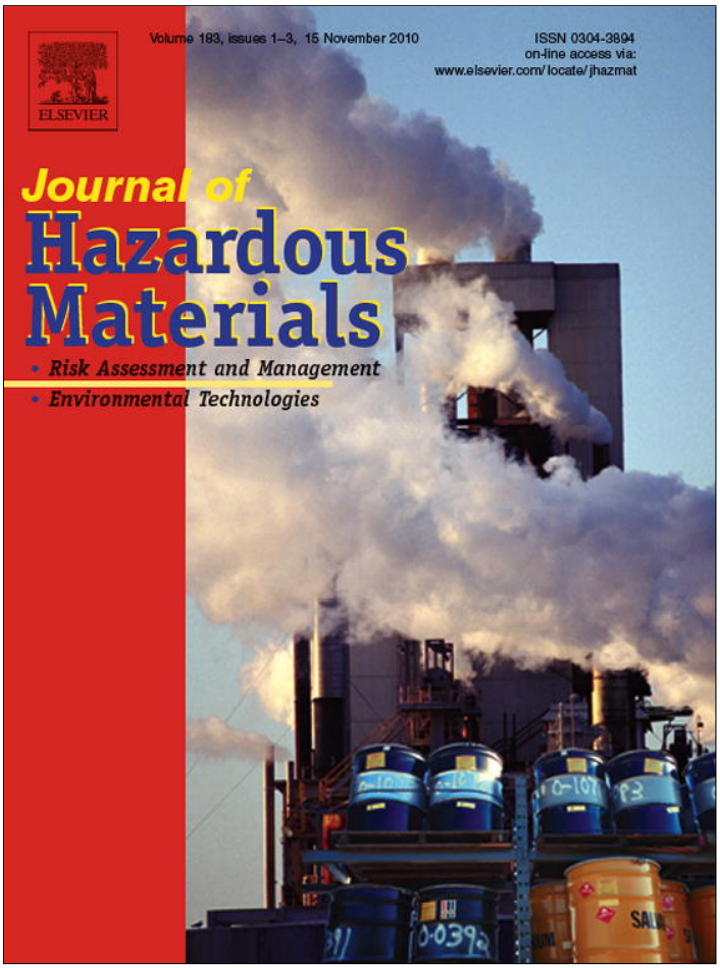

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Comparison of the removal of ethanethiol in twin-biotrickling filters inoculated with strain RG-1 and B350 mixed microorganisms

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ABSTRACT

This study aims to compare the biological degradation performance of ethanethiol using strain RG-1 and B350 commercial mixed microorganisms, which were inoculated and immobilized on ceramic particles in twin-biotrickling filter columns. The parameters affecting the removal efficiency, such as empty bed residence time (EBRT) and inlet concentration, were investigated in detail. When EBRT ranged from 332 to 66 s at a fixed inlet concentration of 1.05 mg L^{-1}, the total removal efficiencies for RG-1 and B350 both decreased from 100% to 70.90% and 47.20%, respectively. The maximum elimination capacities for RG-1 and B350 were 38.36 (removal efficiency = 89.20%) and 25.82 g m^{-3} h^{-1} (removal efficiency = 57.10%), respectively, at an EBRT of 83 s. The variation of the inlet concentration at a fixed EBRT of 110 s did not change the removal efficiencies which remained at 100% for RG-1 and B350 at concentrations of less than 1.05 and 0.64 mg L^{-1}, respectively. The maximum elimination capacities were 39.93 (removal efficiency = 60.30%) and 30.34 g m^{-3} h^{-1} (removal efficiency = 46.20%) for RG-1 and B350, respectively, at an inlet concentration of 2.03 mg L^{-1}. Sulfate was the main metabolic product of sulfur in ethanethiol. Based the results, strain RG-1 would be a better choice than strain B350 for the biodegradation of ethanethiol.

1. Introduction

Ethanethiol is a toxic organic pollutant. It is a colorless liquid with a low odor threshold of 0.7 μg L^{-1} and has a flammable vapor and a gas density that is heavier than air. It can emit noxious odors into the air and lead to chronic harmful effects on the kidneys, heart, lungs, and the nervous system of human beings. Thus, the maximum allowable concentration for ethanethiol is strictly regulated and should not exceed 10.0 mg L^{-1} according to the Occupational Safety & Health Administration [1]. Ethanethiol can be emitted both naturally and anthropologically [2,3]. The industrial applications of ethanethiol in isethionate and phorate pesticides, as well as its product, can also lead to high local atmospheric concentrations during chemical reactions [1]. Therefore, the removal of odorous organic pollutants, such as ethanethiol, from various waste gases is important in the field of environmental engineering.

Various technologies have been developed to purify waste gas containing volatile organic compounds (VOCs) and volatile organic sulfur compounds (VOSCs) [4,5]. In most cases, conventional physical and chemical technologies are often unsatisfactory for the treatment of organic gases. The main reason is that organics may be transferred from the gas to other phases and still not be fully destroyed [5,6]. Comparatively, biological treatment has been validated as a promising technology for the removal of VOCs as well as VOSCs from waste gases because of its low investment and operating costs as well as small energy requirements [7–11]. Additionally, with biological treatment under optimal conditions, the biodegradable contaminants can be converted to harmless end-products without the accumulation of intermediates or dead-end metabolites [12]. A number of VOSCs, such as methanethiol [13,14], dimethyl disulfide [15,16], diethyl disulfide [17], and dimethyl sulfide [18] have been found to be biologically degradable. However, ethanethiol cannot be effectively degraded in anaerobic conditions [19]. Even under aerobic conditions, only one paper been studied by using an aerobic biotrickling filter inoculated microorganism to purify the waste gas containing ethanethiol [20]. No report has been published concerning the biodegradation of ethanethiol as a sole target in biotrickling filters.

Among the biological waste gas treatment technologies, biotrickling filter has attracted considerable interests in the past few years [21] because of their superiority over other biological treatment technologies, such as biofilter and bioscrubber, in terms of mineralization efficiency, especially for highly concentrated acidifying pollutants in waste gas streams. These pollutants include

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sulfur-, chlorine-, or nitrogen-containing organic pollutants [22]. These pollutants are initially adsorbed onto the carrier material by a sorption process and subsequently degraded by biofilms immobilized on the surface of the carrier material. Thus, microorganisms, which are the catalysts for biodegradation of organics, are expected to be the most important factor of the bioreactor. For example, toluene-degrading bacterium *Pseudomonas putida* [23], *P. putida (MTCC 102)* [24], trichloroethene treating bacterium *Dehalococcoides* sp. [25] and monochlorobenzene-oxidizing microorganism *Acinetobacter calcoaceticus* [26], and so on have been isolated for VOCs treatment. However, compared with the microorganisms for treatment VOCs, the species isolated for biodegradation VOSCs are very little [5]. Further, most studies have focused on the selection of carrier materials and optimization of process parameters to improve the removal efficiency of VOSCs [27,28]. Few studies have focused on the microbiological aspects, such as the selection and optimization of biological strains. The commercial mixed microorganism culture, B350, containing 28 species of microorganisms, cellulase, amylase, and hydrolase, has been proven to exhibit high removal capacities for treating phenol and oil-filled wastewater containing aromatic compounds [29–31]. In addition, a newly isolated *Lysinibacillus sphaericus* strain, RG-1, capable of utilizing ethanethiol as the sole carbon and energy source was isolated from activated sludge in our laboratory [32], yet no comparative study of the two biological strains has been reported.

