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Efficient bio-deodorization of thioanisole by a novel bacterium *Brevibacillus borstelensis* GIGAN1 immobilized onto different parking materials in twin biotrickling filter

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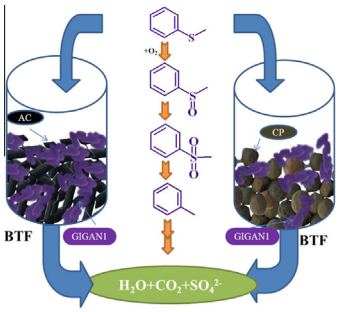
HIGHLIGHTS

- A thioanisole-utilizing bacterium was successfully isolated and identified.
- Performance of a twin BTF for thioanisole removal was compared in detail.
- Higher RE and EC was obtained in these two BTF than previous reports.
- Long-term performance of BTF was discussed by measuring pressure drop and biomass.
- The thioanisole degradation pathways and deodorization mechanism were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Biological treatment of odorous gas is an alternative to conventional physicochemical processes. A newly-isolated and identified *Brevibacillus borstelensis* GIGAN1 was seeded on active carbon (AC) and ceramic particle (CP) in a twin biotrickling filter (BTF) to comparatively probe the removal performance of gaseous thioanisole, respectively. At empty bed residence time (EBRT) of 66 s, 100% of thioanisole ($\leqslant$3 mg L^{-1}) could be removed on AC; while 100% of thioanisole could only be achieved for $\leqslant$1.2 mg L^{-1} on CP. Further increase thioanisole concentration to 3 mg L^{-1}, higher elimination capacity was obtained on AC (162.51 g m^{-3} h^{-1}) than CP (139.93 g m^{-3} h^{-1}). Further, longer EBRT was also beneficial to thioanisole removal. Additionally, the biomass accumulation did not lead to the column clogging. The biodeodorization mechanism of thioanisloe were also tentatively proposed. Overall, an unprecedented performance could be achieved by the novel GIGAN1 in BTF for thioanisole biodegradation.

1. Introduction

Volatile organic sulfur compounds (VOSCs) have received much attention in recent years due to their low odor thresholds, potential corrosive effect as well as chronic adverse effect on human and other biota (Barea et al., 2014; Rumsey et al., 2014). VOSCs including thioanisole, dimethyl sulfide and dimethyl disulfide can be emitted from various activities, such as aerobic and anaerobic waste and sewage treatment processes, agricultural operations, food industries and craft pulp manufacturing (Li et al., 2012). Among these odorants, thioanisole is one of VOSCs that were extremely difficult to be eliminated and might in turn cause the accumulation of the contaminants. With the increasing public expectations on air quality, the removal of these odorants from the atmosphere to provide nuisance free breathable air is therefore highly desired and attracted considerable interesting in recent decades (Mudliar et al., 2010).

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As a promising biological technology, this environmental friendly and cost-effective waste air treatment method (Jin et al., 2007) employed various reactors including bioscrubber, biofilter, biotrickling filter (BTF) and membrane bioreactor to purify polluted gas (Delhomenie and Heitz, 2005). Although a wide and various bioreactors can be selected, the principle of them is almost the same. That is, volatile contaminants were firstly adsorbed onto the biofilm when they passed through the reactor, then transformed into simple, odorless end products (Hort et al., 2009; Liu et al., 2009). Nevertheless, BTF is by far proved to be the most perspective bioreactor for odor treatment from industrial and municipal airstreams due to its superiority in the elimination of high concentrated gaseous pollutants (He et al., 2009). Compared with other bioreactors, BTF possessed circulated trickling nutrimental solution, which is conducive to control the operational environment (Shareefdeen and Singh, 2005). Besides, the packing materials of BTF such as resins, ceramic particles (CP) (Wan et al., 2011c), Celite, polyurethane foam and molecular sieve (He et al., 2009; Mudliar et al., 2010) are also beneficial to the flow of gas and liquid through the bed, as well as the formation of biofilm. Furthermore, the outstanding removal efficiency of off-gas emission in BTF packed with CP and activated carbons (AC), which have excellent absorption capacity, microporous structural properties and good resistance to crush, has already been demonstrated in previous studies (An et al., 2010; Duan et al., 2007).

Recently, many studies were focused on the removal of VOSCs in aqueous solution by microorganisms. For instance, ethanethiol and dimethyl disulfide could be effectively biodegraded by a new *Lysinibacillus sphaericus* RG-1 (Wan et al., 2010) and *Bacillus cereus* GIGAN2 (Liang et al., 2015), respectively. Further, extensive literatures were also focused on using BTF to control various odorants, such as inorganic odor H_2S (Mannucci et al., 2012; Zhang et al., 2009), and organic odor like dimethyl sulfide, ethanethiol, dimethyl disulfide, and methanethiol (Arellano-Garcia et al., 2009; Lebrero et al., 2012; Wan et al., 2011b). However, only two papers were focused on the abatement of thioanisole-containing odorous vapors by BTF inoculated with commercialized B350 or self-isolated *L. sphaericus* RG-1 (Wan et al., 2011a,b). Nevertheless, it is very essential to highlight that no paper has been published concerning the isolation of a new bacterium to efficiently remove thioanisole both in aqueous solution and gaseous atmosphere, as well as the bio-deodorization of the sole thioanisole with single dominant microorganism.

