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Co-treatment of single, binary and ternary mixture gas of ethanethiol, dimethyl disulfide and thioanisole in a biotrickling filter seeded with *Lysinibacillus sphaericus* RG-1

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ABSTRACT

The work reports the aerobic co-treatment characteristics of single, binary and ternary mixture gas of ethanethiol, dimethyl disulfide (DMDS) and thioanisole in a biotrickling filter seeded with *Lysinibacillus sphaericus* RG-1. 100% removal efficiency (RE) was achieved for sole ethanethiol, DMDS and thioanisole at inlet concentration below 1.05, 0.81 and 0.33 mg/L, respectively, at empty bed resident time 110 s. In addition, 100% RE was also obtained with binary ethanethiol and DMDS (1:1) and ternary ethanethiol, DMDS and thioanisole (3:2:1). Michaelis–Menten equation was modified to incorporate the plug flow behavior of the bioreactor. The maximum removal rate (V_{max}) was calculated as 56.18, 57.14 and 22.78 g/m^3/h for sole ethanethiol, DMDS and thioanisole, respectively, while the V_{max} was 41.84 and 14.56 g/m^3/h for DMDS and thioanisole in binary and ternary systems, respectively. Overall, these suggest that not only sole but also binary and ternary mixture can be efficiently removed in this system.

1. Introduction

Odorous waste gases are a special group of air pollutants, including phenols, hydrogen sulfide, ammonia, trimethylamine, volatile fatty acids and volatile organic sulfur compounds (VOSCs) [1–3]. They can enter the atmosphere as contaminants during their manufacture, use, and disposal of the organic or inorganic matters from agriculture and food industry [4], paper making industry [5], and waste and sewage treatment process [6,7]. It is worth noting that some of the VOSCs, such as ethanethiol, dimethyl disulfide (DMDS) and thioanisole, usually can be found in these processes. The removal of them has received intensive attention because of their very low odor threshold values, high toxicity, and potential corrosive effect. It is estimated that 10^8 or 10^9 molecules of odorant vapor in the nose is enough to trigger people's odor detection process. To put this in perspective, 1 μg of ethanethiol in air constitutes approximately 10^{16} molecules, which is 10^7 or 10^8 times higher than the amount necessary for detection [8]. Especially for DMDS, it has the lowest odor threshold value of 0.10 μg/m^3 among all odorous compounds [9]. The development of effective technologies for odorous waste gas treatment is therefore highly desirable.

Various technologies have been developed to reduce/eliminate odorous gases for improving the quality of air. Three sort methods, biological technologies (biofilters, bioscrubbers, activated sludge, etc.), chemical technologies (chemical scrubbers, thermal oxidation, catalytic oxidation, ozonation, etc.), and physical technologies (condensation, adsorption with activated carbon or clean water scrubbers, etc.) have been often used for this purpose [7,10]. In most cases, some conventional physical technologies are often unsatisfactory due to organic pollutants only being transferred from gaseous to other phases, and still not being fully destroyed; while chemical technologies are always expensive [11]. However, biological process has been found to be a very promising technology for the removal of odorous or toxic volatile organic compound waste gas because of low operating costs, low energy requirements as well as no by-products produced for further treatment or disposal [12,13]. For instance, no other by-product was detected except CO_2, H_2O and H_2SO_4 in the acidophilic bacteria oxidizing CS_2 or mixtures of CS_2 and H_2S system [14]. Another important advantage of the technology is that it can simultaneously deal with several contaminants [15,16]. Among the bioreactors used, biotrickling filter facilitates more continuous operation than natural media biofilter due to convenient control of overall pressure drop, pH and nutrient [17]. In addition, biotrickling filter has an advantage over other biological treatment technologies in terms of mineralized efficiency, especially for high concentration acidifying pollutants containing

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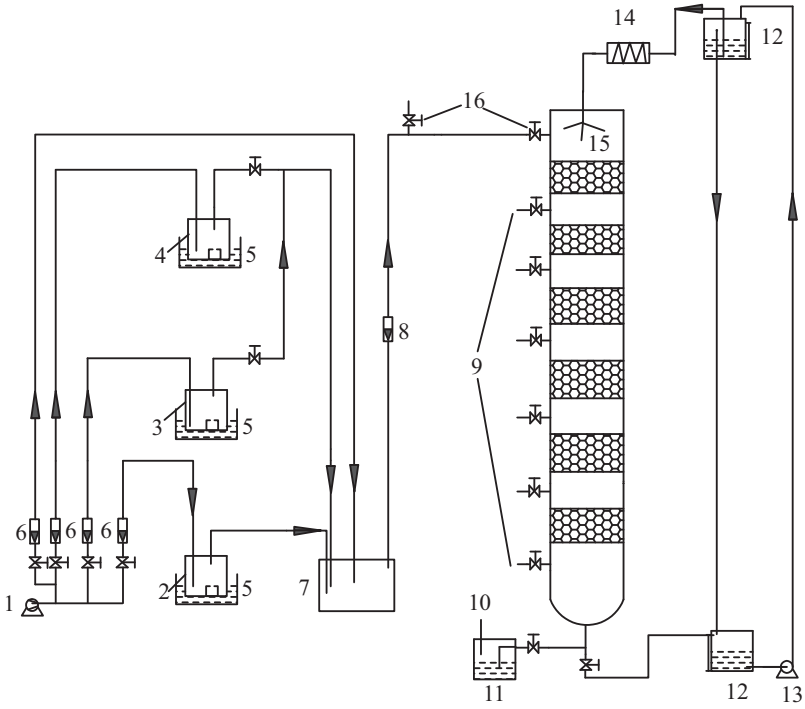

