfide;B350

INTRODUCTION

Odorous compounds, including volatile organic compounds (VOCs),[1,2] volatile fatty acids,[3] H_2S,[4] amines (e.g. trimethylamine and dimethylamine),[5] as well as volatile organic sulfide compounds (VOSCs, e.g. ethanethiol (EtSH), dimethyl disulfide (DMDS) and methanethiol),[6] are emitted mainly from the anaerobic or aerobic decomposition of organic waste in various activities, such as waste and sewage treatment processes,[7] agricultural operations and food industries,[8] and papermaking industry activity.[9] Compared with other organic odorous pollutants, it is noted that a variety of VOSCs are major species of odorous pollutants, and also recognized as important pollutants in air.

The concentrations of VOSCs in gas emissions are usually very dilute, however, they have low odor threshold values; DMDS has the lowest value at 0.10 μg m^{-3} among all odorous compounds.[10] These VOSCs are responsible for complaints because they are detectable by humans at extremely low concentrations. In addition, VOSCs not only reduce the quality of air because of their special odor, but also have negative impacts on human health including headaches, nausea, eye irritation, paralysis, and even death if people are exposed to VOSCs-contaminated air for a long time.[11] Therefore, the demand for odor control systems to provide nuisance-free breathable air is increasing, and various physical, chemical and biological odor abatement technologies have been developed and applied.[12,13] Physical–chemical techniques have proven their efficiency and reliability and will continue to occupy their niche, but several disadvantages remain. Among them, high investment and operating costs, and the possible generation of secondary waste streams are the main drawbacks.[14] Biological techniques have many intrinsic advantages, for example, low cost, high efficiency, good stability and reliability as well as operational simplicity.[13,15] Biological techniques are thus believed to be one of the most economical options for VOSCs removal and have received much attention because of the reduced secondary wastes produced.

* *Correspondence to: Guiying Li and Taicheng An, The State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. E-mail: antc99@gig.ac.cn; ligy1999@gig.ac.cn*

a *The State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

b *Graduate School of Chinese Academy of Sciences, Beijing 100049, China*

Among the biological techniques, the biofilter is one of the earliest developed biological devices for VOCs elimination.[13,16–20] Conventional compost or soil bed biofilters are limited to the elimination of odorous compounds and non-chlorinated VOCs. This is because some environmental conditions, such as pH, humidity and mineral nutrients, cannot be properly controlled in biofilters and potentially toxic dead-end metabolites can inhibit the activity of microorganisms. However, biotrickling filters present a liquid mobile phase inside the bioreactor, which can purge potentially toxic dead-end metabolites from the system, and some other drawbacks of a biofilter can also be overcome simultaneously. Therefore, a wide range of pollutants can potentially be treated by biotrickling filters.

Previously, the biotrickling filter has been studied widely for the control of various odorous compounds.[21–24] However, most studies of the system have been limited to a sole contaminant. However, in general, practical odorous gaseous pollutants are a mixture of various species rather than a single one.[20] Unfortunately, very few publications to date have reported on biofiltration processes in the presence of multiple composition VOSCs using biotrickling filters. In our previous study, a *Lysinibacillus sphaericus* strain RG-1 was isolated from activated sludge, and have the ability to biodegrade EtSH.[25] The performance of a biotrickling filter inoculated with a single strain RG-1 to purify waste gas containing multiple composition VOSCs was investigated.[26] In addition, B350 group microorganisms can also treat waste gas containing EtSH.[27] The biotrickling filter with inoculated strain RG-1 has better removal efficiency for single pollutant EtSH than B350 group microorganisms under the same operating conditions.[27] However, theoretically, compared with a single strain such as RG-1, B350 group microorganisms might have a broader spectrum and an ability to treat multiple composition VOSCs, which can be potentially applied to cost-effectively decompose mixture VOSCs in a pilot scale.

Herein, the main objective is to investigate the feasibility of biodegradation of sole and mixed VOSCs in an EtSH-acclimated biotrickling filter seeded with B350 microorganisms. DMDS, methyl phenyl sulfide (MPS) as sole pollutant, the binary mixture of EtSH and DMDS, as well as the ternary mixture of EtSH, DMDS and MPS were selected as target compounds to be treated. Some factors influencing the biodegradation of selected VOSCs, i.e. the empty bed residence time (EBRT), inlet concentration of pollutants and the mixing ratio have been investigated in detail. To understand the kinetic behavior of the biotrickling filter, a Michaelis–Menten type kinetic equation was applied to obtain the kinetic constants maximum removal rate (V_{max}) and half saturation concentration (K_m). Long-term stable operation and rebooting of the biotrickling filter were also investigated. The experimental results obtained here can provide useful information concerning the design criteria and operating criteria for controlling single DMDS, EtSH/DMDS or EtSH/DMDS/MPS mixed gas at pilot scale. The results strongly support the application of the biotrickling filter to purify waste gas containing odorous multi-pollutants released from industrial processes.

MATERIALS AND METHODS

Microorganisms and culture medium

The B350 containing 28 species of microorganisms, cellulase, amylase, and hydrolase was purchased from Bio-System Co., USA. DMDS (99.5%, Tianjin, China), EtSH and MPS (99+%, Acros, Geel, Belgium) were used as carbon sources and energy sources. All other chemicals were analytical grade reagents, and obtained from Guangzhou Chemical Reagent Co., Inc., China. In all experiments, an inflow medium was provided from a nutrient tank which contained (g L^{-1}): 1.20 $K_2HPO_4{\cdot}3H_2O$, 1.20 KH_2PO_4, 0.20 $MgSO_4{\cdot}7H_2O$, 0.40 NH_4Cl, 0.01 $FeSO_4{\cdot}7H_2O$, and 1.0 mL of trace element stock solution as previously described.[27]