In the present study, a novel strain, which serve as the catalyst, was isolated and used to examine its function of deodorizing high concentration waste gas containing thioanisole in a twin BTF packed onto AC and CP. First of all, an aerobic bacterium capable of removal thioanisole was isolated and successfully identified as *Brevibacillus borstelensis* GIGAN1 using thioanisole as sole carbon and energy source. Secondly, the effect of key factors, such as inlet concentration and the gas flow rate (empty bed residence time, EBRT) on the removal efficiencies (REs) as well as elimination capacities (ECs) were in depth optimized and compared by using this novel bacterium inoculated in a twin BTF packed onto AC and CP. Finally, the bio-deodorization mechanism of thioanisole was tentatively proposed to gain a full insight into the atmospheric fate of thioanisole based on the identified intermediates.

2. Methods

2.1. Chemicals and reagents

Thioanisole (99%) selected as the representative odorous waste gas, and the authentic standards of methyl phenyl sulfoxide (98.0%) and methyl phenyl sulfone (99%), were all obtained from J&K Chemical Ltd. All other chemicals were of analytical grade from Guangzhou Chemical Reagent Co., Inc., China. The specific recipe of mineral medium (MM) used for strain isolation or flow nutrient medium of BTF is listed in the Supporting information (SI).

2.2. Strain isolation and identification

The seeded bacterium was isolated from a river sludge in Guangzhou, China. The isolation procedure was similar to our previous study about the ethanethiol degrading strain isolation (Wan et al., 2010). Physiological, cultural and biochemical characteristics of the bacterium were performed according to the standard techniques (Volova et al., 2005). Scanning electron microscope (SEM) was used to observe the cell morphology. Genomic DNA was extracted using genomic DNA isolation kit (Sangon Biotech Co., Ltd., Shanghai), and used as the template for PCR amplification. Universal bacterial primers: 27 F (5′ – AGAGTTTGATCCTGGCTCAG – 3′) and 1492 R (5′ – GGTTACCTTGTTACGACTT – 3′) (Park et al., 2012) was designed to amplify the 16 sRNA gene by PCR. Experimental details are listed in the SI.

2.3. Biotrickling filter system setup

All experiments were carried out in a home-made twin BTF with effective volume of 9.23 L, a height of 1.2 m and an inner diameter of 0.14 m. The schematic diagram of BTF and the experimental set up were provided in our previous work (Wan et al., 2011b). The difference from previous work is the microorganism and packing materials. In this work, a newly-isolated strain was seeded on CP and AC in BTF for thioanisole abatement. As Table 1 shows, CP possesses a notably lower specific surface area and moisture content (200–500 $m^2\ g^{-1}$ and 15–25%, respectively) than AC (800–900 $m^2\ g^{-1}$ and 35–45%), indicating that AC might provide an attractive nutrient-rich environment for the bacterial growth.

The BTF consists of two columns, and each includes six layers filled with AC or CP to a height of 10 cm, respectively. The air pump, thioanisole reservoir, nutrient medium distributor and peristaltic pump were controlled by microcomputers. With these, the thioanisole vapor with determinate concentration could be controlled by adjusting the gas flow rate, and thioanisole-containing gas could be continuously fed into BTF from the top. Prior to the startup, the inlet and outlet concentration of thioanisole was constantly measured to assess the adsorption equilibrium of the packing materials. Then BTF was inoculated with the isolated strain. MM was intermittently irrigated from the top of the reactor six times per day at 7 L h^{-1} for 15 min to keep the moisture of packing material and to supply nutrition for the bacteria growth. Meanwhile, the pH value in the re-circulated medium was adjusted to the optimal value of 7.0 for the reproduction of the strain. The system was operated at room temperature throughout all the experiment, and was successful started up after 1 month immobilization and the acclimatization of bacteria.

Table 1
The physical–chemical parameters of two packing materials used in this study.

Packing materials	Ceramic particles	Activated carbons
Shape	Circle	Column
Pile density (g cm^{-3})	0.75–1.1	0.9–1
Particle diameter (mm)	4–6	2–4
Specific surface area ($m^2\ g^{-1}$)	200–500	800–900
Porosity (%)	45–55	45–50
Moisture content (%)	15–25	35–45

2.4. Analytical methods

Thioanisole concentration from the inlet, various sampling ports and outlet, biofilm mass and pressure drop were periodically measured as follows: a 300 μL gas sample was injected into a HP 6890 II gas chromatography (GC) equipped with a HP-5MS capillary column (0.25 mm × 0.25 μm × 30 m) and a flame ionization detector (Hewlett–packard, USA) with a splitless mode to determine thioanisole concentration. Oven, injector and detector temperatures were maintained at 50, 200 and 230 °C, respectively. The programmed temperature of the column increased from 50 to 150 °C at 15 °C min^{-1} (held for 2 min), followed by a further increased to 230 °C at a rate of 25 °C min^{-1}. The biofilm formed onto the packing material was observed by SEM (Quanta 400 FEG, FEI, USA). The thickness of the biofilm was measured according to an early reference (Irving and Allen, 2011), and the mass was measured by weight loss (Arnaiz et al., 2007). Pressure drop across the BTF was also determined using a U-tube pressure meter with a minimum reading of 1 mm water column.