Fig. 1. Schematic diagram of the biotrickling filter: (1) air pump; (2–4) VOSCs reservoir; (5) water bath; (6 and 8) mass-flow controller; (7) mixing gas tank; (9) gas sampling and pressure determination ports; (10) gas out; (11) exhaust gas recycling bottles; (12) nutrient recirculation tank; (13) mass-flow pump; (14) peristaltic pump; (15) nutrient distributor; (16) valves.

waste gas streams, such as, sulfur, chlorine or nitrogen containing compounds [18].

It has been reported that single VOSC substrate such as methanethiol or dimethyl sulfide can be effectively degraded in biotrickling filter [19–21]. To our knowledge, only one paper has been published using an aerobic biotrickling filter system for removal of waste gas containing ethanethiol [22] besides our previous paper [23]. And three studies were carried out to purify waste gas containing DMDS *via* biofilter [24–26]. Few researches have been reported to biologically treat thioanisole waste gas. It is worthwhile to point out that the various odorous pollutants always co-exist in real environment [27]. Nevertheless, in strong contrast to the level of understanding towards the degradation of single organic compound, little has been known regarding the biotreatment of waste gas mixture, especially the binary mixture gas of ethanethiol and DMDS and ternary mixture gas of ethanethiol, DMDS and thioanisole, which is more often encountered in the practical case. Some isolated microorganisms, such as *Hyphomicrobium* MS3, *Hyphomicrobium* VS, *Thiobacillus thioparus* E6, DW44 and TK-m could grow on VOSCs [11]. But there were no direct evidence for the degradation of mixture VOSCs, such as ethanethiol and DMDS, in biotrickling filter inoculated with these bacteria. However, in our previous study, a new *Lysinibacillus sphaericus* (*L. sphaericus*) RG-1 has been isolated, which can use ethanethiol as sole carbon and energy [28]. 100% of ethanethiol can be removed in the biotrickling filter inoculated with the strain RG-1 with initial concentration less than 1.0 mg/L at EBRT 110 s [23]. Ethanethiol, DMDS, and thioanisole all belong to VOSCs; therefore, the mixture of them may be efficiently co-metabolized in a biotrickling filter inoculated with the strain RG-1. To date, however, no report has been published on the co-biodegradation of the binary and ternary mixture gas of ethanethiol, dimethyl disulfide and thioanisole as a carbon and energy source in biotrickling filter inoculated with a single strain.

The prime objectives of this study are to systematically investigate biodegradation process of single and the mixture of VOSC by a biotrickling filter inoculated with a newly isolated *L. sphaericus* RG-1, which could be a potential microorganism to purify the waste gas containing some other VOSCs, because high removal efficiency (RE) of ethanethiol in aqueous (96.3%) and gaseous media (100%) was achieved by this strain according to our previous work [23,28]. Therefore, ethanethiol, DMDS and thioanisole were used as test compounds to represent VOSCs. RE and elimination capacity (EC) of single, binary and ternary mixture of selected compounds were evaluated with different inlet concentrations at fixed empty bed resident time (EBRT). A Michaelis–Menten type kinetic equation was modified to obtain the maximum removal rate (V_{max}) and the half saturation concentration (K_m). Experimental results obtained will provide useful information concerning the design criteria and operation for controlling waste gas containing VOSCs.

2. Methods

2.1. Microorganisms and biotrickling filter

The seeded bacterium is *L. sphaericus* RG-1, which was originally isolated from activated sludge. This strain has been found to possess high removal capacity of ethanethiol in aqueous and gaseous media by our research group [23,28]. Ethanethiol (99+%, Acros, Geel Belgium), thioanisole (99+%, Acros, Geel Belgium) and DMDS (99.5%, Tianjin, China) were used as the carbon sources and energy sources. Other chemicals used as received were of analytical grade and obtained from Guangzhou Chemical Reagent Co., Inc., China unless otherwise stated. The bioreactor used was a custom-made biotrickling filter (Fig. 1). The biotrickling filter column was made of rigid Plexiglas, with an inner diameter of 140 mm and a total height of 1200 mm. 100 mm height of each layer was packed with ceramic particles (moisture content: 15–25%; pile density: 0.75–1.1 g/cm^3; particle diameter: 4–6 mm; Brunauer–Emmett–Teller (BET) surface area: 2–5 × 10^4 cm^2/g; manufactured by Transing Chemical Packing CO., LTD, Jiangxi, China) and the volume of packing materials was 9.23 L. Four air streams were supplied by an air-pump.