In this study, single, newly identified strain RG-1 and B350 were compared as biological strains for twin-biotrickling filters in the removal of ethanethiol from a synthetic waste gas. The influence of inlet concentration and empty bed residence time (EBRT) on removal efficiencies and elimination capacities of ethanethiol were also studied in detail. The pressure drop (Δp) across the biotrickling filter and the pH values of the re-circulating liquid were also investigated to clarify the superiority of the biotrickling filter.

2. Materials and methods

2.1. Microorganisms and culture medium

The mixed microorganism culture, B350, was purchased from Bio-System Co. USA. The strain RG-1 was isolated from activated sludge, which has been identified as *Lysinibacillus sphaericus* [32]. Ethanethiol (99+%, Acros, Belgium) was selected as the representative odorous organic pollutant in the synthetic waste gas. All other reagents were of analytical grade and obtained from Guangzhou Chemical Reagent Co., Inc. China. The microorganisms were grown in mineral salt medium with ethanethiol as the sole carbon and energy source. The mineral salts medium 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. The trace element stock solution contained ($g\,L^{-1}$): 0.20 $CaCl_2{\cdot}2H_2O$, 0.20 $MnSO_4{\cdot}4H_2O$, 0.10 $CuSO_4{\cdot}2H_2O$, 0.20 $ZnSO_4{\cdot}7H2O$, 0.09 $CoCl_2{\cdot}6H_2O$, 0.12 $Na_2MoO_4{\cdot}2H_2O$, and 0.006 H_3BO_3. The pH value of the mineral medium was adjusted to 7.0–7.5 with 1 M NaOH.

2.2. Experimental set-up

All experiments were performed in a mid-scale biotrickling filter system, as shown in our previous work [33]. It consisted of a gas source (air pump and VOSCs reservoir), mixing gas tank, a gas flow rate control unit, a waste gas treatment unit (twin-biotrickling filters), nutrient recirculation unit and waste gas adsorption bottles. Biotrickling filter was made of transparent rigid plexiglass with an inner diameter of 140 mm and a height of 1200 mm. Each column was divided into six equal-height layers, with 7 sampling ports at fixed interval of 150 mm along the height of the column to measure the gas ethanethiol concentrations. Each layer of the biotrickling filter column was packed to a height of 100 mm (the percentage of the carrier material related to the reactor volume is about 50%) with autoclaved ceramic particles in each layer (moisture content: 15-25%; pile density: 0.75–1.10 $g\,cm^{-3}$; particle diameter: 4–6 mm; BET surface area: $2–5 \times 10^4\,cm^2\,g^{-1}$; maximum porosity volume for pile: no less than 36%; manufactured by Transing Chemical Packing Co., Ltd., Jiangxi, China). The effective volume in the biotrickling filter was 9.23 L, and was calculated according to the inner diameter of the biotrickling filter and the total high of the packing materials. Ceramic particles were inoculated with B350 group microorganisms in the A column and RG-1 in the B column of the twin-biotrickling filter. The bacterial strains used were inoculated into liquid culture and grown 24 h at 30 °C by constant agitation (120 rpm) under aerobic conditions. After incubation, 300 mL cell broth of strain RG-1 and B350 were seeded to the A column and B column of the biotrickling filters, respectively. The growth condition was controlled at 30 °C and a pH range of 7.0–7.5. Mineral salt medium was trickled over the bed upper surface to maintain an adequate level of bed filling moisture content and provide the necessary nutrients for bacterial growth, as well as remove the excess biomass from the biotrickling filters. Synthetic waste gas with a low concentration of ethanethiol (about 0.10–0.60 $mg\,L^{-1}$) was blown into both columns to provide energy and carbon source for microorganisms. In addition, the air and ethanethiol were continuously fed into the biotrickling filter by using 10 mm outer diameter Teflon tubing and fittings, thus, the biotrickling filter is a continuous and open system for oxygen transfer. After the immobilization and acclimatization stage (38 days in this study), ethanethiol removal efficiencies and elimination capacities were evaluated using RG-1 and B350, respectively.

2.3. Operating conditions

Both biotrickling filter column were operated with gas and liquid flowing co-currently (down-flow) mode. Waste gas was supplied by an air-pump (Guangdong Risheng Group CO., Ltd., China). Waste gas flow rate was controlled with flow meters from 100 to 500 $L\,h^{-1}$, corresponding to an EBRT range of 332–66 s, at fixed inlet ethanethiol concentration, respectively, to determine the optimal EBRT. The inlet ethanethiol concentrations were ranged from 0.42 to 2.03 $mg\,L^{-1}$ at fixed optimal EBRT to further investigate the effect of inlet concentration on the performance of the biotrickling filter. The re-circulated liquid was introduced from the top of the biotrickling filters using peristaltic liquid pump at a rate of 7.5 $L\,h^{-1}$ for 10 min each time, sixteen times a day to maintain the moisture of the biotrickling filters and supply nutrient to the strain RG-1 and B350. In addition, the re-circulated liquid containing mineral salt volume was maintained at 30 L by periodically adding distilled water, and the pH value of re-circulated liquid was irregularly adjusted to neutral with 0.1 M NaOH.

The pressure drop across the column and pH value of the system was measured every day or two using a U-tube water manometer and pH meter, respectively. The concentration of sulfate in the re-circulated liquid was determined every 10 days using standard photometric method [34].

2.4. Analytical methods

The gas concentrations of ethanethiol were determined using an HP 5890 gas chromatography system (Hewlett-Packard, USA) equipped with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. Nitrogen was used as the carrier gas at 20 $mL\,min^{-1}$. The temperatures of the injector and detector were 280 and 300 °C, respectively. The programmed temperature of the column was maintained at

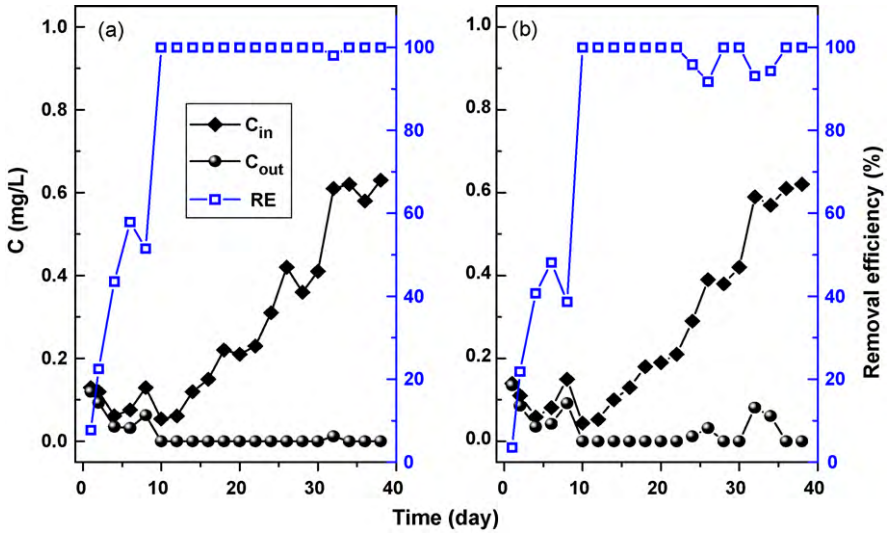

Fig. 1. Performance of twin-biotrickling filters with (a) RG-1 and (b) B350 during the start-up period.

40 °C for 2 min and then increased to 80 °C at a rate of 5 °C min^{-1}. Gas samples were collected at regular intervals from the inlet and outlet using an airtight syringe (Agilent 500 μL). A 300 μL gas sample was injected into the column for concentration determination in the splitless mode. The ceramic particles (ca. 50 g) were sampled from twin-biotrickling filters, and the mass of the biofilm (expressed in mg per gram of dry ceramic particles) was determined by weight loss [35]. An optical microscope (Leica DMRX, Wetzlar, Germany) and scanning electron microscope (SEM, JSM-6360, Japan) were employed to observe biofilm formation on the ceramic particles. The thickness of the biofilm in both reactors were calculated according to the method described by Zhao et al. [36]. The pressure of the bioreactor was measured by a pressure meter with a minimum reading of 1 mm water column.