System setup

All biodegradation experiments were performed using an EtSH-acclimated biotrickling filter packed with ceramic particles and seeded with B350 microorganisms. A schematic diagram of the system is given in our previous report.[27] The whole system consisted of a gas source, mixing gas tank, a gas flow rate control unit, a waste gas treatment unit (biotrickling filter), nutrient recirculation unit and waste gas adsorption unit. The biotrickling filter was made from a transparent rigid Plexiglas tube with an inner diameter of 140 mm and a height of 1200 mm. The column of the biotrickling filter was divided into six equal-height layers, each layer being filled to a height of 100 mm with an equal amount of ceramic particles. To support the filter-bed and to ensure homogeneous distribution of the input gas and liquid, a Plexiglas mesh was installed at the base of each layer. Seven ports were located along the column at fixed interval of 150 mm for gas sampling and pressure measurement. The difference from the previous experiment is that each VOSC has its own reservoir in this study. The EtSH, DMDS and MPS vapors supplied from separate VOSCs reservoirs were diluted with compressed air and flowed downwards from the top of the biotrickling filter. Nutrient medium was intermittently sprayed over the bed upper surface at a rate of 7.5 L h^{-1} for 10 min 16 times a day to not only maintain an adequate level of bed filling moisture content and provide the necessary nutrients for bacterial growth, but also to remove excess biomass from the biotrickling filter. The effluent nutrient medium from bioreactor was collected in the lower water tank, then pumped to the upper water tank and cycled by peristaltic pumps. The biotrickling filter was usually allowed to stabilize for 24 h after adjusting the inlet concentration of pollutants or when changing EBRT, and to then take gas samples from different ports to determine the performance of the biotrickling filter in the next 48 h (or longer) period of time. In order to dismiss nutrient medium physical absorption effects in removal efficiency (RE) and elimination capacity (EC) evaluation, the gas samples were collected after 20 min spraying of nutrient medium. All parameters and operating conditions are summarized in Table 1.

Analytical methods

EtSH, DMDS and MPS concentrations (g m^{-3}; the unit can be converted to ppmv using the equation described in http://www.ppmv.org/) were determined using an HP 5890 gas chromatography equipped with an HP-5 MS capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. The temperatures of the injector and detector were 280 and 300 °C, respectively. The oven temperature was programmed to hold at 80 °C for 2 min, and increase from 80 to 150 °C at 10 °C min^{-1}. A 300 μL gas sample was collected at regular intervals from the inlet and outlet of the different layers along the column using a 500 μL airtight syringe (Agilent), and injected into the column for concentration determination in the splitless mode. In addition, to obtain data correctly, each gas sample concentration was determined for three replicates. Ceramic particles (*ca* 50 g) were withdrawn from the biotrickling filter and used for determination

Table 1. Biotrickling filter operating conditions

Filtering medium	Ceramic particles (moisture content: 15–25%; pile density: 0.75–1.10 g cm^{-3}; particle diameter: 4–6 mm; BET surface area: 2–5 × 10^4 cm^2 g^{-1}; maximum porosity volume for pile: no less than 36%)
Pollutant	EtSH, DMDS, MPS
Packing bed height	100 mm × 6 layers
Column diameter	Inner diameter of 140 mm
Volume of the packing materials	9.23 L
Microorganisms	B350 group microorganisms
Inlet ethanethiol concentration	0.6 g m^{-3}
Inlet DMDS concentration	0.3–1.0 g m^{-3}
Inlet thioanisole concentration	0.1–0.5 g m^{-3}
Airflow rate	100–500 L h^{-1}
EBRT	66–332 s

of the mass of biofilm (expressed in mg per gram of dry ceramic particles) with weight loss as described by Arnaiz *et al*.[28] Pressure drops across the biotrickling filter were measured by a U-tube pressure meter with a minimum reading of 1 mm water column. The optimal pH value is approximated 7.0 for growth and reproduction of microorganisms. Thus, the pH of the nutrient solution was re-adjusted to 7.0 with 0.1 mol L^{-1} NaOH.

Calculation of removal efficiency, inlet load and elimination capacity

The performance of the biotrickling filter was evaluated in terms of the RE (%), inlet load (IL, g m^{-3} h^{-1}) and elimination capacity (EC, g m^{-3} h^{-1})) as described in our previously published papers.[26,27]

RESULTS AND DISCUSSION

Effect of EBRT on bioreactor performance for DMDS

When DMDS was supplied as sole carbon and energy source for B350 microorganisms in the EtSH-acclimated biotrickling filter, the effect of EBRT on treatment performance was investigated at fixed EBRT 332, 166, 110, 83 and 66 s (corresponding to flow rate 100, 200, 300, 400, and 500 L h^{-1}, respectively), at a fixed inlet DMDS concentration of 1.0 g m^{-3}. As shown in Fig. 1(a), the DMDS concentration at the outlets dropped gradually as the distance from the inlet was increased. Total REs of 100% were achieved at EBRT 332 and 166 s as the DMDS gas pass through the first fifth and sixth layers of the biotrickling filter, respectively, and more than 64.4% DMDS was removed by the first three layers of the biotrickling filter. With further shortening the EBRT from 110 to 66 s, the total and first three layers REs decreased from 87.1 and 53.0% to 50.2 and 29.8%, respectively. This proved that EBRT is an important parameter in the application of the biotrickling filtration. Comparatively, the REs of DMDS were larger than those of EtSH as sole substrate in the biotrickling filter seeded with B350 as reported earlier.[27] For instance, REs were 87.1 and 73.2% for DMDS and EtSH, respectively, at EBRT 110 s.

The biotrickling filter performance was also evaluated in terms of the ECs for various inlet loads (Fig. 1(b)). As the EBRT was reduced from 332 to 110 s, total ECs of the layers 1–3 and 4–6 increased from 8.70 to 17.0 g m^{-3} h^{-1} and from 2.69 to 10.96 g m^{-3} h^{-1}, respectively. It is worth noting that the total ECs of layers 4–6 were much lower than those of layers 1–3. This is because the system was operated in a down-flow mode, and a large quantity of gaseous DMDS was eliminated in the first three layers before passing through the remaining three layers. With EBRT further decreased to 83 s, the total ECs of the first three and the last 3 layers increased gradually to 17.6 and (maximum) 13.6 g m^{-3} h^{-1}. With further decrease of EBRT to 66 s, the total ECs of layers 1–3 reached a peak of 17.6 g m^{-3} h^{-1}, and that of layers 4–6 fell slightly to 12.0 g m^{-3} h^{-1}. In addition, it is clear that the total ECs of layers 1–6 increased abruptly from 11.4 to 28.0 g m^{-3} h^{-1}, and reached its maximum of 31.2 g m^{-3} h^{-1} with RE of 72.5% at EBRT of 83 s. The declining EC at decreasing EBRT can be explained by the change from mass transfer rate-controlled to reaction rate-controlled.