Three air streams were separately fed into ethanethiol, DMDS and thioanisole reservoirs to produce their vapors, respectively. Another dry air stream was used to dilute and blend the generated vapors in the mixing gas tank. Thus, the mixture of air and pollutants was continuously fed into the biotrickling filter by the air-pump using Teflon tubing with an outer diameter 10 mm and fittings (biotrickling filter is a continuous and open system for oxygen transfer). The detailed procedures of biotrickling filter operation were described in our previous publication [23]. The nutrient solution containing (g/L) 1.20 $K_2HPO_4{\cdot}3H_2O$, 1.20 KH_2PO_4, 0.20 $MgSO_4{\cdot}7H_2O$, 0.40 NH_4Cl and 0.01 $FeSO_4{\cdot}7H_2O$ was introduced from the top of the biotrickling filter using a peristaltic liquid pump at a rate of 7.5 L/h for 10 min each time, sixteen times a day to maintain the moisture of the carrier material and to supply nutrient to the strain RG-1.

2.2. Analytical methods

Waste gas concentrations were determined using a HP 5890 gas chromatography (Hewlett-Packard, USA) equipped with a HP-5MS 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, increased from 80 to 150 °C at 10 °C/min. Gas samples were collected at regular time intervals from the inlet, outlet and various sampling ports using a 500 μL airtight syringe (Agilent, Australia). A 300 μL gas sample was injected into the column for the concentration determination in the splitless mode.

The performance of the biotrickling filter is evaluated in terms of the RE which is given in Eq. (1):

$$\mathrm{RE}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the inlet and outlet concentrations (mg/L) of pollutants, respectively. In addition, the performance of the biotrickling filter is also commonly quantified in terms of EC of pollutants for various inlet loads (IL). The IL is an important parameter for designing a biotrickling filter (presented in Eq. (2)). The changes of the IL are from the change of the inlet concentration at a fixed flow rate. EC is defined as the amounts of pollutant degraded per unit volume of the packing materials per unit time (g/m^3/h) which is given in Eq. (3):

$$\mathrm{IL} = \frac{QC_0}{1000V} \tag{2}$$

$$\mathrm{EC} = \frac{Q(C_0 - C_e)}{1000V} \tag{3}$$

where Q is gas flow rate (L/h) and V is volume of packing materials (m^3).

Ceramic particles (about 50 g) were withdrawn from the biotrickling filter and used for the determination of biofilm mass (expressed in mg/g of dry ceramic particles) with weight loss [29]. In brief, the ceramic particles were transferred into a weighed crucible and all unbound moisture was removed in an oven at 105 °C for 24 h. The crucible was reweighed and placed in a furnace at 560 °C for 1 h to burn off all the biomass present, followed by a further reweighing. The 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 about 7.0 for growth and reproduction of *L. sphaericus* RG-1. Too low or too high pH will ultimately decrease the activity of microorganisms. Thus, the pH value of the nutrient solution was re-adjusted to 7.0 every 3–5 days with 0.1 mol/L NaOH or HCl solution.

2.3. Kinetic analysis

Macrokinetics of a biotrickling filter can be expressed by a Michaelis–Menten type relationship by assuming that oxygen limitation is not present in the system since the system is aerobic [5]. At steady state, the growth rate of microorganisms was balanced by their own decay rate, resulting in the biological equilibrium of the system. Hence, kinetic constants remained stable over the investigated period. Gas flowing through the biotrickling filter can be characterized as pseudo plug flow with minimal back mixing. Therefore, such an ideal plug flow bioreactor without dispersion at steady state can be modeled by the following equation:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial H} + R_r \tag{4}$$

where A is the cross-section area of the biotrickling filter column (m^2), t is the time interval (h), H is the distance in the bed (m), and R_r is the overall reaction rate defined as follows:

$$R_r = \frac{V_{max}C}{K_m + C} \tag{5}$$

where V_{max} is the maximum biodegradation rate (g/m^3/h) and K_m is the saturation (Michaelis–Menten) constant (mg/L) in gas phase. At steady state, the accumulation term $\partial C/\partial t$ equals to zero. Eq. (4) was integrated under the following conditions $C = C_0$ at $H = 0$ and $C = C_e$ at $H = H_e$, by solving Eqs. (4) and (5), Eq. (6) or (7) is obtained.

$$\frac{V/Q}{C_0 - C_e} = \frac{K_m}{V_{max}C_{\ln}} + \frac{1}{V_{max}} \tag{6}$$

$$\frac{Q(C_0 - C_e)}{V} = \frac{V_{max}C_{\ln}}{K_m + C_{\ln}} \tag{7}$$

where $C_{\ln}$ is natural logarithm mean concentration $((C_0 - C_e)/\ln(C_0/C_e))$. According to 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 [30–33].