2.5. Calculation of the removal efficiency, EBRT, inlet load and elimination capacity

The performance of the biotrickling filter were evaluated in terms of the removal efficiency (%), EBRT (s), inlet load (IL, g^{-3} h^{-1}) and elimination capacity (g^{-3} h^{-1}), which were calculated by the following equations:Removal efficiency:

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

Empty bed residence time:

$$\mathrm{EBRT} = \frac{V}{Q}$$

Inlet load:

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

Elimination capacity:

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

where Q is the gas flow (L h^{-1}), V is the effective volume in the biotrickling filter (m^{-3}), C_0 and C_e are the inlet and outlet gaseous ethanethiol concentration (mg L^{-1}), respectively.

3. Results and discussion

3.1. Bioreactor start-up

During the start-up period, about 0.10 mg L^{-1} gaseous ethanethiol was first introduced to the columns of the biotrickling filter. The inlet concentration was increased gradually to 0.64 mg L^{-1} at a fixed EBRT of 332 s. The performance of the RG-1 and B350 from 1 to 38 days is shown in Fig. 1a and b, respectively. Analysis of the removal efficiencies during the whole start-up period demonstrated that the removal efficiencies were very low during the first 9 days. However, 100% of the removal efficiencies was achieved for RG-1 and B350 at low initial concentration (<0.20 mg L^{-1}) after the 10th day. Comparatively, RG-1 was robust enough to consistently absorb and completely degrade ethanethiol, although a wide range of concentrations from 0.05 to 0.64 mg L^{-1} was employed (Fig. 1a). The results reveal that almost no acclimation time was needed for RG-1 to be fully functionalized. For B350 (Fig. 1b) on the 24th day, the decrease in removal efficiency from 100% to 95.9% corresponded to the increase in inlet concentration from 0.21 to 0.29 mg L^{-1}. This could be because the process of biofilm formation was not completed or the microorganisms could not adapt to the sudden increase in ethanethiol concentration. However, after another 4 days of acclimation, 100% removal efficiency can be achieved once again. A similar phenomenon was observed on the day 32, indicating that an acclimation period was necessary for B350.

To obtain crucial qualitative information about biofilm formation, the morphology of the ceramic particles before and after cultivation was characterized by optical microscopy and SEM. As shown in Fig. 2a1 and 2a2, the surface of a clean ceramic particle is coarse and porous, which is favorable for the immobilization of microorganisms. The surface morphologies of immobilized microorganisms with RG-1 and B350 on the ceramic particle after 38 days of the start-up period are shown in Fig. 2b and c, respectively. The biofilm was successfully developed during the start-up period. An abundance of rod and zoogloea bacteria adhered onto the surface of the ceramic particles (Fig. 2b2 and c2). In addition, the biomass immobilized on the surface of the ceramic particles was also determined during the start-up period. Initially, no bacteria grew on the ceramic particles. The attached bacteria increased gradually with an increase in the start-up time. On the day 20, the biomass increased to 4.18 mg g^{-1} for RG-1 and 3.95 mg g^{-1} for

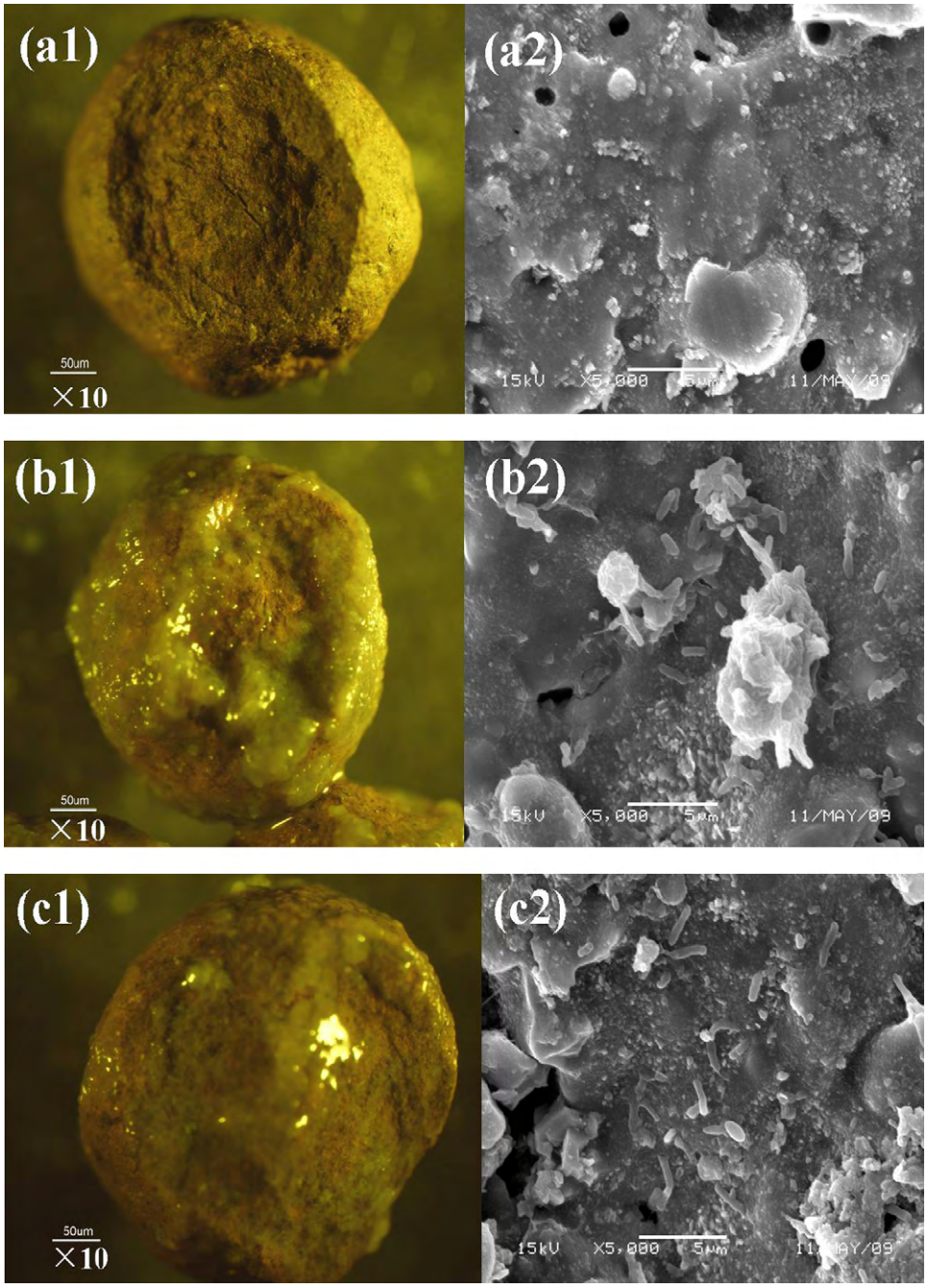

Fig. 2. Optical micrographs and SEM images of ceramic particles: (a1) without biofilm (10×); (a2) without biofilm (5000×); (b1) with RG-1 biofilm (10×); (b2) with RG-1 biofilm (5000×); (c1) with B350 biofilm (10×); (c2) with B350 biofilm (5000×).