Generally, REs always decreased with decrease of EBRT at fixed inlet concentration for microorganisms to purify waste gas. This is because the REs for the biotrickling filter are controlled by mass transfer of DMDS from air to the biofilm, which, in turn, is controlled by the EBRT.[29] A longer EBRT results in higher REs because of adequate time for microorganisms to completely

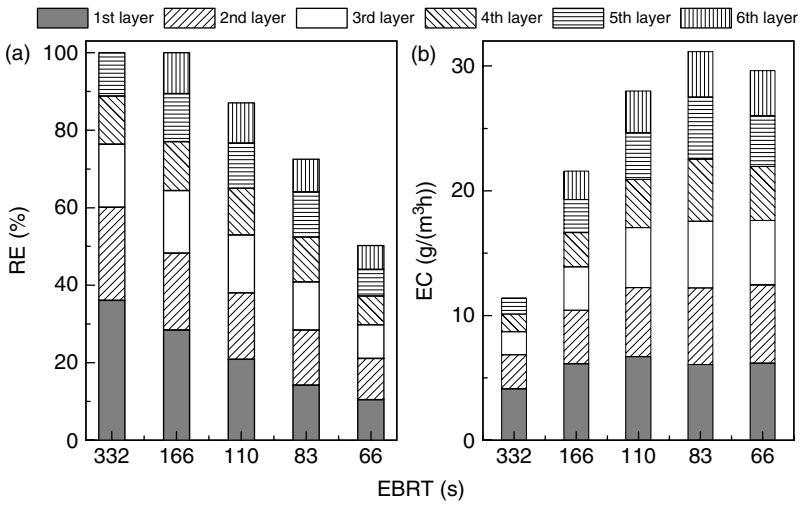

Figure 1. (a) REs and (b) ECs at different EBRTs and fixed DMDS inlet concentration 1.0 g m^{-3}.

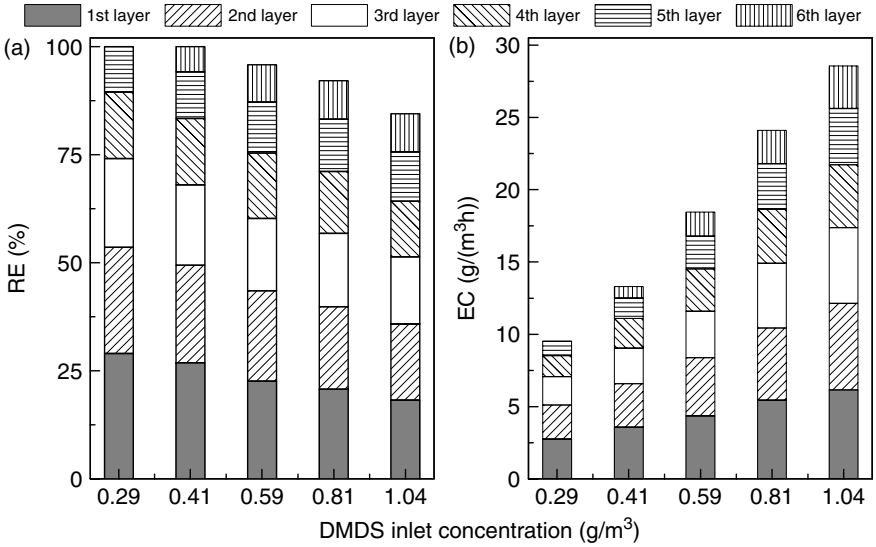

Figure 2. (a) REs and (b) ECs of biotrickling filter inoculated with B350 at different DMDS inlet concentrations and fixed EBRT 110 s.

biodegrade DMDS entering the biofilm. In the case of shorter EBRTs, REs were very low owing to the short residence time of DMDS at the biofilm. Thus, microorganisms had insufficient time to perform the required degradation on the available amount of DMDS, and similar results have been found in previously published works[23,30] It is noteworthy that the biotrickling filter is an open system and that air was continuously fed into the bioreactor. Although the oxygen solubility may be very low in the liquid, it should be noted that oxygen transfer is a dynamic balance between the gas phase and the biofilm. Thus, oxygen should be sufficient for the microorganisms to degrade DMDS and for their own growth.

Effect of inlet concentration on bioreactor performance for DMDS

The effect of inlet DMDS concentration on biodegradation performance was investigated at a fixed EBRT of 110 s. As shown in Fig. 2(a), REs of 100% were obtained at inlet concentrations of 0.29 and 0.41 g m^{-3} as the waste gas passed through the 5th and 6th layer of the column, respectively. When the concentration was increased to 0.59 and 1.04 g m^{-3}, the biotrickling filter responded with an accumulation of DMDS at the outlets, and the total REs gradually decreased to 95.8 and 84.4%, respectively, indicating that RE is a decreasing function of the inlet concentration. In fact, increase of the inlet DMDS concentration has two effects; one is to enhance the transfer rate of DMDS to the biofilm, the other is to inhibit the metabolic activity of the microbial population.

The relationship between ECs and inlet concentrations is shown in Fig. 2(b). As inlet concentration was increased from 0.29 to 1.04 g m^{-3}, the total ECs of layers 1–3 and 4–6 increased steadily from 7.1 to 17.4 g m^{-3} h^{-1} and from 2.5 to 11.2 g m^{-3} h^{-1}, respectively. The total ECs always increased with increase of inlet concentration or inlet loading. At a concentration of 0.29 g m^{-3}, the total EC was only 9.5 g m^{-3} h^{-1}, while total EC increased to 28.6 g m^{-3} h^{-1} as inlet concentration was further increased to 1.04 g m^{-3}. When the inlet concentrations were greater than 0.41 g m^{-3}, the REs and ECs of B350 in this system were slightly lower than those obtained in an identical biotrickling filter seeded with strain RG-1.[26] For instance, RE and EC were 92.1% and 24.1 g m^{-3} h^{-1}, respectively, for B350 microorganisms, and 100% and 26.2 g m^{-3} h^{-1} for strain RG-1. In addition, Ho *et al.*[31] used a biofilter packed with granular activated carbon to eliminate DMDS, and obtained EC_{max} of 5.0 g m^{-3} h^{-1}. A much higher EC_{max} of 13.3 g m^{-3} h^{-1} (RE=100%) for DMDS was achieved in this present study at an inlet concentration 0.41 g m^{-3} and EBRT 110 s.