3. Results and discussion

3.1. Removal of sole VOSC (ethanethiol, DMDS or thioanisole)

The inlet pollutant concentration is a key parameter for the biofiltration process. The effect of inlet concentrations on REs was investigated by adjusting the single gaseous ethanethiol, DMDS and thioanisole concentrations within the range of 0.42–2.03 mg/L, 0.29–1.04 mg/L and 0.13–0.51 mg/L at fixed EBRT 110 s, respectively. Fig. 2 shows the REs in each and total layer plotted against inlet concentrations of three VOSCs. It can be seen that higher REs were obtained at lower inlet concentrations and vice versa lower REs at higher inlet concentrations. For ethanethiol, total 100% of REs were achieved when the inlet concentration was less than 1.05 mg/L. As the inlet concentration decreased, total 100% RE could be achieved more swiftly, for instance, at the 3rd layer for 0.42 mg/L ethanethiol, more than 90% of ethanethiol was removed after passing the first two layers of the biotrickling filter. With the further increase of the inlet concentration, the biotrickling filters responded with an accumulation of ethanethiol and the total RE was only 93.2% at inlet concentration 1.21 mg/L. Comparatively, the maximum REs of 100% were achieved at inlet concentration below 0.81 mg/L for DMDS. Even if the inlet concentration decreased to 0.59 mg/L, all of the DMDS was removed after passing through the first 5 layers. Similar to ethanethiol degradation trend, as the inlet concentration increased further, the RE decreased slightly. However, the strain RG-1 had a higher capability to degrade ethanethiol than to DMDS. For instance, total 100% and 94.3% REs were obtained at about 1 mg/L of ethanethiol and DMDS, respectively. By comparison, the 100% REs were achieved only at inlet concentration

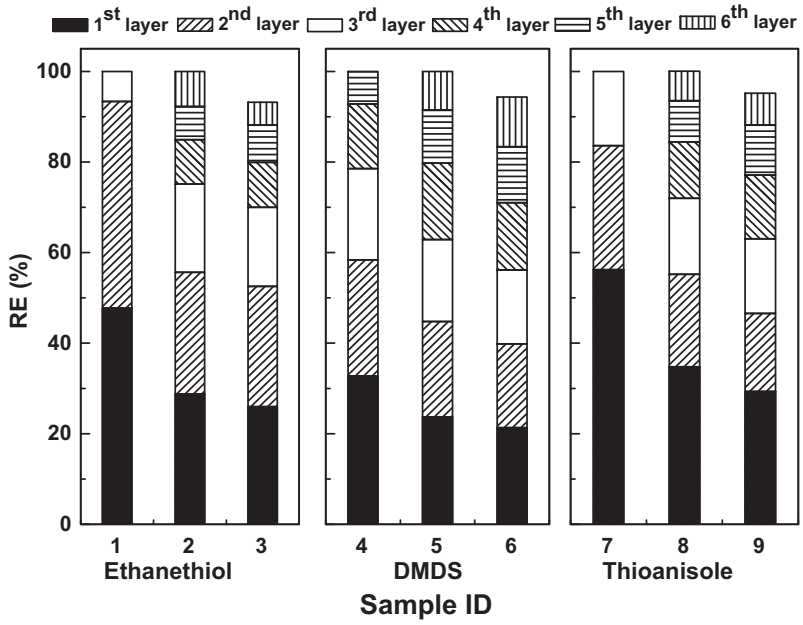

Fig. 2. REs of ethanethiol, DMDS and thioanisole as a single substrate at different inlet concentrations (mg/L): (1) 0.42; (2) 1.05; (3) 1.21; (4) 0.29; (5) 0.81; (6) 1.04; (7) 0.13; (8) 0.33; (9) 0.41.

below 0.33 mg/L for thioanisole. As the inlet concentration further increased to 0.41 mg/L, the biotrickling filter responded with an accumulation of thioanisole and the total RE was dropped to 95.2%.

The ECs of ethanethiol, DMDS and thioanisole as single substrate at different inlet concentrations at fixed EBRT 110 s are also shown in Table 1. It revealed that the total ECs always increased with increasing inlet concentrations for them within tested range. For ethanethiol, the total EC increased dramatically to 32.82 g/m^3/h at the concentration of 1.05 mg/L, which is 2.4 times higher than that at the concentration of 0.42 mg/L. With further rise in the concentration, the EC increased slowly, although the total RE descended slightly from 100 to 93.2%. Comparatively, all of the results showed that both much higher RE and EC were achieved in this work than other reported references. For example, Luis et al. [22] seeded with an alkaliphilic sulfo-oxidizing bacteria in a biotrickling filter to purify ethanthiol under the alkaline condition, and achieved only 3.65 g/m^3/h of maximum EC with a 50% RE at EBRT 40 s. Hort et al. [27] reported an approximately 100% of RE of a biofilter packed with compost and sludge for 16 and 45 ppbv ethanethiol and DMDS at EBRT 60 s, respectively. For DMDS and thioanisole, similar increase trend of total ECs and decrease of REs with increase of the inlet concentrations as ethanethiol were observed. Cho et al. [25] used a fibrous peat biofilter inoculated with aerobically digested night soil sludge to purify the DMDS waste gas, and a maximum EC of 3.2 g/m^3/h was obtained. Ho et al. [26] used a biofilter packed with granular activated to eliminate DMDS, the maximum EC of 5.03 g/m^3/h can be reached. Comparatively, much higher maximum EC of 31.92 g/m^3/h (RE = 94.3%) for DMDS was achieved in this study at inlet concentration 1.04 mg/L at fixed EBRT 110 s. Nevertheless, the total ECs of ethanethiol were slightly higher than ECs of DMDS at similar inlet concentrations at EBRT 110 s. Considering the REs and ECs of three compounds, the biodegradation capability of strain RG-1 followed an order of ethanethiol > DMDS > thioanisole. Overall, the optimal concentrations for strain RG-1 degradation were 1.05, 0.81 and 0.33 mg/L for ethanethiol, DMDS and thioanisole at EBRT 110 s, respectively.