B350. The biomass increased from 15.02 to 33.95 mg g^{-1} for RG-1 and from 8.72 to 19.25 mg g^{-1} for B350 when the inlet ethanethiol concentration varied from 0.41 to 0.63 mg L^{-1} when the operation time further increased from 30 to 40 days, respectively. According to the reference [37], the density of biofilm changed between 20 and 105 mg cm^{-3} when the biofilm thickness increased from 30 to 1300 μm. In our experiment, the average diameter of ceramic particles is 4.42 ± 0.94 mm, and contains an average of 10 particles of per gram. On the assumption that the average density of biofilm was 62.5 mg cm^{-3}, the thicknesses of biofilm were calculated as 105,164 and 669 μm for RG-1 and 99, 209 and 421 μm for B350 on the 20th, 30th and 40th day, respectively. All the results indicated that the microorganisms were successfully immobilized on the surface of the ceramic particles.

3.2. Effect of EBRT on bioreactor performance

Empty bed residence time is one of the most important parameters in biotrickling filtration processes [18]. The effect of EBRT on the treatment performance of the biotrickling filter inoculated with RG-1 or B350 was investigated at a fixed concentration of 1.05 mg L^{-1}. As shown in Fig. 3, higher removal efficiencies were obtained at higher EBRT, while a lower EBRT led to lower removal efficiencies for both RG-1 and B350 treatment. However, RG-1 and B350 had different degradation trends. For RG-1, the total removal efficiencies of 100% was achieved at an EBRT of 332, 166, and 110 s (Fig. 3a), and more than 50% of ethanethiol was degraded after passing through the first three layers of the biotrickling filter. With further shortening of the EBRT, total removal efficiencies decreased

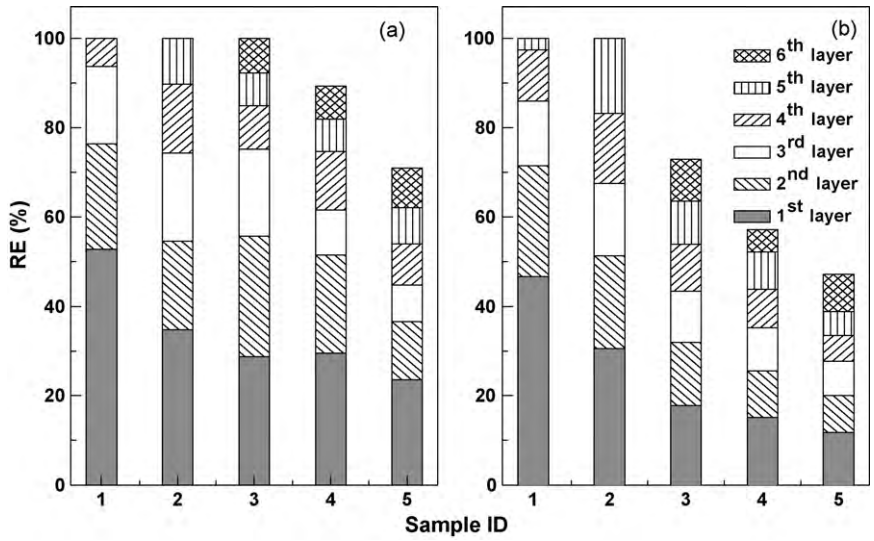

Fig. 3. Removal efficiencies of (a) RG-1 and (b) B350 at a fixed inlet concentration of 1.05 mg L^{-1} at different EBRTs (1: 332 s; 2: 166 s; 3:110 s; 4: 83 s; 5: 66 s).

to 89.20% and sharply decreased to 70.90% at EBRTs of 83 and 66 s, respectively. In contrast, B350 had lower total removal efficiencies at the same conditions (Fig. 3b). Even at an EBRT of 332 s, 100% removal efficiency could only be obtained at the fifth layer. With a further decrease of EBRT, a significant drop in total removal efficiencies, e.g., 73.20, 57.10, and 47.20%, were achieved at EBRTs of 110, 83, and 66 s, respectively.

The performance of the biotrickling filter was also evaluated in terms of the elimination capacity of ethanethiol with various EBRTs and inlet loads (Fig. 4). The elimination capacities of RG-

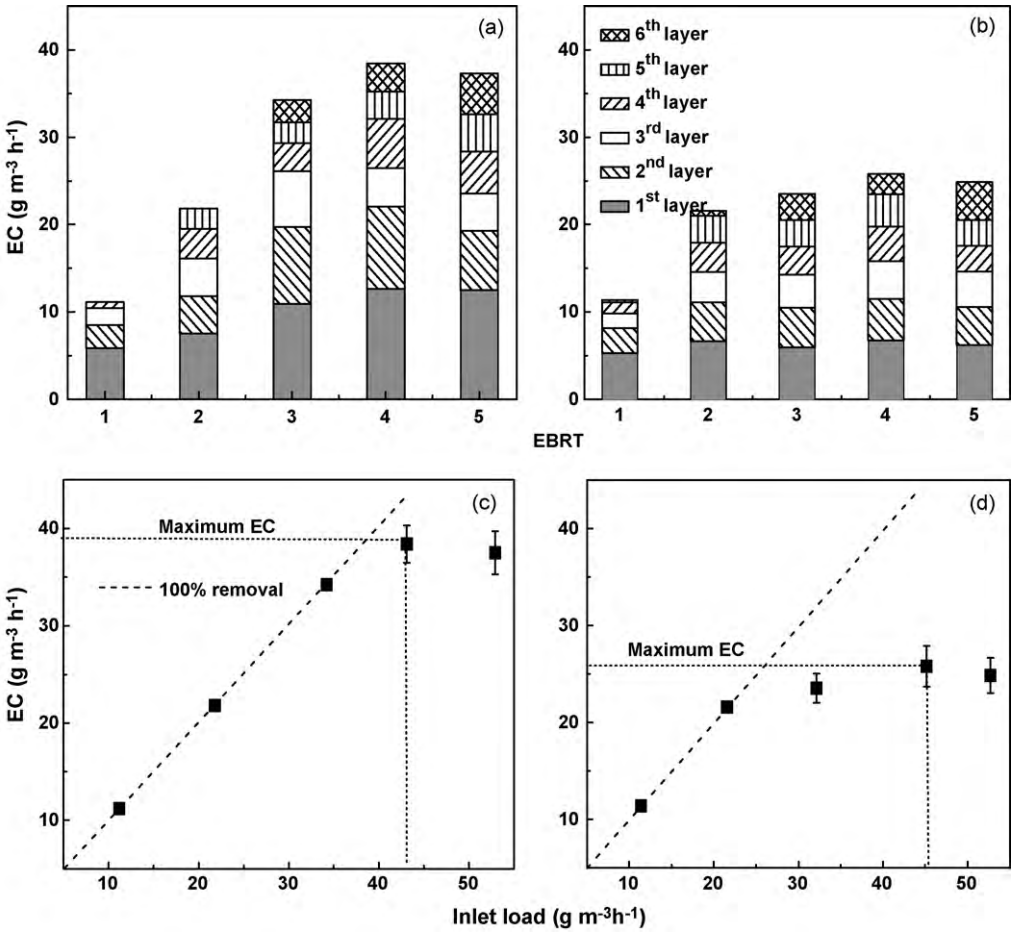

Fig. 4. Elimination capacities with (a) RG-1 and (b) B350 at an inlet concentration of 1.05 mg L^{-1} at different EBRTs (1: 332 s; 2: 166 s; 3:110 s; 4: 83 s; 5: 66 s); Elimination capacities with (c) RG-1 and (d) B350 versus the inlet load of ethanethiol at various EBRTs.