Two parameters, removal efficiency (RE, %) and elimination capacity (EC, g m^{-3} h^{-1}), were used to evaluate treatment performance of twin-BTF, and the detailed calculation method referred to our previous work (Wan et al., 2011b).

2.5. Identification of metabolites

Biodegradation intermediates in gas samples and re-circulating liquid were both identified by a GC (Agilient 7890) – Mass Spectrometer (MS) (5975C) detector with a DB-5MS (30 m × 0.25 mm × 0.25 μm film thickness) capillary column using full scan model (*m/z*: 30–500 amu). Generally, gas phase products (300 μL) could be directly determined after concentrating by Entech 7100 A Preconcentrator, while the metabolites in the re-circulated liquid (100 mL) were further processed as following procedure before injected into GC–MS. That is, samples were consecutively extracted three times using 30 mL dichloromethane, then concentrated to 1 mL by a rotary evaporator and dried with a gentle stream of high-purity nitrogen, followed by the re-dissolved in 100 μL hexane. Column temperature was programed as followed: 60 °C for 2 min, rose to 150 °C at the rate of 10 °C min^{-1} and then to 250 °C at 15 °C min^{-1}.

3. Results and discussion

3.1. Properties of thioanisole-degrading strain

By far, the shortage of high efficient strain in conventional biological treatment of the increasing number of thioanisole-containing waste gas, have created an urgent need for the investigation of this microorganism and may have important significance to the removal of these compounds. In this study, an aerobic bacterium capable of removal thioanisole was successfully isolated using thioanisole as sole carbon and energy source. The morphological, physiological and biochemical characteristics of the isolated strain (Table S1 and Fig. S1) showed that the colonies of the strain on the solid agar plate were round, opaque, cream with a diameter of 1–2 mm, and it is a rod shaped (0.5–0.8 × 6–8 μm), Gram positive strain with flagella. In addition, it was positive for nitrate reduction, citrate utilization, gelatin liquefaction and the hydrolysis of DNA, while negative for using mannitol, arabinose, glucose and xylose as the sole carbon source and for *V–P* test, catalase and the hydrolysis of starch. Although this strain cannot grow under relatively harsh condition such as 15 °C, pH 5.5 or 9.0 and 2.0–5.0% NaCl solution, it can still grow under the temperature of 50 °C, which supply good conditions for the environmental application of the strain to mineralize the contaminants both in gas and water phase. Furthermore, to identify the genus of this strain, the phylogenetic tree was also constructed based on the 16S rRNA sequence with 1436 bp length (Genbank accession number: KC693053) using Neighbor-joining method after the alignment with the related sequences from the genebank database. As Fig. 1 shows, this strain is clustered in the phylogenetic branch of family *Brevibacillus* and has a similarity up to 100% to *B. borstelensis*. Thus, this novel isolated strain was classified into the genus *Brevibacillus* and names as *B. borstelensis* GIGAN1.

3.2. Bioreactor start-up

To overcome the difficulty of atmospheric application of this newly-isolated bacterium and to investigate the operation condition of BTF bioreactor as well as to evaluate the removal efficiency of thioanisole in this reactor, the start-up of BTF was carried out. During the start-up period, gaseous thioanisole was gradually introduced to the BTF columns from 0.5 to 1 mg L^{-1} at fixed EBRT of 88 s. It was found that the REs were very low at the first few days, then increased slightly to 100% by day 30, suggesting that the BTF was ready to use after a month start-up. Furthermore, the biofilm onto the CP and AC was observed using SEM at 30th day. As Fig. S2a and c shows, before immobilization, the surface of CP is irregular and smooth, while AC is porous and coarse. However, after 1 month start-up, the microorganisms were immobilized onto the packing materials, and more rod-shaped microorganisms could be observed onto AC than CP (Fig. S2b and d). This is due to larger surface area of AC, which is facilitate the growth of microorganisms on the surface. This conclusion also can be confirmed by the biomass analysis. That is, the biomass rose gradually from 0 to 130.61 mg g^{-1} onto AC, while only to 12.78 mg g^{-1} for CP during 30 days start-up process. It is hence no surprising that the CP need more time to form the biofilm than AC, and the REs of the AC-packed BTF will far outweigh than CP-packed bioreactor.

3.3. Influence of inlet concentration on the removal performance

Following the rapid start-up, the effect of thioanisole concentration on the BTF treatment performance was evaluated at fixed

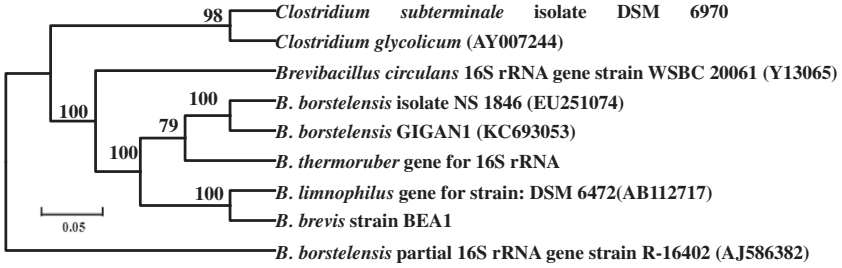

Fig. 1. Phylogenetic tree based on 16S rRNA sequence analysis (1000 bootstrap for the confidence level).