Table 1
Total ECs and REs for different initial concentrations sole substrate at fixed EBRT 110 s.

Inlet concentration (mg/L)	Inlet loading (g/m^3/h)	EC (g/m^3/h)	RE (%)
Ethanethiol			
0.42	13.64	13.64	100
1.05	32.82	32.82	100
1.21	39.33	36.67	93.2
DMDS			
0.29	9.53	9.53	100
0.81	26.20	26.20	100
1.04	33.83	31.92	94.3
Thioanisole			
0.13	4.16	4.16	100
0.33	10.66	10.66	100
0.41	13.20	12.56	95.2

As described, the slight decrease of total REs and increase of total ECs were found as the inlet concentrations rose above the optimal concentration. This can be interpreted as follows. Generally, biodegradation includes two main processes, diffusion of the compounds through the biofilm and their degradation in the biofilm in the presence of microorganisms [34]. The REs and ECs may be controlled by diffusion limitation and reaction limitation [35,36]. When the inlet concentration is below the optimal concentration, biodegradation process can be described as a diffusion limitation regime. The increase of the inlet concentration at fixed EBRT can enhance the transfer rate of pollutants from the gas phase to the biofilm and more microorganisms participate in the biodegradation activity. Therefore, REs remained constant and the ECs increased with the increase of inlet concentration at a diffusion limitation regime. As the inlet concentration increases further above the upper limit of the diffusion limitation regime, higher concentration gradients are produced, which will transfer more pollutants to the biofilm, and resulted in a reaction limitation regime. At reaction limitation regime, the bacterial activity became a limiting step to eliminate pollutants. Therefore, the decrease of the REs and slightly increase of ECs were found as the reaction limitation occurred. This result agrees with the viewpoint that the inlet concentration is a significant limiting parameter in the biotrickling filter as described in the previous references [37,38]. In addition, high inlet concentration may enhance the production of biomass, which subsequently increases the biofilm thickness, decreases the porosity of carrier material and walls up the air flow in the biotrickling filter [39]. In the present experiment, EC increased firstly in the diffusion lim-

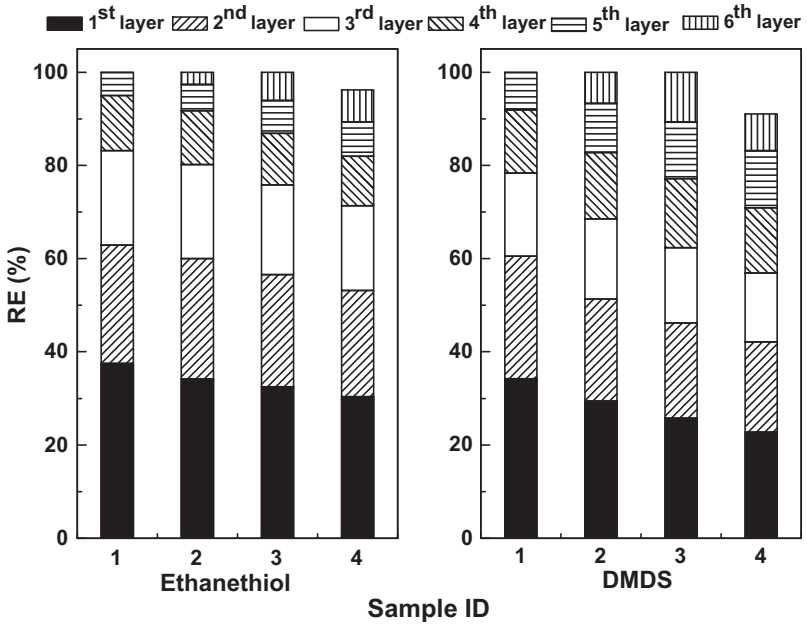

Fig. 3. REs of binary mixture of ethanethiol and DMDS at different concentration ratios (ethanethiol:DMDS = E:D): (1) E:D = 3:1; (2) E:D = 3:2; (3) E:D = 1:1; (4) E:D = 3:4.

itation regime and almost maintained the maximum value in the reaction limitation regime. The increase of inlet load seems to have no inhibition effect on the pollutant removal for strain RG-1.

3.2. Removal of the binary mixture of ethanethiol and DMDS

The REs and ECs for different ratios of the binary mixture of ethanethiol and DMDS at fixed EBRT 110 s are illustrated in Fig. 3 and Table 2. In this section, the inlet concentration of ethanethiol was maintained at about 0.60 mg/L with step-increase of the inlet concentrations of DMDS from 0.21 to 0.81 mg/L. The response of the biotrickling filter was determined by regularly monitoring the outlet concentrations of ethanethiol and DMDS, respectively, of each layer. After adjusting DMDS concentrations, the system was allowed to stabilize for 24 h before again changing the DMDS concentration. As shown in Fig. 3, no significant changes occurred with the REs of ethanethiol for the strain RG-1 in the presence of DMDS. Above 80% of ethanethiol was degraded after passing through the first four layers at all DMDS tested concentration range. Eventually, ethanethiol was completely removed at the fifth or sixth layer as the DMDS concentrations were less than 0.61 mg/L. However, with further increase of the concentration to 0.81 mg/L, RE was slid to 96.2%. Clearly, under the conditions tested herein, the REs were not significantly affected by addition of DMDS below 0.61 mg/L. For DMDS, the outlet concentration always remained under the detection limit at DMDS inlet concentrations lower than 0.61 mg/L. Similar to the biodegradation trend as ethanethiol, an abrupt drop of total RE was observed, for example, 91.0% RE was achieved for DMDS at the concentration 0.81 mg/L. Compared with sole substrate, the REs of ethanethiol and DMDS decreased slightly in the binary system, which is due to the bacterial activity becoming the rate-limiting step for pollutant removal.