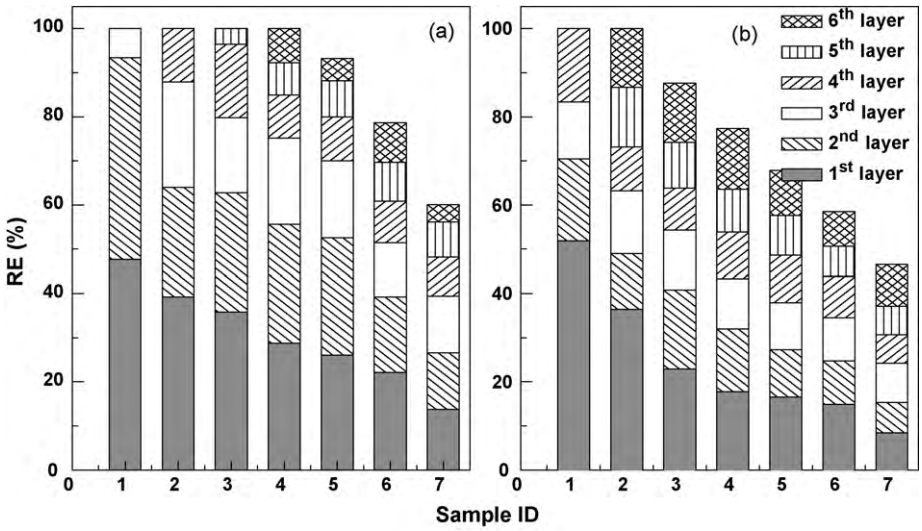

Fig. 5. Removal efficiencies with (a) RG-1 and (b) B350 at a fixed EBRT of 110 s with different inlet concentrations (1: 0.42 mg L^{-1}; 2:0.64 mg L^{-1}; 3: 0.78 mg L^{-1}; 4: 1.05 mg L^{-1}; 5: 1.21 mg L^{-1}; 6: 1.50 mg L^{-1}; 7: 2.03 mg L^{-1}).

1 and B350 were almost equal at larger EBRTs, such as 332 and 166 s (Fig. 4a and b). However, with a decrease of EBRT to 83 s, the total elimination capacities of RG-1 increased swiftly and peaked at 38.36 g m^{-3} h^{-1} (removal efficiency = 89.20%), while the total elimination capacities of B350 increased very slowly and reached its maximum at 25.82 g m^{-3} h^{-1} (removal efficiency = 57.10%). As the EBRT decreased further to 66 s, the elimination capacities slightly decreased to 37.54 and 24.86 g m^{-3} h^{-1} for RG-1 and B350, respectively. The first three layers play an important role in both biotrickling columns, and more than half of ethanethiol could be eliminated as the waste gas passed through the columns. The elimination capacities plotted against inlet loads for RG-1 and B350 are illustrated in Fig. 4c and d, respectively. Based on Fig. 4c, 100% removal could be achieved as inlet loads were less than 34.23 g m^{-3} h^{-1}. Moreover, only 89.20% of ethanethiol was removed when the maximum total elimination capacity was achieved at an EBRT of 83 s for RG-1. By comparison, for B350, 100% removal efficiency could only be achieved as the ethanethiol inlet loads were in the range of 0–21.58 g m^{-3} h^{-1}. At an EBRT of 83 s, only 57.10% ethanethiol can be removed as the maximum total elimination capacity was achieved. Comparatively, all of the results showed that both much higher removal efficiency and elimination capacity were achieved in this work than other reported references. For example, Luis et al. inoculated with an alkaliphilic sulfo-oxidizing bacteria in a biotrickling filter to purify ethanethiol under the alkaline condition, and achieved only 3.65 g m^{-3} h^{-1} of maximum elimination capacity with a 50% removal efficiency [20].

Generally, removal efficiencies always dropped with a decrease of EBRT for both strains. It was noteworthy that the biotrickling filers were a continuous and open system. During the biodegradation, assuming that ethanethiol was completely converted into carbon dioxide, water and sulfuric acid by microorganisms according to the following stoichiometric reaction:

$$C_2H_5SH + 5O_2 \rightarrow 2CO_2 + 2H_2O + H_2SO_4$$

For the biotrickling filter inoculated strain RG-1, the maximum elimination capacity was 38.36 g m^{-3} h^{-1} at the gas flow rate 400 L h^{-1}. The actual maximum oxygen consumption is 98.99 g under the current system according to the stoichiometric reaction. However, the 400 L h^{-1} of air in the biotrickling filter can provide 119.75 g oxygen. Thus, oxygen is sufficient for the strain RG-1 and B350 to degrade ethanethiol in this continuous and open system. So the probable reason is that removal efficiencies are controlled by the mass transfer of ethanethiol from the air to the biofilm (diffusion limitation) and by the biodegradation process (reaction limitation) in the biotrickling filters [9,38]. A longer EBRT results in higher removal efficiencies because there is adequate time for organic molecules to enter the biofilm to complete biodegradation. Thus, the overall removal efficiencies are controlled only by the diffusion limitation. On the contrary, reaction limitation may occur in the case of a shorter EBRT. With a decrease of EBRT, the inlet loads into the biotrickling filters increased and enhanced the transfer rate of ethanethiol from the gas phase to the biofilm. Thus, the microorganisms did not have sufficient time to degrade excessive amounts of ethanethiol. Consequently, elimination capacities initially increased to its maximum value and then remained constant or decreased, whereas removal efficiencies dropped gradually because of the limited contact time between the biofilm and ethanethiol. Therefore, the EBRT is a significant parameter in a biotrickling filter [39,40]. The RG-1 strain had higher removal efficiencies and elimination capacities than B350 at the same treatment conditions. In this research, 110 s was chosen as the optimum EBRT for the degradation of ethanethiol.

3.3. Effect of inlet concentration on bioreactor performance

The inlet concentration of the organic pollutant is another key parameter in the biotrickling filtration process. The effect of ethanethiol concentration on bioreactor performance was investigated by adjusting gaseous concentrations within a range of 0.42–2.03 mg L^{-1} at a fixed EBRT of 110 s. Removal efficiencies at each layer and total removal efficiencies depending on the different inlet concentrations were plotted in Fig. 5. One hundred percent removal efficiency was obtained when the inlet concentrations increased from 0.42 to 1.05 mg L^{-1} for RG-1 (Fig. 5a) and from 0.42 to 0.64 mg L^{-1} for B350 (Fig. 5b). Total removal efficiencies of 100% can be achieved at the third, fourth, fifth, and sixth layer for RG-1 at inlet concentrations of 0.42, 0.64, 0.78 and 1.05 mg L^{-1}, respectively. While for B350, total removal efficiencies of 100% can only be obtained at the fourth and sixth layer at inlet concentrations of 0.42 and 0.64 mg L^{-1}, respectively. With a further increase of the inlet concentration, the total removal efficiencies dropped steadily from 100% to 60.30% for strain RG-1 and to 46.20% for B350 when the inlet concentrations increased to 2.03 mg L^{-1}. The removal efficiency decreased as a function of inlet concentration.