The results demonstrate that RE and EC are dependent on the inlet concentration. Generally, biodegradation includes two main processes; diffusion of the substrate from gas to biofilm and subsequent degradation within the biofilm by the microorganisms[32,33] The REs and ECs may be controlled by diffusion limitation or reaction limitation.[34] When the inlet concentration is below the optimal concentration, the biodegradation can be described as a diffusion-limited regime. Increase of the inlet concentration at fixed EBRT can enhance the transfer rate of substrates from gas to biofilm so that more microorganisms participate in the biodegradation activity. Therefore, 100% REs remain constant and ECs are increased with increase of inlet concentration with a diffusion-limited regime. As the inlet concentration increases further, above the upper limit of the diffusion-limited regime, higher concentration gradients are produced, which transfer more pollutants to the biofilm, resulting in reaction limitation. With a reaction-limited regime, the bacterial activity becomes the limiting step to the elimination of pollutants. Therefore, a decrease in REs and slight increase in ECs were found as reaction limitation occurred. This confirms the viewpoint that inlet concentration is also a significant limiting parameter in the application of biotrickling filters.[23]

Removal of a mixture of EtSH and DMDS

The biotrickling filter inoculated with B350 was used mainly to purify waste gas containing EtSH and the concentration was optimized at 0.60 g m^{-3} at EBRT 110 s, as described in our previous paper.[27] Simultaneously, it has been proved that the same biotrickling filter acclimated with EtSH has the ability to biodegrade DMDS as described above. Thus, to investigate the effect of a co-substrate with DMDS on the performance of the biotrickling filter, the inlet concentration 0.60 g m^{-3} EtSH was maintained constant throughout a test with step-increases of DMDS from 0.20 to 0.81 g m^{-3}. Outlet concentrations of EtSH and DMDS were measured after steady operation for 24 h at a fixed DMDS concentration. The REs and ECs for different ratios of EtSH

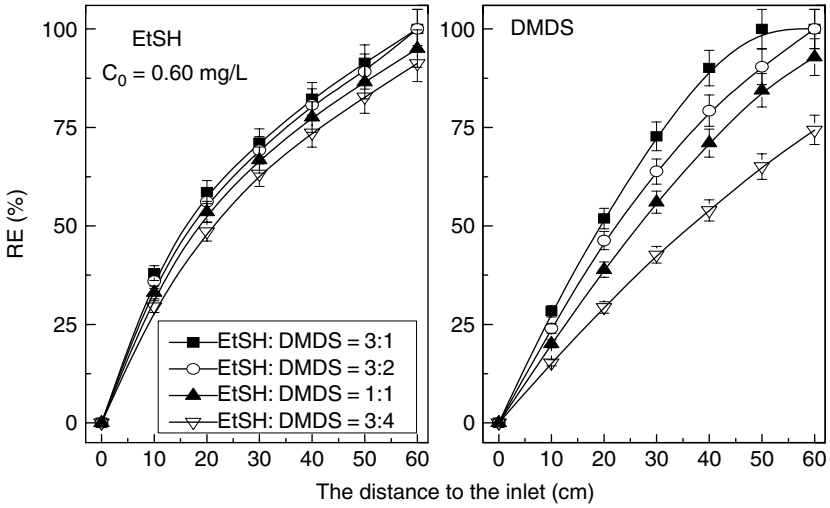

Figure 3. REs of the mixture of EtSH and DMDS at different concentration ratios.

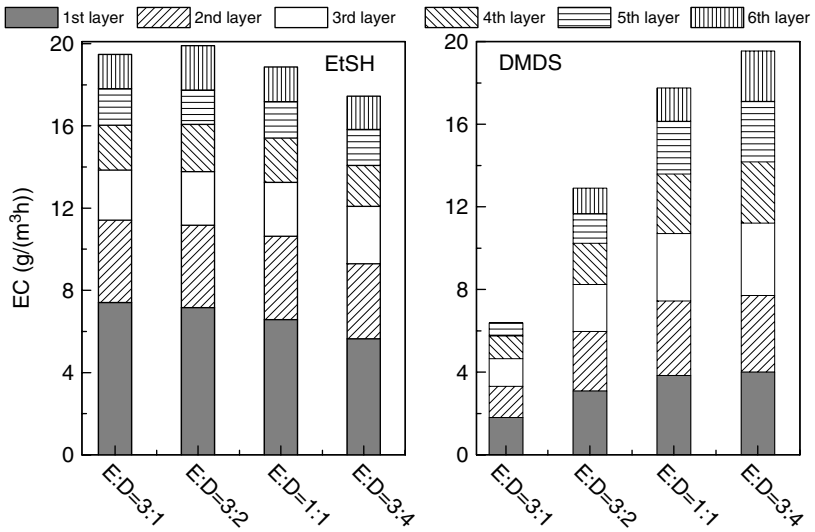

Figure 4. ECs of the mixture of EtSH and DMDS at different concentration ratios (EtSH : DMDS=E : D).

to DMDS at fixed EBRT 110 s are illustrated in Figs 3 and 4, respectively. Overall, higher EtSH and DMDS REs were obtained at lower concentrations of DMDS, while higher concentrations of DMDS led to lower REs. For DMDS, 100% REs were obtained at DMDS concentrations below 0.40 g m^{-3}. As inlet DMDS concentration was increased to 0.59 g m^{-3}, RE slightly decreased to 92.9%. With further increase of DMDS concentration, an abrupt drop in total RE was observed; for example, to 74.4% at 0.81 g m^{-3} DMDS. These results indicate that the REs of DMDS were dramatically affected by the presence of EtSH. The REs of EtSH decreased from 100 to 91.2% as DMDS concentration was increased from 0.20 to 0.81 g m^{-3}, thus the changes obtained for the REs of EtSH in the presence of DMDS were much less significant.

The ECs of EtSH and DMDS at different ratios are shown in Fig. 4. The total ECs of EtSH were maintained nearly constant (19.5, 19.9, 18.9 and 17.4 g m^{-3} h^{-1}) throughout as DMDS concentration was increased from 0.20 to 0.81 g m^{-3}. Arellano-García *et al.*[21] reported that the maximum EC was only 3.7 g m^{-3} h^{-1} with RE of 50% for EtSH in a biotrickling filter seeded with alkaliphilic sulfo-oxidizing bacteria under alkaline conditions. Compared with this study, the ceramic particles biotrickling filter inoculated with B350 can more effectively eliminate EtSH (EC >17.4 g m^{-3} h^{-1} and RE >91.2%) at EBRT 110 s. In contrast, the total ECs for DMDS increased swiftly from 6.4 to 17.8 g m^{-3} h^{-1} with increase of inlet concentration from 0.20 to 0.59 g m^{-3}. As concentration was further increased to 0.81 g m^{-3}, total EC increased slightly to 19.5 g m^{-3} h^{-1}. As described above, reaction limitation may occur as the inlet pollutants loading exceeds the diffusion limitation regime. Thus, RE always decreased with increasing DMDS concentration, and ECs may slightly increase or remain constant. According to the changes of RE and EC, the optimal ratio of EtSH to DMDS in a mixed gas was 3 : 2 for B350 at fixed EBRT 110 s, which is larger than the optimal ratio 1 : 1 obtained with the identical parallel biotrickling filter seeded with strain RG-1 under the same operating conditions.[26] The performance of the biotrickling filter seeded with B350 was good for the removal of a mixture of EtSH and DMDS as discussed above.