Table 2
Total ECs and REs of binary mixture of ethanethiol and DMDS with different ratios at fixed EBRT 110 s.

Inlet concentration (mg/L)	Inlet loading ($g/m^3/h$)	EC ($g/m^3/h$)	RE (%)
Ethanethiol			
0.61 (E:D[a] = 3:1)	19.80	19.80	100
0.60 (E:D = 3:2)	20.17	20.17	100
0.60 (E:D = 1:1)	19.59	19.59	100
0.59 (E:D = 3:4)	19.23	18.49	96.2
DMDS			
0.21 (E:D = 3:1)	6.78	6.78	100
0.41 (E:D = 3:2)	13.39	13.39	100
0.61 (E:D = 1:1)	19.91	19.91	100
0.81 (E:D = 3:4)	26.27	23.92	91.0

[a] Ethanethiol:DMDS.

The total ECs, which reflect the capacity of the biotrickling filters to purify the mixed gas containing ethanethiol and DMDS, are listed in Table 2. Ethanethiol elimination capacities remained virtually the same as during startup with ethanethiol only (data not show), and ECs maintained about 20 $g/m^3/h$ as the inlet ethanethiol concentration was about 0.6 mg/L and DMDS increased from 0.21 to 0.61 mg/L. With the further increase of the DMDS concentration to 0.81 mg/L, the EC then fell slightly to 18.49 $g/m^3/h$. While for DMDS, the total EC increased gradually from 6.78 to 19.91 $g/m^3/h$ as DMDS rose from 0.21 to 0.61 mg/L, and then slightly to 23.92 $g/m^3/h$ at concentration 0.81 mg/L. This can also be explained using biophysical model proposed by Ottengraf and Van Den Oever [40] for single VOCs with the additional aspects added to account for mixed substrates. That is, at diffusion limitation regime, the increase of the DMDS inlet concentration enhanced the transfer rate of DMDS from gas phase to biofilm as ethanethiol concentrations were kept constant. Thus, the ECs to DMDS gradually rose with increasing amount of DMDS transferred to the biofilm, while the ECs to ethanethiol were maintained constant in the present study. Nevertheless, at reaction limitation regime, slight increase of total ECs accompanied by mild decrease of REs to the binary mixture was observed when the DMDS inlet concentration further increased from 0.61 to 0.81 mg/L. Summarily, according to REs and ECs, the optimal ratio was 1:1 for binary mixture of ethanethiol and DMDS at fixed EBRT 110 s.

3.3. Removal of ternary mixture of ethanethiol, DMDS and thioanisole

Co-treatment of ternary mixture of ethanethiol, dimethyl disulfide and thioanisole using *L. sphaericus* RG-1 was also conducted to evaluate the performance of the biotrickling filter. The inlet concentrations of ethanethiol (0.60 mg/L) and DMDS (0.40 mg/L)

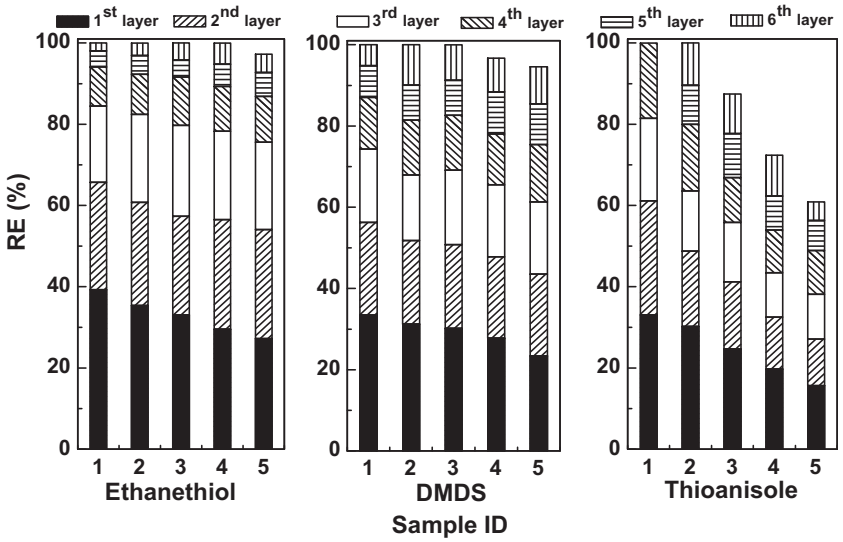

Fig. 4. REs of ternary mixture of ethanethiol, DMDS and thioanisole at different ratios (ethanethiol:DMDS:thioanisole = E:D:T): (1) E:D:T = 6:4:1; (2) E:D:T = 3:2:1; (3) E:D:T = 6:4:3; (4) E:D:T = 3:2:2; (5) E:D:T = 6:4:5.

were maintained constant throughout the test with step-increase of the inlet concentrations of thioanisole from 0.12 to 0.51 mg/L. The outlet concentrations of ethanethiol, DMDS and thioanisole were detected respectively.