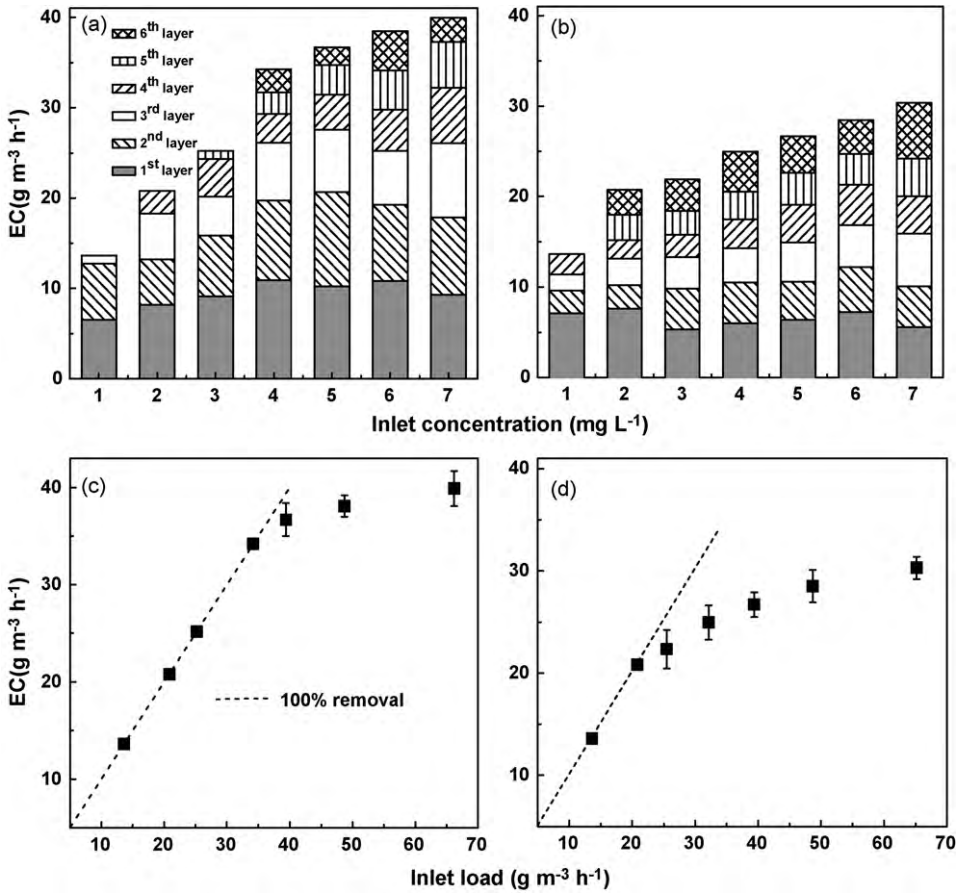

Fig. 6. Elimination capacities with (a) RG-1 and (b) B350 at a fixed EBRT of 110 s at different inlet concentrations (1: 0.42 mg L^{-1}; 2:0.64 mg L^{-1}; 3: 0.78 mg L^{-1}; 4: 1.05 mg L^{-1}; 5: 1.21 mg L^{-1}; 6: 1.50 mg L^{-1}; 7: 2.03 mg L^{-1}); Elimination capacities with (c) RG-1 and (d) B350 versus the inlet load of ethanethiol at various inlet concentrations.

For inlet concentrations lower than 0.64 mg L^{-1}, ethanethiol can be completely degraded by both RG-1 and B350.

The performance of the biotrickling filter was also evaluated in terms of elimination capacities of ethanethiol for various inlet concentrations and inlet loads at a fixed EBRT of 110 s (see Fig. 6). The total elimination capacities always increased with a rise of the inlet concentration for both strains. The elimination capacities of RG-1 versus inlet concentrations and inlet loads are shown in Fig. 6a and c, respectively. At concentrations of 0.42 mg L^{-1}, the total elimination capacity was only 13.64 g m^{-3} h^{-1}. As the inlet concentration further increased to 1.05 mg L^{-1}, the total elimination capacity climbed to 34.23 g m^{-3} h^{-1} or more than twice the total elimination capacity at 13.64 g m^{-3} h^{-1} (Fig. 6a). At an inlet concentration less than 1.05 mg L^{-1} (Fig. 6c), 100% removal efficiencies were achieved. However, the total elimination capacity increased to 39.93 g m^{-3} h^{-1}, corresponding to an abrupt drop to 60.3% of the removal efficiency when the inlet concentration further increased to 2.03 mg L^{-1}.

Comparatively, elimination capacities of B350 (Fig. 6b and d) showed an almost similar trend with the increase of inlet concentration as RG-1, except that B350 had lower elimination capacities at an identical condition. The total elimination capacity increased from 13.64 to 20.76 g m^{-3} h^{-1} when the concentration increased from 0.42 to 0.64 mg L^{-1}. The further increase of the concentration caused the amount of ethanethiol at the outlet to increase slowly, although a significant increase of the total elimination capacities was observed from 20.76 to 30.34 g m^{-3} h^{-1} (removal efficiency = 46.20%) for B350.

As mentioned in Section 3.2, this behavior can also be described as a diffusion limitation and a reaction limitation. The increase of the inlet concentration at a fixed EBRT can enhance the transfer rate of ethanethiol from the gas phase to the biofilm. It produces higher concentration gradients, which improve mass transfer in the biotrickling filter, and results in a reaction limitation. At the reaction limitation area, the bacterial activity became a limiting factor for the elimination of ethanethiol. In addition, high inlet concentration may enhance the production of biomass. An excessive amount of biomass increased the thickness of the biofilm, decreasing the porosity of ceramic particles and blocking the air flow in the biotrickling filter [41]. On the contrary, elimination capacity first increased in the diffusion limitation area and remained at an almost maximum elimination capacity in the reaction limitation area. In the present experiment, the increase of inlet load appeared to have no inhibition effect on the ethanethiol biodegradation for both RG-1 and B350.

3.4. Pressure drop

Pressure drop is a valuable indicator of the development and accumulation of biomass, cracks in the ceramic particles, and resultant short-circuiting of the biotrickling bed for a biotrickling filter. This is because the increase in pressure drop can increase the operating cost of the biotrickling filters [42]. In this research, the whole experimental period (3 months) was split into five consecutive stages, from S1 to S5, according to the different gas flow rates ranging from 100 to 500 L h^{-1}. Fig. 7 shows the total pressure drop (Δp) plotted against the operation time. The total pressure drop in the bioreactor increased linearly with R^2 values of 0.9965 and 0.9881 for RG-1 and B350 as the flow rate increased from 100 to 500 L h^{-1}, respectively. These results confirmed that an increase in pressure

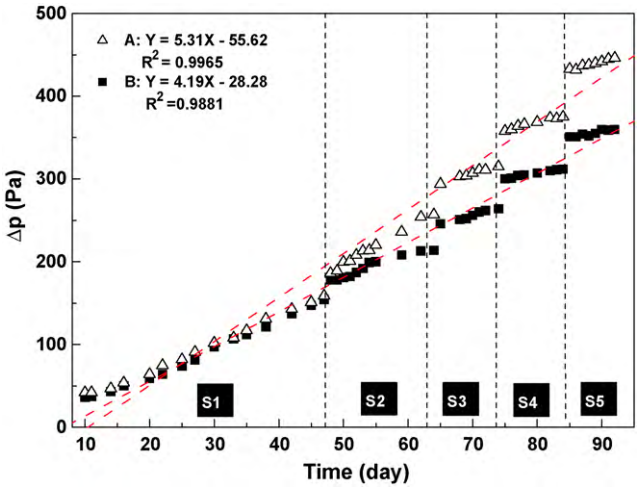

Fig. 7. Evolution of pressure drop through biotrickling filters versus time. (A) biotrickling filter with RG-1; (B) biotrickling filter with B350. S1: 100 L h^{-1}; S2: 200 L h^{-1}; S3: 300 L h^{-1}; S4: 400 L h^{-1}; and S5: 500 L h^{-1}.

drop is reasonably linear with an increasing the flow rate [43]. Although an increase in pressure drop values was observed with an increase of flow rate, the values of pressure drop were quite low. Additionally, the results revealed that the pressure drop was relatively steady at each EBRT with an increase of operation time. Moreover, no clogging or breakdown problems occurred during the 3-month period. The low pressure drop and long-term stability of the biotrickling filters were attributed to good mechanical strength and reasonable size of ceramic particles. These configurations resulted in an ideal hydrodynamic environment and effective mass transfer to prevent the accumulation of biomass and maintain higher performance. The microbial cells within the ceramic particles can be constantly renewed with new bacterial cells to avoid blocking problems in the biotrickling filters.