Effect of EBRT on bioreactor performance

The effect of EBRT on the treatment of a mixed gas of EtSH and DMDS was investigated with EBRT ranged from 110 to 66 s at a

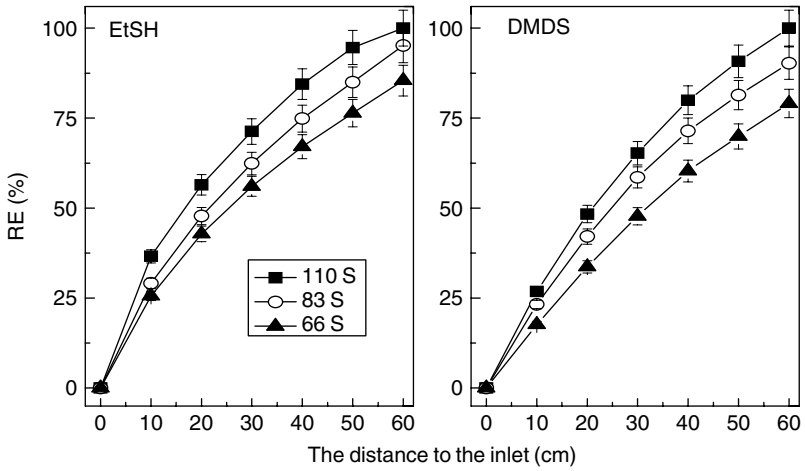

Figure 5. RE for EtSH and DMDS at fixed ratio (3 : 2) at different EBRTs.

Table 2. Total ECs and REs of binary mixture of EtSH and DMDS with different EBRT at fixed ratios

Inlet concentration (gm^{-3})	EBRT (s)	Inlet loading ($g\ m^{-3}\ h^{-1}$)	EC ($g\ m^{-3}\ h^{-1}$)	RE (%)
EtSH				
0.61(E : D*=3 : 2)	110	19.8	19.8	100
0.59(E : D=3 : 2)	83	25.5	24.3	95.2
0.63(E : D=3 : 2)	66	34.0	29.0	85.4
DMDS				
0.41(E : D=3 : 2)	110	13.4	13.4	100
0.39(E : D=3 : 2)	83	17.0	15.3	90.2
0.42(E : D=(3 : 2)	66	22.6	17.9	79.1

* : EtSH : DMDS.

fixed ratio of EtSH to DMDS ($0.60\ g\ m^{-3}$:$0.40\ g\ m^{-3}$ =3 : 2). As shown in Fig. 5, RE decreased from 100 to 85.4% for EtSH and to 79.1% for DMDS as the EBRT was shortened from 110 to 66 s. RE decreased more abrupt for DMDS. Greater than 50% EtSH and 45% DMDS were degraded by layers 1–3 at EBRT shortened to 66 s. Total ECs of EtSH and DMDS are listed in Table 2. They were increased from 19.8 to 29.0 $g\ m^{-3}\ h^{-1}$ for EtSH, and from 13.4 to 17.9 $g\ m^{-3}\ h^{-1}$ for DMDS with decrease of EBRT from 110 to 66 s. Overall, REs of EtSH and DMDS always decreased with decreasing EBRT at a fixed ratio of EtSH to DMDS.

As described, the increase in inlet loaded pollutants can enhance their transfer rate from the gas to the biofilm and thus more microorganisms may participate in the biodegradation activity at short EBRT. When the inlet loading exceeds the microorganisms' biodegradation ability, reaction limitation may occur. Thus, the biodegradation reaction becomes the most important step. Total REs of EtSH and DMDS gradually decrease with the amount of EtSH and DMDS transferred to the biofilm with decreasing EBRT, leading to a slight increase in ECs for the gas mixture of EtSH and DMDS.

Removal of ternary mixture of EtSH, DMDS and MPS

To investigate the application of the biotrickling filter to the degradation of other pollutants a third pollutant, MPS instead of a mixture of EtSH and DMDS was supplied to the biotrickling filter. The effect of inlet concentration on biodegradation was investigated for MPS concentrations within the range 0.10 to 0.50 $g\ m^{-3}$ at a fixed EBRT of 110 s. The REs and ECs of B350 in total and for each layer at different inlet concentrations is plotted in Fig. 6. From Fig. 6(a), it can be seen that REs of 100% were obtained after passing the first four layers at an inlet MPS concentration of 0.13 $g\ m^{-3}$, and after the first five layers at 0.23 $g\ m^{-3}$. When the inlet concentration was increased to 0.33 and 0.51 $g\ m^{-3}$, the biotrickling filter responded with an accumulation of MPS at the outlet of the 6th layer, and total REs decreased to 95.1 and 78.2%, respectively. The ECs of MPS as sole substrate for each layer and for the total layer are plotted against inlet concentrations in Fig. 6(b). As inlet concentrations was increased from 0.13 to 0.51 $g\ m^{-3}$, the ECs of layers 1–3 and 4–6 increased from 3.6 to 8.0 $g\ m^{-3}\ h^{-1}$ and from 0.5 to 5.0 $g\ m^{-3}\ h^{-1}$, respectively. Total ECs steadily increased from 4.2 to 13.0 $g\ m^{-3}\ h^{-1}$ with increasing inlet concentration. These results show that the biotrickling filter can effectively purify waste gas containing solely EtSH and DMDS, mixtures of EtSH and DMDS, and also solely MPS.

Hence, co-treatment of a ternary mixture of EtSH, DMDS and MPS by B350 was also conducted to further evaluate the performance of the biotrickling filter. All experiments were performed in a gaseous mixture containing fixed inlet concentrations of EtSH ($0.60\ g\ m^{-3}$) and DMDS ($0.40\ g\ m^{-3}$), with MPS concentrations ranging from 0.12 to 0.51 $g\ m^{-3}$ at a fixed EBRT of 110 s.