The REs of ethanethiol, DMDS and thioanisole at different mixed ratio are plotted in Fig. 4. It can be seen that 100% REs of ethanethiol were obtained as inlet thioanisole concentration ranging from 0.12 to 0.41 mg/L, followed with the decrease of the total RE to 97.3% with increasing thioanisole concentration to 0.51 mg/L. Comparatively, similar degradation trend was observed for DMDS, although 100% REs were achieved only at thioanisole concentration below 0.29 mg/L. By comparison, total removal of thioanisole was obtained at lower thioanisole inlet concentration for instance, less than 0.19 mg/L. When the inlet concentration increased to 0.51 mg/L, the total RE of thioanisole dropped dramatically to 60.9%. It must be noted that the REs of ethanethiol and DMDS were not completely affected compared to the REs of those in the sole and binary system at the same treatment conditions when the thioanisole concentration was less than 0.29 mg/L. However, the co-existence of ethanethiol and DMDS reduced the REs of thioanisole noticeably at the same treatment conditions.

The total ECs of ethanethiol, DMDS and thioanisole at different inlet concentrations are also listed in Table 3. The total ECs of ethanethiol and DMDS almost remained constant at nearly same inlet concentrations, such as 0.6 and 0.4 mg/L for ethanethiol and DMDS, respectively, as the thioanisole concentrations increased from 0.12 to 0.51 mg/L, respectively. The minimum EC of 19.24 and 12.48 g/m^3/h for ethanethiol and DMDS, respectively, is still higher than those reported for other biological system [22,26]. In contrast, thioanisole had the different degradation trend, the total ECs increased gradually from 3.80 to 8.33 g/m^3/h with increasing thioanisole inlet concentrations from 0.12 to 0.29 mg/L. As concentrations further increased to 0.41 and 0.51 mg/L, the total ECs increased slightly to 9.63 (RE = 72.4%) and 10.02 g/m^3/h (RE = 60.9%), respectively. The possible reason is the same as explained previously. Briefly, the mass transfer of three compounds from gas phase to liquid phase and the biofilm is not the rate determining step of the process and the REs and ECs of ternary mixture were mainly limited by the biochemical reaction within the biofilm. According to REs and ECs, the optimal concentration ratio was 3:2:1 for ternary mixture of ethanethiol, DMDS and thioanisole at fixed EBRT 110 s.

3.4. Biodegradation kinetics for single, binary and ternary mixture gas

The V_{max} and K_m for ethanethiol, DMDS and thioanisole either in a single or in a mixture gas supply were calculated over the first four layers of the biotrickling filter *via* Eq. (6). The V_{max} values were 56.18, 57.14 and 22.78 g/m^3/h, and K_m was calculated as 0.15, 0.34 and 0.10 mg/L for ethanethiol, DMDS and thioanisole as sole substrate, respectively. Obviously, the maximum removal rates of RG-1 were almost same for ethanethiol and DMDS, but were much larger than that for thioanisole, which agreed well with the experimental results as described in Section 3.1. Compared with sole system, the V_{max} and K_m of DMDS were only 41.84 g/m^3/h and 0.27 mg/L in the binary system. While for the ternary mixture gas, the V_{max} and K_m of thioanisole were 14.56 g/m^3/h and 0.09 mg/L, respectively, at fixed concentration of ethanethiol and DMDS. Obviously, the V_{max} for DMDS and thioanisole in the mixture system was much less than those in the single gas system. The probable reason is that additional carbon source is available from ethanethiol or ethanethiol and DMDS mixture, and results in a reaction limitation. At the reaction limitation area, the bacterial activity became a limiting

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

Inlet concentration (mg/L)	Inlet loading (g/m^3/h)	EC (g/m^3/h)	RE (%)
Ethanethiol			
0.61 (E:D:T[a] = 6:4:1)	19.59	19.59	100
0.59 (E:D:T = 3:2:1)	19.28	19.28	100
0.62 (E:D:T = 6:4:3)	20.32	20.32	100
0.61 (E:D:T = 3:2:2)	19.91	19.91	100
0.61 (E:D:T = 6:4:5)	19.78	19.24	97.3
DMDS			
0.39 (E:D:T = 6:4:1)	12.75	12.75	100
0.41 (E:D:T = 3:2:1)	13.23	13.23	100
0.39 (E:D:T = 6:4:3)	12.56	12.56	100
0.42 (E:D:T = 3:2:2)	13.67	13.22	96.7
0.41 (E:D:T = 6:4:5)	13.18	12.48	94.6
Thioanisole			
0.12 (E:D:T = 6:4:1)	3.80	3.80	100
0.19 (E:D:T = 3:2:1)	6.30	6.30	100
0.29 (E:D:T = 6:4:3)	9.54	8.33	87.4
0.41 (E:D:T = 3:2:2)	13.30	9.63	72.4
0.51 (E:D:T = 6:4:5)	16.46	10.02	60.9

[a] Ethanethiol:DMDS:thioanisole.