EBRT of 66 s by adjusted gaseous concentration ranging from 0.5 to 3.0 mg L^{-1}. The REs of packed BTF onto CP and AC at different initial thioanisole concentrations are presented in Fig. S3a and b, respectively. The total REs decreased with increased inlet concentration, and 100% total REs were achieved after gas passing through 4th (0.5 mg L^{-1} thioanisole) and 5th layer (0.8–1.2 mg L^{-1} thioanisole) for the BTF packed with CP. When the inlet concentrations were further increased from 1.5 to 3.0 mg L^{-1}, total REs fell substantially from 93.2% to 86.1%. Comparatively, superior biodegradation efficiency was achieved with BTF packed with AC. That is, 100% of thioanisole could be removed when thioanisole pass through 3rd (0.5–0.8 mg L^{-1}), 4th (1.0–1.2 mg L^{-1}), 5th (1.5–2.5 mg L^{-1}) and 6th (3 mg L^{-1}) layer. It is important to highlight that REs achieved with both packing materials in the present work were higher than previous works with identical BTF. For instance, at fixed EBRT of 110 s, 100% of thioanisole could be removed only when the thioanisole concentration was less than 0.33 and 0.23 mg L^{-1} by *L. sphaericus* RG-1 and B350 group with a CP packed BTF, respectively (Wan et al., 2011a,b), which is much less than 1.2 mg L^{-1} achieved in this work.

Besides, ECs is also considered to be associated with the performance of BTF under various inlet loads, which are plotted in Fig. S3c and d. Even after increasing inlet thioanisole from 0.5 to 1.2 mg L^{-1}, the same ECs (increased suddenly from 27.09 to 65.01 g m^{-3} h^{-1}) was able to maintain for both packed BTFs. However, when the inlet concentration was increased further, different effect on the thioanisole removal was also observed. For AC packed BTF, the total ECs increased dramatically from 81.26 to 162.51 g m^{-3} h^{-1}, while relatively lower ECs (varied from 75.74 to 139.93 g m^{-3} h^{-1}) for CP packed BTF were achieved as the concentration increased from 1.5 to 3 mg L^{-1}. It is worth pointing out that the increase of ECs may be related to an improved thioanisole mass transfer from the air to the biofilm (Fortuny et al., 2011). Furthermore, higher ECs achieved in BTF packed with AC than that of CP may be explained by higher bacterial coverage, which result in a bigger interfacial surface-to-volume ratio inside the reactor.

To further explore which layers played a major role in the elimination of thioanisole in BTF, the relationship between ECs of different layers and the inlet concentrations were investigated (Tables S2 and S3). For CP-packed BTF, the total ECs of layers 1–3 and 4–6 rose dramatically from 25.72 to 118.20 g m^{-3} h^{-1} and 1.37 to 21.73 g m^{-3} h^{-1}, respectively, as the inlet concentrations correspondingly increased from 0.5 to 3 mg L^{-1}. Comparatively, the AC-packed BTF possessed much higher ECs of layers 1–3 and 4–6, which varied from 27.09 to 148.43 g m^{-3} h^{-1}, and 0 to 14.09 g m^{-3} h^{-1} under the same conditions, than that of CP-packed BTF. Thus, it can be concluded that thioanisole was mainly biodegraded at the first to third layers of the BTF for both packed materials.

3.4. Influence of EBRT on the removal performance

The increase of EBRT (from 42 to 110 s, corresponding to gas flow rate from 800 to 300 L h^{-1}) for the biological system was expected to cause a direct effect on the twin BTF performance. As Fig. 2a and b shows, at fixed thioanisole concentration of 1.2 mg L^{-1}, although the biodegradation trends are different from each other, higher EBRT generally results in better REs for both packing materials because the inlet load would exceed the removal capability of GIGAN1 in such a short EBRT. Overall, for CP packed BTF, total REs of 100% was achieved as the thioanisole-containing gas passing through 5th and 6th layer at the EBRT 110 to 63 and 55 s. With further shortening the EBRT to 47 and 42 s, the total REs slowly decreased from 93.6% to 91.0%. The reason is that lower gas flow (responding to longer EBRT) would provide adequate time for microbes to completely eliminate thioanisole and result in

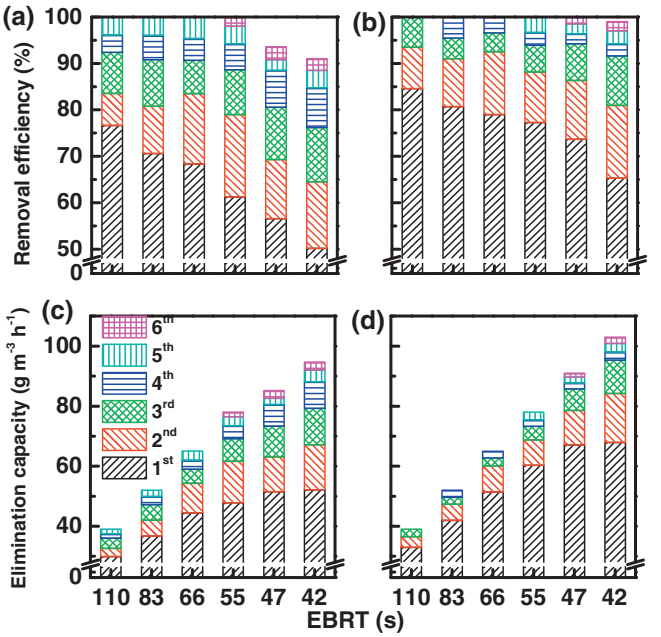

Fig. 2. Comparative studies of the performance of EBRT on the effect of REs in BTF packed with CP (a) and AC (b), as well as ECs in BTF packed with CP (c) and AC (d) at fixed concentration of 1.2 mg L^{-1}.