REs of EtSH, DMDS and MPS at different mixture ratios are plotted in Fig. 7. 100% REs for EtSH were obtained at inlet MPS concentrations less than 0.29 $g\ m^{-3}$, then RE dropped to 91.5% at 0.51 $g\ m^{-3}$. A similar degradation trend was also observed for DMDS. 100% REs of DMDS were achieved at MPS concentrations below 0.29 $g\ m^{-3}$. By comparison, 100% REs of MPS was obtained only at inlet concentrations less than 0.19 $g\ m^{-3}$. When MPS inlet concentration was increased to 0.51 $g\ m^{-3}$, the RE of MPS dropped dramatically to 51.6%. Obviously, the REs of EtSH and DMDS were hardly affected by the coexisting MPS under the same treatment conditions when the MPS concentration was less than 0.29 $g\ m^{-3}$. However, the co-existence of EtSH and DMDS affected the RE of MPS more noticeably under the same treatment conditions. Interestingly, the trend in REs for a ternary mixture of EtSH, DMDS and MPS using B350 is similar to those for RG-1,[26] although specific data indicated a clear distinction between B350 group microorganisms and single strain RG-1. For example, 100% REs were achieved at EtSH : DMDS : MPS=6 : 4 : 1,

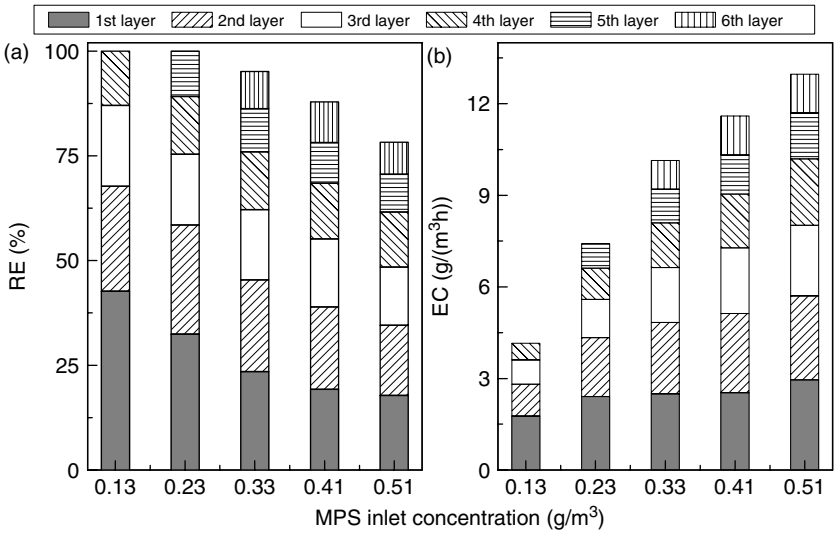

Figure 6. (a) REs and (b) ECs of biotrickling filter at different inlet concentrations of MPS at fixed EBRT 110 s.

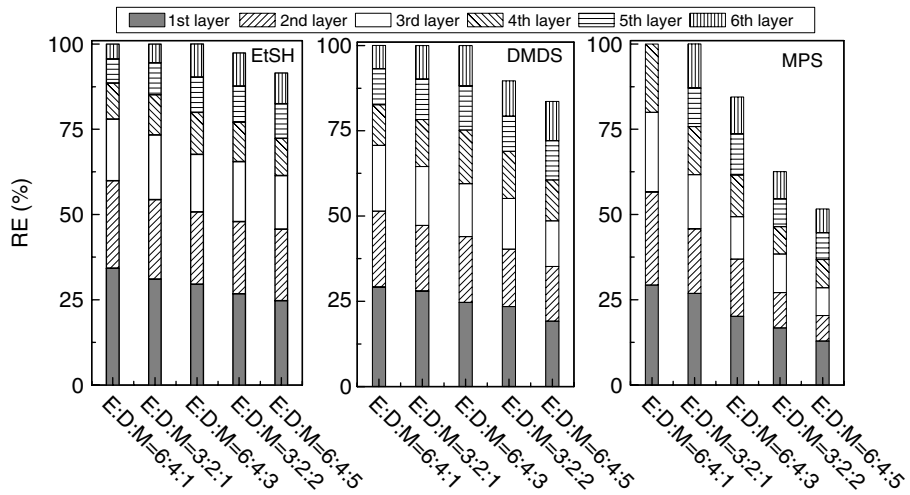

Figure 7. REs of ternary mixture of EtSH, DMDS and MPS at different ratios (EtSH : DMDS: MPS=E : D : M).

3 : 2 : 1 and 6 : 4 : 3 for B350, whereas 100% REs were achieved at EtSH : DMDS : MPS=6 : 4 : 1, 3 : 2 : 1, 6 : 4 : 3 and 3 : 2 : 2 for strain RG-1. It seems that the strain RG-1 is better for the purification of waste gas than B350. However, both have the same optimal ratio as EtSH : DMDS : MPS=3 : 2 : 1.

Total ECs of EtSH, DMDS and MPS at different inlet concentrations are listed in Table 3. Total ECs of EtSH and DMDS remain almost constant near their inlet concentrations, such as 0.6 and 0.4 g m^{-3} for EtSH and DMDS, respectively, with increase in MPS concentration from 0.12 to 0.51 g m^{-3}. In contrast, for MPS, total ECs increased gradually from 3.8 to 8.1 g m^{-3} h^{-1} with increasing MPS inlet concentration from 0.12 to 0.29 g m^{-3}. As concentration was further increased to 0.51 g m^{-3}, total ECs increased very slightly to 8.6 g m^{-3} h^{-1}. The possible reason is the same as explained previously. Briefly, the mass transfer of three compounds from gas phase to biofilm is not a rate determining step of the process and the REs and ECs of the ternary mixture were mainly limited by the biochemical reaction within the biofilm. Thus, according to REs and ECs, the optimal concentration ratio was 3 : 2 : 1 for the ternary mixture of EtSH, DMDS and MPS at a fixed EBRT of 110 s.

Biodegradation kinetics for single, binary and ternary mixture gas

The kinetics parameters need to be calculated to fully understand the kinetic behavior of the biotrickling filter. In this study, macrokinetic determination was calculated according to the following equation derived from the Michaelis–Menten equation as described by Wani *et al*.:[35]

$$(V/Q)/(C_0 - C_e) = K_m/(V_{max}C_{ln}) + 1/V_{max} \quad (1)$$

where V_{max} is maximum removal rate, K_m refers to saturation constant (g m^{-3}) and C_{ln} represents the natural logarithm mean concentration($(C_0 - C_e)/\ln(C_0/C_e)$). From the linear relationship between $1/C_{ln}$ and $(V/Q)/(C_0 - C_e)$, V_{max} and K_m were calculated from the intercept and slope, respectively. In addition, the Michaelis–Menten Equation (1) has also been applied to determine the kinetics constants in other work.[36,37]

The V_{max} and K_m for EtSH, DMDS, and MPS either alone or as a mixed gas supply were calculated over the first five layers of the biotrickling filter by the biodegradation kinetic analysis as shown in Table 4. The V_{max} values were 28.7 and 13.9 g m^{-3} h^{-1}, and

Table 3. Total REs and ECs of ternary mixture gas of EtSH, DMDS and MPS with different ratios at fixed EBRT 110 s