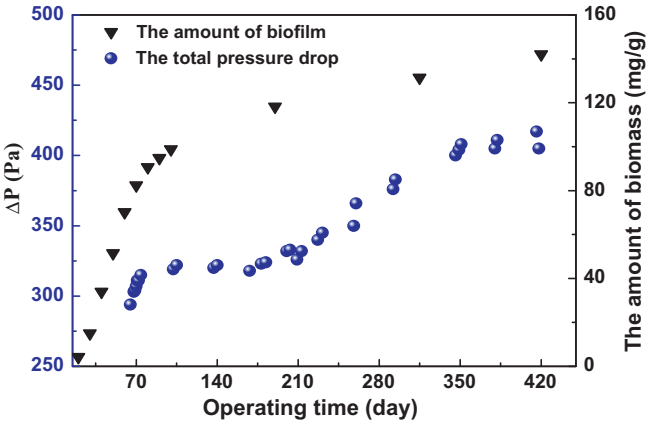

Fig. 5. Development of the amount of biomass and the total pressure drop across the biotrickling filter bed with the increase of the operating time at fixed EBRT 110 s.

factor for the elimination of ethanethiol. Additionally, there was a decrease in K_m for DMDS and thioanisole in the binary and ternary systems. Generally, if we inferred a physical meaning for K_m analogous to enzymatic kinetics, a higher K_m value indicated a lower enzymatic affinity for pollutants [41]. Therefore, the presence of ethanethiol or ethanethiol and DMDS mixture may strengthen the binding ability of the enzyme with DMDS and thioanisole. Overall, considering all the data relevant to REs and ECs, there was no significant inhibitory effect in the binary and ternary mixture gas at the optimal ratios in the present experiment conditions.

3.5. Long term performance of the biotrickling filter

The pressure drop (Δp) across the biotrickling filter is a key indicator of biotrickling filter performance, because it not only relates to the development and accumulation of biomass in the biotrickling filter, but also affects the energy consumption of the blower which contributes most of the operation costs [42,43]. In this work, therefore, long-term performance of the biotrickling filter was investigated by determining both pressure drop at fixed EBRT 110 s and the amount of biofilm (see Fig. 5). The total pressure drop in the bioreactor increased gradually from 8 Pa (without the microorganisms and the data not shown) to 315 Pa (with the microorganism) during 74-day start-up period. This can be attributed to the microorganisms' multiplication with VOSCs feeding, which might minimize the external porosity of the ceramic particles and thus led to high pressure drop across the bed. The pressure drop almost remained constant from the 102th day to 168th day because of low ethanethiol inlet concentration and low-temperature environment. From the 168th day, the biotrickling filter was operated at different EBRTs and feed with different single substrates, even a mixture of variety of substrates (e.g. the mixture of ethanethiol and DMDS). Although a slight increase of the pressure drop was noticed from the 168th to 416th day, it is worth mentioning that these values were quite low. From the figure, it can also be observed that the amounts of the biomass were increased dramatically from 0 to 98.83 mg/g during the first 100 days of operation, and then increased slowly to 118.19 and 142.06 mg/g on the 190th and 420th days, respectively. It is clear that no other carbon and energy source (besides ethanethiol, DMDS or thioanisole) and microorganisms (besides strain RG-1) were introduced to the biotrickling filter as described above. In fact, strain RG-1 utilizes these pollutants through the assimilation to grow and produce large amounts of biomass, and the growth of strain RG-1 guarantees the biotrickling filter with high removal efficiency for different pollutants during long-term operation. Moreover, no clogging or aging problems of the ceramic particles were encountered during all the long operation period. The low pressure drop and long-term stability of the biotrickling filter were attributed to the good mechanical strength and the appropriate size of ceramic particle. Besides, the dead microbial cells in the ceramic particles bed were constantly washed out of the biotrickling filter by the periodically introduced nutrient solution.

4. Conclusion

In this study, a biotrickling filter inoculated with *L. sphaericus* RG-1 is confirmed to have a high capacity and long-term stability to eliminate ethanethiol, DMDS and thioanisole as sole or mixture substrates in the biotrickling filter. For concentrations below 1.05, 0.81 and 0.33 mg/L for sole ethanethiol, DMDS and thioanisole, respectively, 100% RE can be achieved at an EBRT of 110 s. This system can also successfully remove binary (ethanethiol and DMDS) and ternary (ethanethiol, DMDS and thioanisole) mixture. The optimal ratios were 1:1 and 3:2:1 for binary and ternary mixture at an EBRT of 110 s, respectively. The presence of other substrates did not affect the removal efficiencies of ethanethiol or ethanethiol and DMDS at optimal conditions. High immobilization efficiency of strain RG-1 on the surface of ceramic particles can lead to the growth of biofilm during 420 days operation and result in stable long-term high removal efficiencies. Therefore, based on the results, the strain RG-1 has significant potential for treating ethanethiol, DMDS and thioanisole from real waste gas containing high concentrations of ethanethiol, DMDS and thioanisole, even the mixture of them.

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