higher REs (Li et al., 2008; Mirmohammadi et al., 2014). Comparatively, AC-packed BTF possessed higher REs than that of CP-packed BTF, and 100% of thioanisole could be eliminated at EBRT $\geqslant$ 47 s. This could be interpreted that bigger specific surface area of AC material is beneficial for the formation of the biofilm and the subsequent biodegradation of thioanisole by microorganisms.

Unlike REs, the ECs of both packed BTFs showed opposite changing trend (Fig. 2c and d). The ECs increased from 39.00 to 94.65 g m^{-3} h^{-1} for CP-packed BTF, while to 102.97 g m^{-3} h^{-1} for AC-packed BTF with the falling of EBRT from 110 to 42 s. In addition, Tables S4 and S5 also display that thioanisole concentrations at the outlet dropped dramatically as the distance from the inlet increased. As the EBRT reduced from 110 to 42 s, large quantity of thioanisole was removed at layers 1–3 with ECs increased from 36.03 to 79.27 g m^{-3} h^{-1} for CP-packed BTF, as well as from 39.00 to 95.30 g m^{-3} h^{-1} for AC-packed BTF. Notably, it is relevant to stress that ECs of last three layers was far less than that of first three layers, just increased from 7.60 to 14.80 g m^{-3} h^{-1} for BTF packed with CP, and from 0 to 7.4 g m^{-3} h^{-1} for BTF packed with AC, respectively. This phenomenon is likely attributed to the orientation of the gas flow from the top to bottom, which provide enough carbon and energy source for the growth of GIGAN1 bacteria to form thicker biofilm in the layers 1–3 of BTF reactor (Wan et al., 2011a).

In conclusion, the above results illustrated that both much higher REs and ECs were achieved in AC-packed BTF than that of CP-packed BTF under the same conditions. Prior to applying into the environment, further research is needed to observe the limitations of this system, such as the accumulation of the sulfate, as well as the excess biomass in the packing bed and the change of pH value during the long operation of these reactors.

3.5. Long-term performance of the biotrickling filter

Generally, the formation and accumulation of the biomass on the surface of the packing materials would not only change the effective porosity and pore shape of the carriers, but also result in the variation of resistance to the gas flow and circulated liquid

in BTF (Chen et al., 2012). Thus, the pressure drop of the continuous operation of BTF was measured as the gas flow increased from 300 to 800 L h^{-1} (Fig. 3). It can be revealed that the total pressure maintained around 80 and 104 Pa by day 20, for CP-packed and AC-packed BTF, respectively, then rose sharply due to biomass growth and finally responding stayed at 224 and 251 Pa by day 40 at gas flow rate of 500 L h^{-1}. Obviously, the pressure drop remained low when the waste gas passing through the first three layers or when the gas flow rate was set at lower values. However, the increase of gas flow rate resulted in an additional increase in the pressure drop. For instance, the total pressure in CP-packed BTF rose sharply from 91 to 525 Pa by day 40 as the flow rate accordingly rose from 300 to 800 L h^{-1}, which is a little lower than that of AC-packed BTF with the pressure drop increased from 104 to 579 Pa. The probable reason for this phenomenon was that excess thioanisole gas fed to BTF can lead to a significant growth of microorganisms, which in turn result in the increase of the pressure drop. In addition, it is worth mentioning that the pressure drop changed with the distance from the inlet, at 10 to 60 cm from the inlet of BTF, the pressure drop increased from 33 to 48 Pa for CP-packed BTF, and 39 to 48 Pa for AC-packed BTF. Furthermore, the accumulation of the microorganisms with thioanisole feeding can be reflected by the amounts of the biomass. As Fig. 4 shows, the mass of biofilm onto CP material suddenly increased from 12.78 to 48.6 mg L^{-1} at day 30 to 45, and then rose slightly to 99.37 at day 75. Comparatively, the biomass onto AC was larger than that of CP with the thickness grew from 130.61 to 330.95 mg g^{-1} at day 30 to 75. This can be explained that thioanisole is much easier to be adsorbed onto AC-packed biofilm, which subsequently led to faster growth of microorganisms and produced larger amounts of the biomass than that of CP. From the above results, it can be concluded that no clogging was encountered during the long operation period in both columns packed with CP and AC, and AC-packed BTF with a higher pressure drop due to biomass accumulation in the bed, involved material with more porosity and better mechanical strength than that of CP-packed BTF.