Inlet concentration (g m^{-3})	Inlet loading (g m^{-3} h^{-1})	EC (g m^{-3} h^{-1})	RE (%)
EtSH			
0.60 (E:D:M* = 6:4:1)	19.6	19.6	100
0.59 (E:D:M = 3:2:1)	19.3	19.3	100
0.63 (E:D:M = 6:4:3)	20.3	20.3	100
0.61 (E:D:M = 3:2:2)	19.9	19.4	97.4
0.61 (E:D:M = 6:4:5)	19.8	18.1	91.5
DMDS			
0.39 (E:D:M = 6:4:1)	12.8	12.8	100
0.41 (E:D:M = 3:2:1)	13.2	13.2	100
0.39 (E:D:M = 6:4:3)	12.6	12.6	100
0.42 (E:D:M = 3:2:2)	13.7	12.3	89.7
0.41 (E:D:M = 6:4:5)	13.2	11.0	83.6
MPS			
0.12 (E:D:M = 6:4:1)	3.8	3.8	100
0.19 (E:D:M = 3:2:1)	6.3	6.3	100
0.29 (E:D:M = 6:4:3)	9.5	8.1	84.4
0.41 (E:D:M = 3:2:2)	13.3	8.4	62.6
0.51 (E:D:M = 6:4:5)	16.5	8.6	51.6

* : EtSH : DMDS : MPS

K_m were calculated as 0.08 and 0.03 g m^{-3} for DMDS and MPS according to the regression equation, respectively. In addition, the linear regression equation was $y = 0.0044x + 0.0317$ ($R^2 = 0.884$) for EtSH as sole substrate, so the V_{max} and K_m values were calculated as 31.6 g m^{-3} h^{-1} and 0.14 g m^{-3} for EtSH according to our previous study.[27] Obviously, the maximum removal rates of B350 were almost the same for EtSH and DMDS, but were much larger than that for MPS, which agreed well with the experimental results described above. Comparatively, V_{max} and K_m of DMDS were only 22.1 g m^{-3} h^{-1} and 0.062 g m^{-3}, respectively, in the binary system. In the ternary system, the V_{max} and K_m of MPS were 10.1 g m^{-3} h^{-1} and 0.042 g m^{-3} at fixed concentrations of EtSH and DMDS, respectively. Obviously, the V_{max} of DMDS and MPS in the mixture system were much less than those in the single gas system. The probable reason for this is that additional carbon source is available from EtSH, or the mixture of EtSH and DMDS. EtSH may be first biodegraded and then DMDS for the binary EtSH and DMDS, thus, the V_{max} of DMDS decreased from 28.7 to 22.1 g m^{-3} h^{-1}. Moreover, EtSH and DMDS were first utilized by B350 in the ternary EtSH, DMDS and MPS. This indicated that the presence of EtSH and DMDS may weaken the binding ability of the enzyme with MPS. However, the binding ability of the enzyme with pollutants is not the most important factor during the biodegradation process. The total maximum ECs can reach 32.8 and 38.8 g m^{-3} h^{-1} for the binary and the ternary mixture, respectively, at the optimal concentration ratio. The total ECs of the mixture were larger than those of any sole pollutant at optimal conditions. Considering all the relevant data, no significant inhibitory effect of the binary and ternary mixture gas was observed at the optimal ratios under the present experiment conditions.

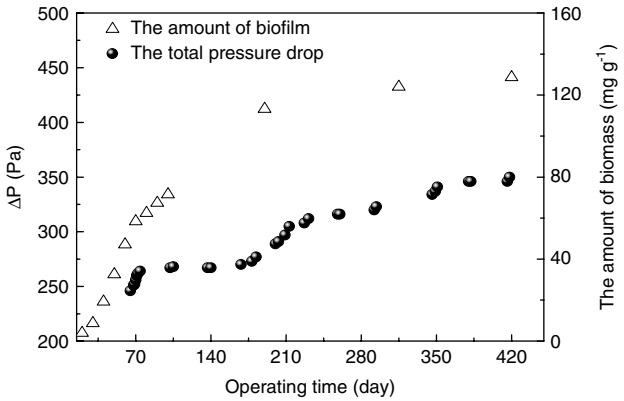

Figure 8. Development of the amount of biomass and the total pressure drop across the biotrickling filter bed with increase of operating time at fixed EBRT 110 s.

Long-term performance of the biotrickling filter

The pressure drop (Δp) across a biotrickling filter is a key indicator of its performance, because it relates to the growth and accumulation of biomass. In this work, therefore, long-term (over 1 year) performance of the biotrickling filter was investigated by measuring the pressure drop and the biomass amount at a fixed EBRT of 110 s. As shown in Fig. 8, the total pressure drop in the bioreactor increased gradually from 8 Pa (without the microorganisms) to 350 Pa (with the microorganisms) during the 420 days operating period. This can be attributed to the multiplication of microorganisms with EtSH, DMDS and MPS feeding, which might minimize the external porosity of the ceramic particles and lead to the increase in pressure drop as the operating time is increased. The biomass amounts increased dramatically from 0 to 71.8 mg g^{-1} during the first 100 days operation, and then only slightly to 113.2 and 128.6 mg g^{-1} on the 190th and 420th day, respectively. Comparatively, the maximum pressure drop and biomass obtained in this study were less than those in the biotrickling filter inoculated with strain RG-1[26]. Hoehn and Ray[38] reported that the density of biofilm grew from 20 to

Table 4. Degradation kinetic parameters V_{max} and K_m

Operating condition	Odor	Linear regression equation	R^2	Kinetic parameter	
				V_{max} (g m^{-3} h^{-1})	K_m (g m^{-3})
Single substrate	EtSH	$y = 0.0044x + 0.0317$	0.884	31.6	0.139
	DMDS	$y = 0.0028x + 0.0348$	0.891	28.7	0.080
	MPS	$y = 0.0017x + 0.0720$	0.905	13.9	0.024
EtSH-DMDS mixture	DMDS	$y = 0.0028x + 0.0453$	0.981	22.1	0.062
EtSH-DMDS-MPS mixture	MPS	$y = 0.0042x + 0.0991$	0.944	10.1	0.042

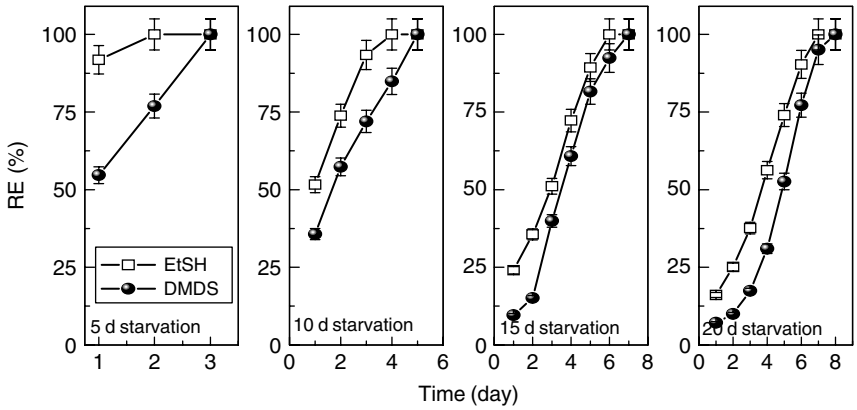

Figure 9. Re-acclimation period after various starvation periods. EBRT: 110 s; EtSH: 0.6 g m^{-3}; DMDS: 0.4 g m^{-3}.