3.5. pH values and sulfate product

The major metabolic products of VOSCs may be sulfate [5]. Because no biotransformation exists to consume sulfate, it will accumulate in the re-circulated liquid, and pH values will drop with an increase in operation time. In this study, the pH values and sulfate concentrations of the re-circulated liquid in the biofiltration system for ethanethiol removal were regularly determined during the 3-month operation period. When the pH dropped to about 6.5, the pH value of the re-circulated liquid was adjusted to 7.0–7.5 with 0.1 M NaOH. The results of the pH value and sulfate concentration measurements were plotted against treatment time in Fig. 8. pH values fluctuated between 7.50 and 6.50 for both RG-1 and B350. The pH decreased more quickly for RG-1 than for B350, indicating a higher metabolic activity in RG-1 treatment compared with that of B350 treatment. Sulfate concentration increased steadily from 0 to 3378.82 and 2442.02 mg L^{-1} (after deduction of sulfate in the mineral salts medium) in the re-circulated liquid containing RG-1 and B350 from 0 to the 92nd day, respectively. The sulfur mass balance between sulfate and ethanethiol were calculated according to the amount of ethanethiol consumption and the amount of sulfate produced. The ratio of ethanethiol conversion were 28.27%, 28.37%, 26.42%, 31.07%, 36.17%, 38.96%, 37.88% and 36.68% for strain RG-1 and 24.84%, 24.13%, 21.35%, 20.83%, 28.40%, 27.06%, 30.90% and 28.26% for B350 on the 20th, 30th, 42nd, 52nd, 62nd, 72nd, 82nd and 92nd day, respectively. This result proved that RG-1 had higher ethanethiol biodegradation ability than B350. In addition, it also indicated that sulfur in ethanethiol was converted to sulfuric acid, and even element sulfur, sulfide and sulfite [44,45]. In summary,

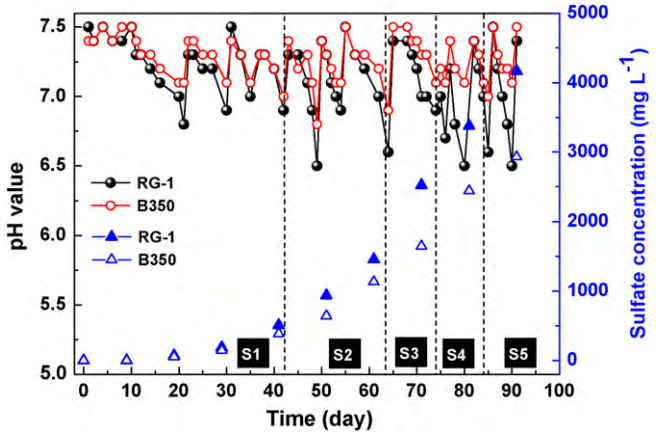

Fig. 8. Evolution of pH values and sulfate concentrations versus time. S1: 100 L h^{-1}; S2: 200 L h^{-1}; S3: 300 L h^{-1}; S4: 400 L h^{-1}; and S5: 500 L h^{-1}.

the variations of pH values and sulfate were not influenced on the removal efficiency of ethanethiol. This may be due to the maintenance of microorganism activities at different pH values.

4. Conclusion

This paper focused on a comparison of the performance of biotrickling filters inoculated with RG-1 and B350 for the removal of ethanethiol vapors. Results showed that removal efficiencies and elimination capacities strongly depended on the inlet concentration and EBRT. The RG-1 strain showed better performance than B350. When the EBRT ranged from 332 to 66 s at a fixed inlet concentration of 1.05 mg L^{-1}, the removal efficiency of ethanethiol decreased from 100% to 70.90% for RG-1 and 47.20% for B350. The maximum elimination capacities of 38.36 and 25.82 g m^{-3} h^{-1} were obtained at an EBRT of 83 s for RG-1 and B350, respectively. The effect of the inlet concentration on removal efficiencies and elimination capacities at a fixed EBRT of 110 s was varied. However, RG-1 exhibited better total removal efficiencies and total elimination capacities than B350. One hundred percent of removal efficiencies were maintained at inlet concentrations less than 1.05 and 0.64 mg L^{-1} for RG-1 and B350, respectively. With a further increase in inlet concentration, removal efficiencies decreased to 60.30% with a maximum elimination capacity of 39.93 g m^{-3} h^{-1} for RG-1 and to 46.20% with a maximum elimination capacity of 30.34 g m^{-3} h^{-1} for B350. In addition, sulfur in the ethanethiol was ultimately converted to sulfuric acid by RG-1 and B350, respectively. Therefore, RG-1 has a stable performance compared with B350 and is more suitable for the degradation of a waste gas containing ethanethiol.

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References

[1] P. Patnaik, A Comprehensive Guide to the Hazardous Properties of Chemical Substances, 3rd ed., Wiley-Interscience, New York, 2007.
[2] C. Easter, C. Quigley, P. Burrowes, J. Witherspoon, D. Apgar, Odor and air emissions control using biotechnology for both collection and wastewater treatment systems, Chem. Eng. J. 113 (2005) 93–104.
[3] S. Rappert, R. Muler, Odor compounds in waste gas emissions from agricultural operations and food industries, Waste Manage. 25 (2005) 887–907.