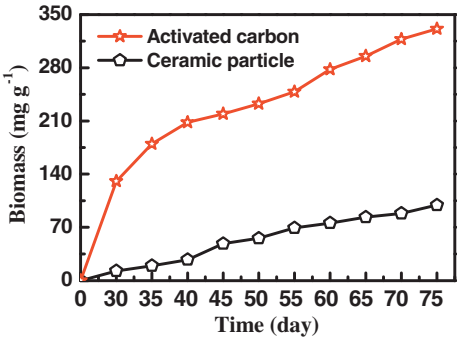

Fig. 4. Development of biomass across CP-packed and AC-packed BTF with increase of the operating time at fixed EBRT of 66 s.

Complete biodegradation of thioanisole leads to the production of hydrogen proton and fluctuation of pH value. Thus, acidification has often been an obstacle to use biotechnological method to deodorize sulfur-containing waste gas and thus controlling pH to appropriate level has proved to be very important step for bioreactor function (Pantoja et al., 2010). Therefore, pH value and major metabolic products of thioanisole in leachate from twin BTF were regularly measured during 65-day operation period. As Fig. 5 shows, the pH value of the re-circulated liquid did not exhibit abrupt fluctuation, only with small fluctuating between 6.73 and 7.86 for AC-packed BTF, and between 7.20 and 7.42 for CP-packed BTF after adjusting with 0.1 M NaOH during the entire operating period. Besides, the sulfate concentration in leachate was regularly monitored, because the production of sulfate can be used as standard to directly confirmed the mineralization of thioanisole. As

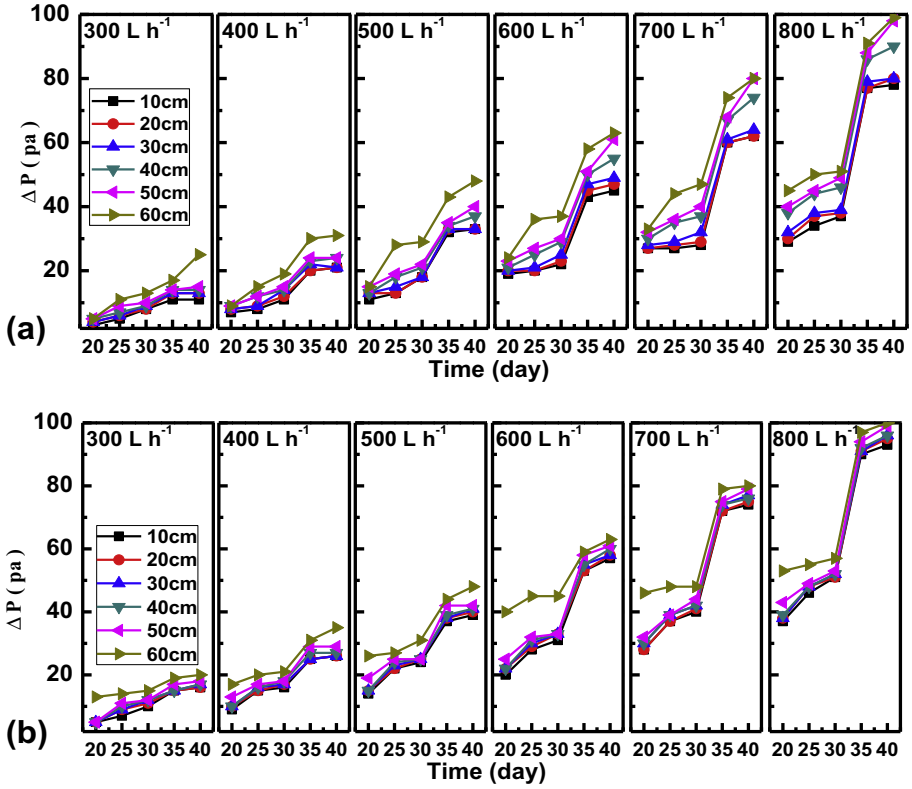

Fig. 3. Pressure drop comparison of twin BTF packed with CP (a) and AC (b) over the time at different gas flow rates.

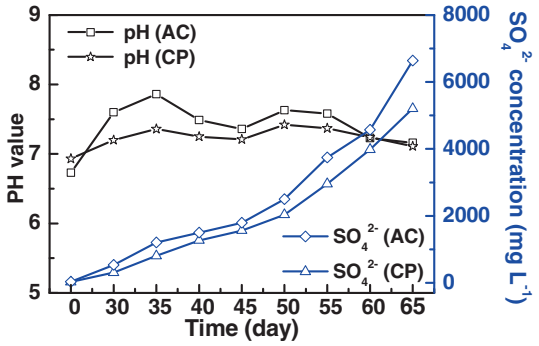

Fig. 5. Evolution of pH values and sulfate concentrations with increase of the operating time.

Fig. 5 illustrates, for AC-packed BTF, the sulfate concentration was slightly increased from 537.06 to 1794.71 mg L^{-1} from 30th to 45th day, then dramatically increased to 6636.65 mg L^{-1} at day 65. However, it is worth noting that sulfate production amount slightly less for CP-packed BTF than that of AC-packed BTF were also encountered, which increased from 307.24 (30th day) to 1562.01 (45th day), then to 5204.98 mg L^{-1} (65th day), probably due to slower or inadequate conversion of thioanisole by GIGAN1 onto CP-packed BTF.