105 mg cm^{-3} when the biofilm thickness increased from 30 to 1300 μm. Generally, the average diameter of raw ceramic particles is 4.42 ± 0.94 mm and contains an average 10 particles g^{-1}. On the assumption that the average density of biofilm was 62.5 mg cm^{-3}, the thickness of B350 biofilm was calculated to be 99, 209 and 421 μm on the 20th, 30th and 40th day, respectively, as described in previous literature.[27] When the operating time was further increased from 50 to 420 days, the biomass increased from 32.6 to 128.6 mg g^{-1}, and the biofilm thickness grew from 647 to 1711 μm, respectively. However, no clogging or aging problems were encountered during the long operating period. The low pressure drop and long-term stability of the biotrickling filter was attributed mainly to good selection for mechanical strength and the appropriate size of the ceramic particles. The dead microbial cells in the ceramic particles bed were constantly washed out from the biotrickling filter by the periodically introduced nutrient solution.

In addition, 100% RE can be achieved for EtSH at an inlet concentration 0.6 g m^{-3} and EBRT of 110 s for all runs of 420 days. Also, EtSH can be completely removed from the binary mixture of EtSH and DMDS at ratio 3 : 2 as well as the ternary mixture of EtSH, DMDS and MPS at ratio 3 : 2 : 1. Overall, the REs remain constant with increase of pressure drop and operating time. Thus, it can be concluded that the long-term VOSCs removal performance (420 days) of the biotrickling filter was very stable.

Biotrickling filter re-acclimation

The performance of a biotrickling filter is usually studied under relatively ideal conditions, such as steady-state operation and the presence of a single pollutant in a laboratory system. However, operational problems undetected in the laboratory may occur when a pilot scale biotrickling filter is operated in industrial settings. In particular, repeated periods of nonuse were identified as one of the factors that caused lower pollutant elimination in the field, preventing the establishment of a dense process culture in the reactor.[39] The pollutant starvation period may be caused by interruptions in the plant operation, such as weekend shutdown and equipment upgrades, which can often lead to temporary lack of feed of waste gas or nutrient medium in real industrial operations.[23] Clearly, understanding the phenomena occurring in the absence of pollutant feed and characterization of the recovery of biotrickling filter performance when resuming normal operation are important for the successful deployment of biotrickling filters.

In the present study, to investigate the possible problems of sudden starvation for the long-term performance of the biotrickling filter, a series of deliberate starvation experiments (at 258 and 346 days) were investigated. During starvation, air without carbon source, such as EtSH or DMDS, was supplied. Then waste gas containing EtSH (*ca* 0.60 g m^{-3}) and DMDS (*ca* 0.40 g m^{-3}) was fed to the biotrickling filter bed at EBRT 110 s after starvation for 5, 10, 15 and 20 days. The effect of starvation was determined by comparing the REs of EtSH and DMDS before and after various starvation intervals. Figure 9 demonstrates the re-acclimation profiles of REs for EtSH and DMDS after restarting at the standard operating conditions for several starvation intervals. Clearly, the RE of EtSH is much higher than that of DMDS during the re-acclimation period after starvation, although the initial RE of EtSH and DMDS decrease gradually with increase of the starvation period. For instance, the REs were 91.8 and 54.7% for EtSH and DMDS, respectively, on the 1st day after 5 days starvation. In addition, for EtSH, 100% REs were obtained on the 2nd, 4th, 6th and 7th day after 5, 10, 15 and 20 days starvation, respectively. Comparatively, 100% REs for DMDS were achieved on the 3rd, 5th, 7th and 8th day under the same experiment conditions. It was also found that the REs were low during the first part of the re-acclimation period, and then increased more sharply with increasing re-acclimation period after longer starvation times.

From these re-acclimation experiments, it was found that a specific feeding time was needed for the biotrickling filter inoculated with B350 to reach its full RE as before starvation. The probable explanation is that a significant decrease in microbial population may occur during starvation due to biomass death, resulting in loss of degrading activity during the period of absence of substrate as previously described.[30] Thus, the removal capacity of live microorganisms falls, and some of them cannot re-acclimatize to EtSH and DMDS instantly after starvation; while some of them recover completely with prolonged re-acclimation time. It is interesting to note that no difference in the REs was observed between before shutdown and after re-acclimation. Thus, it can be concluded that the biotrickling filter seeded with B350 not only has a much higher EtSH and DMDS removal capacity, but also can recover to its full removal capacity swiftly after an unexpected shutdown problem. This infers that the biotrickling filter inoculated with B350 has very high potential for practical application for the removal of odorous pollutants.

CONCLUSIONS

This paper details the performance of an EtSH-acclimated biotrickling filter inoculated with B350 group microorganisms

to treat waste gas containing EtSH, DMDS and MPS as single and mixed odorous vapors. The results showed that the REs and ECs of the pollutants in the biotrickling filter strongly depended on both inlet concentration and EBRT. 100% RE can be achieved at concentrations below 0.41 and 0.23 g m^{-3} for DMDS and MPS, respectively, as sole contaminant at a fixed EBRT of 110 s. Additionally, the biotrickling filter successfully handled a binary mixture of EtSH and DMDS; the optimal ratio was 3 : 2 at a fixed EBRT of 110 s. Furthermore, this effective system can also successfully degrade a ternary mixture of EtSH, DMDS, and MPS. The optimal ratio was 3 : 2 : 1 at a fixed EBRT of 110 s. Kinetic parameters for single, binary and ternary systems revealed that the presence of DMDS or MPS had no significant effect on the removal of EtSH or EtSH and DMDS under optimal conditions. Long-term stability of operation suggested that the biotrickling filter seeded with B350 is a promising cost-effective technology to treat waste gas mixtures of EtSH, DMDS and MPS in practical cases. In addition, the biotrickling filter was capable of withstanding different periods of starvation (5–20 days) with rapid recovery times (3–8 days) to achieve 100% RE after starvation.

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