[4] S. Mudliar, B. Giri, K. Padoley, D. Satpute, R. Dixit, P. Bhatt, R. Pandey, A. Juwarkar, A. Vaidya, Bioreactors for treatment of VOCs and odours—a review, J. Environ. Manage. 91 (2010) 1039–1054.
[5] E. Smet, P. Lens, H. Van Langenhove, Treatment of wastegases contaminated with odorous sulfur compounds, Crit. Rev. Environ. Sci. Technol. 28 (1998) 89–117.
[6] J.E. Burgess, S.A. Parsons, R.M. Stuetz, Developments in odour control and waste gas treatment biotechnology: a review, Biotechnol. Adv. 19 (2001) 35–63.
[7] C. Kennes, F. Thalasso, Review: waste gas biotreatment technology, J. Chem. Technol. Biotechnol. 72 (1998) 303–319.
[8] M.C. Delhoménie, M. Heitz, Biofiltration of air: a review, Crit. Rev. Biotechnol. 25 (2005) 53–72.
[9] H. Jorio, L. Bibeau, G. Viel, M. Heitz, Effects of gas flow rate and inlet concentration on xylene vapors biofiltration performance, Chem. Eng. J. 76 (2000) 209–221.
[10] J.W.V. Groenestijn, N.J.R. Kraakman, Recent developments in biological waste gas purification in Europe, Chem. Eng. J. 113 (2005) 85–91.
[11] J.W. Groenestijn, P.G.M. Hesselink, Biotechniques for air pollution control, Biodegradation 4 (1993) 283–301.
[12] M.A. Deshusses, C.T. Johnson, Development and validation of a simple protocol to rapidly determine the performance of biofilters for VOC treatment, Environ. Sci. Technol. 34 (2000) 461–467.
[13] K.S. Cho, M. Hirai, M. Shoda, Enhanced removal efficiency of malodorous gases in a pilot-scale peat biofilter inoculated with *Thiobacillus thioparus* Dw44, J. Ferment. Bioeng. 73 (1992) 46–50.
[14] J. Sipma, R. Van Bree, A.J.H. Janssen, B. Arena, L.W.H. Pol, G. Lettinga, Degradation of methanethiol in a continuously operated upflow anaerobic sludge-blanket reactor, Water Environ. Res. 74 (2002) 264–271.
[15] T. Ito, T. Miyaji, T. Nakagawa, N. Tomizuka, Degradation of dimethyl disulfide by *Pseudomonas fluorescens* Strain 76, Biosci. Biotechnol. Biochem 71 (2007) 366–370.
[16] M. Hirai, M. Ohtake, M. Shoda, Removal kinetics of hydrogen-sulfide, methanethiol and dimethyl sulfide by peat biofilters, J. Ferment. Bioeng. 70 (1990) 334–339.
[17] R.A. Pandey, S.N. Mudliar, S. Borgalokar, Treatment of waste gas containing diethyldisulphide (DEDS) in a bench scale biofilter, Bioresour. Technol. 100 (2009) 131–135.
[18] M. Luvsanjamba, A. Kumar, H. Van Langenhove, Removal of dimethyl sulfide in a thermophilic membrane bioreactor, J. Chem. Technol. Biotechnol. 83 (2008) 1218–1225.
[19] R.C. Van Leerdam, F.A.M. De Bok, B.P. Lomans, A.J.M. Stams, P.N.L. Lens, A.J.H. Janssen, Volatile organic sulfur compounds in anaerobic sludge and sediments: biodegradation and toxicity, Environ. Toxicol. Chem. 25 (2006) 3101–3109.
[20] A.G. Luis, G.S. Armando, B. Guillermo, H.J. Sergio, R. Sergio, Treatment of carbon disulfide and ethanethiol vapors in alkaline biotrickling filters using an alkaliphilic sulfo-oxidizing bacterial consortium, J. Chem. Technol. Biotechnol. (2010) 328–335.
[21] H.H.J. Cox, M.A. Deshusses, Biological waste air treatment in biotrickling filters, Curr. Opin. Biotechnol. 9 (1998) 256–262.
[22] B. Sercu, D. Núñez, G. Aroca, N. Boon, W. Verstraete, H. Van Langenhove, Inoculation and start-up of a biotricking filter removing dimethyl sulfide, Chem. Eng. J. 113 (2005) 127–134.
[23] Q. Liao, X. Tian, X. Zhu, R. Chen, Y.Z. Wang, Measurements and modeling of heat generation in a trickling biofilter for biodegradation of a low concentration volatile organic compound (VOC), Chem. Eng. J. 140 (2008) 221–234.
[24] K. Singh, R.S. Singh, B.N. Rai, S.N. Upadhyay, Biofiltration of toluene using wood charcoal as the biofilter media, Bioresour. Technol. 101 (2010) 3947–3951.
[25] S.C. Popat, M.A. Deshusses, Analysis of the rate-limiting step of an anaerobic biotrickling filter removing TCE vapors, Process. Biochem. 45 (2010) 549–555.
[26] R.A. Pandey, P.R. Joshi, S.N. Mudliar, S.C. Deshmukh, Biological treatment of waste gas containing mixture of monochlorobenzene (MCB) and benzene in a bench scale biofilter, Bioresour. Technol. 101 (2010) 5168–5174.
[27] E. Smet, G. Chasaya, H.V. Langenhove, W. Verstraete, The effect of inoculation and the type of carrier material used on the biofiltration of methyl sulphides, Appl. Microbiol. Biotechnol. 45 (1996) 293–298.
[28] E.D. Schroeder, Trends in application of gas-phase bioreactors, Rev. Environ. Sci. Biotechnol. 1 (2002) 65–74.
[29] G.H. Zhao, L.C. Zhou, Y.F. Li, X.X. Liu, X.J. Ren, X.L. Liu, Enhancement of phenol degradation using immobilized microorganisms and organic modified montmorillonite in a two-phase partitioning bioreactor, J. Hazard. Mater. 169 (2009) 402–410.
[30] X. Zhao, Y.M. Wang, Z.F. Ye, A.G.L. Borthwick, J.R. Ni, Oil field wastewater treatment in biological aerated filter by immobilized microorganisms, Process. Biochem. 41 (2006) 1475–1483.
[31] P. Fernádez-Ávarez, J. Vila, J.M. Garrido-Fernádez, M. Grifoll, J.M. Lema, Trials of bioremediation on a beach affected by the heavy oil spill of the Prestige, J. Hazard. Mater. 137 (2006) 1523–1531.
[32] S.G. Wan, G.Y. Li, T.C. An, B. Guo, L. Sun, L. Zu, A.L. Ren, Biodegradation of ethanethiol in aqueous medium by a new *Lysinibacillus sphaericus* strain RG-1 isolated from activated sludge, Biodegradation (2010), doi:10.1007/s10532-010-9366-8.
[33] G.Y. Li, Z. He, T.C. An, X.Y. Zeng, G.Y. Sheng, J.M. Fu, Comparative study of the elimination of toluene vapours in twin biotrickling filters using two microorganisms *Bacillus cereus* S1 and S2, J. Chem. Technol. Biotechnol. 83 (2008) 1019–1026.
[34] A.D. Eaton, L.S. Clesceri, A.E. Greenberg (Eds.), Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, 1995.
[35] C. Arnaiz, P. Buffiere, J. Lebrato, R. Moletta, The effect of transient changes in organic load on the performance of an anaerobic inverse turbulent bed reactor, Chem. Eng. Process. 46 (2007) 1349–1356.
[36] Q.L. Zhao, S.Y. Liu, K. Wang, Biomass,thickness and activity of biofilm in hybrid biofilm reactors, J. Harbin Univ. Civil Eng. Archit. 32 (1999) 39–43.
[37] R.C. Hoehn, A.D. Ray, Effects of thickness on bacterial film, J. Water Pollut. Control Fed. 45 (1973) 2302–2320.
[38] Y.M. Jin, M.C. Veiga, C. Kennes, Effects of pH, CO_2, and flow pattern on the autotrophic degradation of hydrogen sulfide in a biotrickling filter, Biotechnol. Bioeng. 92 (2005) 462–471.
[39] Z. He, L.C. Zhou, G.Y. Li, X.Y. Zeng, T.C. An, G.Y. Sheng, J.M. Fu, Z.P. Bai, Comparative study of the eliminating of waste gas containing toluene in twin biotrickling filters packed with molecular sieve and polyurethane foam, J. Hazard. Mater. 167 (2009) 275–281.
[40] M.C. Delhoméie, L. Bibeau, N. Bredin, S. Roy, S. Broussau, R. Brzezinski, J.L. Kugelmass, M. Heitz, Biofiltration of air contaminated with toluene on a compost-based bed, Adv. Environ. Res. 6 (2002) 239–254.
[41] A.B. Cunningham, O. Wanner, Modeling biofilm accumulation and mass transport in a porous medium under high substrate loading, Biotechnol. Bioeng. 47 (1995) 703–712.
[42] D. McNevin, J. Barford, Biofiltration as an odour abatement strategy, Biochem. Eng. J. 5 (2000) 231–242.
[43] Y. Yang, R. Allen, Biofiltration control of hydrogen sulfide. I: design and operational parameters, J. Air. Waste Manage. 44 (1994) 863–868.
[44] Y.C. Chung, C.P. Huang, C.P. Tseng, Operation optimization of *Thiobacillus thioparus* CH11 biofilter for hydrogen sulfide removal, J. Biotechnol. 52 (1996) 31–38.
[45] K.L. Ho, Y.C. Chung, Y.H. Lin, C.P. Tseng, Microbial populations analysis and field application of biofilter for the removal of volatile-sulfur compounds from swine wastewater treatment system, J. Hazard. Mater. 152 (2008) 580–588.