3.6. Degradation mechanism of thioanisole

To further ascertain the detoxification potential of thioanisole in BTF by the novel isolated strain GIGAN1, the possible biodeodorization mechanism and degradation pathway were elucidated based on the degradation products identified. The intermediates in the gaseous mixtures obtained from the outlet of each layer of BTF, as well as in the re-circulated liquid were identified by GC–MS. As Fig. S4 shows, although no any other by-products was presented in gas phase due to the formation of more polar intermediates during the bioconversion of thioanisole, three probable intermediates were still identified in leachate. The mass spectra of these three by-products were compared with the standard spectra of NIST Mass Spectral Library and shown in Table S6 and Fig. S5. The results reveal that, after validation with the authentic standards, a couple *m*/*z* values of 92/91 corresponding to M^+/M^+-1 fragment was identified as toluene (retention time (RT) = 4.320). Also, *m*/*z* values of 140 and 156 corresponding to M^+ fragment were obtained with a molecule weight of methyl phenyl sulfoxide (RT = 19.924) and methyl phenyl sulfone (RT = 21.679), respectively. Thus, based on foregoing identified intermediates and following two published references, the possible biodegradation pathway of thioanisole by this newly-isolated strain GIGAN1 was proposed as Scheme S1. The SCH_3 group rather than benzene ring of thioanisole was first attacked and then converted to methyl phenyl sulfoxide with the presence of O_2 by bacterium GIGAN1. Then, an active biotransformation of the formed sulfoxide to methyl phenyl sulfone occured, which might be due to the contribution of thioanisole oxygenase released from the bacterium. This result is well agreed with previous reports, which in detail discussed the oxidative mechanism of thioanisole by *Rhodococcus rhodochrous* IEGM 66 cells (El'kin et al., 2010) and singlet oxygen under visible light (Li et al., 2011), respectively. Subsequently, toluene was also formed via the methylation of sulfone and all the by-products could be eventually completely metabolized into CO_2, H_2O and sulfate. This results can also inspire us that this isolated *B. borstelensis* GIGAN1 might be used to the environmental remediation application like the removal of toluene and other sulfur-containing compounds.

4. Conclusions

A novel aerobic strain, *B. borstelensis* GIGAN1 was isolated and inoculated into twin BTF to compare thioanisole removal performance. 100% of thioanisole ($\leqslant$1.2 and $\leqslant$3.0 mg L^{-1}) could be removed for CP- and AC-packed BTF at EBRT of 66 s, respectively. Maximum ECs of 94.65 and 102.97 g m^{-3} h^{-1} for CP- and AC-packed BTF can be achieved at 1.2 mg L^{-1} thioanisole. Long-term stability of BTF suggested that no clogging was encountered during entire operation period. Besides, thioanisole metabolic mechanism was also tentatively proposed. Overall, this was the first report that a novel strain was isolated for thioanisole deodorization.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.01.120.

References

An, T.C., Wan, S.G., Li, G.Y., Sun, L., Guo, B., 2010. Comparison of the removal of ethanethiol in twin-biotrickling filters inoculated with strain RG-1 and B350 mixed microorganisms. J. Hazard. Mater. 183, 372–380.
Arellano-Garcia, L., Revah, S., Ramirez, M., Gomez, J.M., Cantero, D., 2009. Dimethyl sulphide degradation using immobilized *Thiobacillus thioparus* in a biotrickling filter. Environ. Technol. 30, 1273–1279.
Arnaiz, C., Buffiere, P., Lebrato, J., Moletta, R., 2007. The effect of transient changes in organic load on the performance of an anaerobic inverse turbulent bed reactor. Chem. Eng. Process. 46, 1349–1356.
Barea, E., Montoro, C., Navarro, J.A.R., 2014. Toxic gas removal – metal–organic frameworks for the capture and degradation of toxic gases and vapours. Chem. Soc. Rev. 43 (16), 5419–5430.
Chen, R., Liao, Q., Tian, X., Wang, Y.Z., Zhu, X., Miao, J.H., 2012. Characterization of the start-up behavior and steady-state performance of biotrickling filter removing low concentration toluene waste gas. Sci. China Technol. Sci. 55, 1701–1710.
Delhomenie, M.C., Heitz, M., 2005. Biofiltration of air: a review. Crit. Rev. Biotechnol. 25, 53–72.
Duan, H.Q., Yan, R., Koe, L.C.C., Wang, X.L., 2007. Combined effect of adsorption and biodegradation of biological activated carbon on H_2S biotrickling filtration. Chemosphere 66, 1684–1691.
El'kin, A.A., Grishko, V.V., Ivshina, I.B., 2010. Oxidative biotransformation of thioanisole by *Rhodococcus rhodochrous* IEGM 66 cells. Appl. Biochem. Microbiol. 46, 586–591.
Fortuny, M., Gamisans, X., Deshusses, M.A., Lafuente, J., Casas, C., Gabriel, D., 2011. Operational aspects of the desulfurization process of energy gases mimics in biotrickling filters. Water Res. 45, 5665–5674.
He, Z., Zhou, L.C., Li, G.Y., Zeng, X.Y., An, T.C., Sheng, G.Y., Fu, J.M., Bai, Z.P., 2009. 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, 275–281.
Hort, C., Gracy, S., Platel, V., Moynault, L., 2009. Evaluation of sewage sludge and yard waste compost as a biofilter media for the removal of ammonia and volatile organic sulfur compounds (VOSCs). Chem. Eng. J. 152, 44–53.
Irving, T.E., Allen, D.G., 2011. Species and material considerations in the formation and development of microalgal biofilms. Appl. Microbiol. Biotechnol. 92, 283–294.
Jin, Y.M., Veiga, M.C., Kennes, C., 2007. Co-treatment of hydrogen sulfide and methanol in a single-stage biotrickling filter under acidic conditions. Chemosphere 68, 1186–1193.
Lebrero, R., Rodriguez, E., Estrada, J.M., Garcia-Encina, P.A., Munoz, R., 2012. Odor abatement in biotrickling filters: effect of the EBRT on methyl mercaptan and hydrophobic VOCs removal. Bioresour. Technol. 109, 38–45.
Li, G.Y., He, Z., An, T.C., Zeng, X.Y., Sheng, G.Y., Fu, J., 2008. 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, 1019–1026.
Li, W.L., Xie, Z.G., Jing, X.B., 2011. BODIPY photocatalyzed oxidation of thioanisole under visible light. Catal. Commun. 16, 94–97.
Li, G.Y., Wan, S.G., An, T.C., 2012. Efficient bio-deodorization of aniline vapor in a biotrickling filter: metabolic mineralization and bacterial community analysis. Chemosphere 87, 253–258.
Liang, Z.S., An, T.C., Li, G.Y., Zhang, Z.Y., 2015. Aerobic biodegradation of odorous dimethyl disulfide in aqueous medium by isolated *Bacillus cereus* GIGAN2 and identification of transformation intermediates. Bioresour. Technol. 175, 563–568.
Liu, Q., Li, M., Chen, R., Li, Z.Y., Qian, G.R., An, T.C., Fu, J.M., Sheng, G.Y., 2009. Biofiltration treatment of odors from municipal solid waste treatment plants. Waste Manage. 29, 2051–2058.
Mannucci, A., Munz, G., Mori, G., Lubello, C., 2012. Biomass accumulation modelling in a highly loaded biotrickling filter for hydrogen sulphide removal. Chemosphere 88, 712–717.
Mirmohammadi, M., Bayat, R., Shirazi, H.K., Sotoudeheian, S., 2014. Effect of empty bed residence time on biotrickling filter performance: case study-triethylamine. Int. J. Environ. Sci. Technol. 11, 183–190.
Mudliar, S., Giri, B., Padoley, K., Satpute, D., Dixit, R., Bhatt, P., Pandey, R., Juwarkar, A., Vaidya, A., 2010. Bioreactors for treatment of VOCs and odours – a review. J. Environ. Manage. 91, 1039–1054.
Pantoja, J.L.R., Sader, L.T., Damianovic, M.H.R.Z., Foresti, E., Silva, E.L., 2010. Performance evaluation of packing materials in the removal of hydrogen sulphide in gas-phase biofilters: polyurethane foam, sugarcane bagasse, and coconut fibre. Chem. Eng. J. 158, 441–450.
Park, I., Lee, J., Cho, J., 2012. Degradation of phytate pentamagnesium salt by *Bacillus* sp T4 phytase as a potential eco-friendly feed additive. Asian Australasian J. Anim. Sci. 25, 1466–1472.
Rumsey, I.C., Aneja, V.P., Lonneman, W.A., 2014. Characterizing reduced sulfur compounds emissions from a swine concentrated animal feeding operation. Atmos. Environ. 94, 458–466.
Shareefdeen, Z., Singh, A., 2005. Biotechnology for Odor and Air Pollution Control. Springer.
Volova, T.G., Kozhevnikov, I.V., Dolgopolova, Y.B., Trusova, M.Y., Kalacheva, G.S., Aref'eva, Y.V., 2005. Physiological and biochemical characteristics and capacity for polyhydroxyalkanoates synthesis in a glucose-utilizing strain of hydrogen-oxidizing bacteria, *Ralstonia eutropha* B8562. Microbiology 74, 684–689.
Wan, S.G., Li, G.Y., An, T.C., Guo, B., Sun, L., Zu, L., Ren, A.L., 2010. Biodegradation of ethanethiol in aqueous medium by a new *Lysinibacillus sphaericus* strain RG-1 isolated from activated sludge. Biodegradation 21, 1057–1066.
Wan, S.G., Li, G.Y., An, T.C., 2011a. Treatment performance of volatile organic sulfide compounds by the immobilized microorganisms of B350 group in a biotrickling filter. J. Chem. Technol. Biotechnol. 86, 1166–1176.
Wan, S.G., Li, G.Y., An, T.C., Guo, B., 2011b. 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. J. Hazard. Mater. 186, 1050–1057.
Wan, S.G., Li, G.Y., Zu, L., An, T.C., 2011c. Purification of waste gas containing high concentration trimethylamine in biotrickling filter inoculated with B350 mixed microorganisms. Bioresour. Technol. 102, 6757–6760.
Zhang, L.H., Wang, Q.H., Tian, S.L., Wang, X.Q., Xie, W.M., Sun, P.T.C., 2009. Biodegradation of hydrogen sulphide by inoculated *Rhodococcus* sp. zw11 in a pilot-scale biotrickling filter. Int. J. Environ. Pollut. 37, 450–465.