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RESEARCH PAPER

Treatment of Volatile Organic Compounds from a Typical Waste Printed Circuit Board Dismantling Workshop by a Pilot-scale Biotrickling Filter

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Abstract A pilot-scale biotrickling filter (BTF) was designed to treat volatile organic compounds (VOCs) emitted from a typical waste printed circuit board (WPCB) pyrolysis workshop. Measured by gas chromatography-mass spectrometry (GC-MS), the main components of VOCs and their concentrations were benzene, toluene, chlorobenzene, ethyl-benzene, xylene, styrene, benzaldehyde, and trimethyl-benzene. The removal efficiencies of the BTF for these compounds ranged from 81.1 to 97.8% after 90 days of operation. The maximum elimination capacity of 25.94 g/m^3 h was obtained with the inlet loading of 30.72 g/m^3 fixed the fixed empty-bed residence time (EBRT) of 9.80 sec. Hazard ratio index based on threshold limit value for time weighted average (TLV-TWA) and VOCs concentrations indicated that the cancer risk of VOCs was significantly reduced after the BTF treatment. The microbial community analysis revealed initial inoculum and some emerging bacteria played crucial roles in the improvement of BTF performance with the biodegradation of this kind of VOCs by the polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) technique and pyrosequencing analyses indicated that proteobacteria phylum was the dominant in the BTF. All above results indicated that VOCs with multicomponent and fluctuant concentrations from a typical waste printed circuit board pyrolysis workshop were removed efficiently and in an environmentally friendly way by the biofiltration method.

Keywords: waste printed circuit boards (WPCBs), volatile organic compounds (VOCs), biotrickling filter (BTF), health risks, microbial community

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1. Introduction

The environmental pollution problem resulting from electronic waste (e-waste) dismantling process has become a global concern [1]. Waste printed circuit boards (WPCBs), one of the most important kinds of E-waste, are complex heterogeneous mixtures consisting of organic material, metal and fiberglass, which are welded to electronic components including transformers, batteries, LED screens, potentiometers, resistors, capacitors, diodes, transistors, *etc.* [2,3]. Pyrolysis WPCB processes develop gradually a recycling manufactory system because WPCBs contain many valuable metals, such as copper, lead, iron, tin and noble metals (silver, gold and palladium are present in small quantities) [4]. Due to the primitive pyrolysis process and the absence of reliable purification measures, a huge number of volatile organic compounds (VOCs) were produced and emitted into the surrounding atmosphere.

These VOCs include aromatic hydrocarbons such as benzene and its derivatives, alkanes, alcohols, aldehydes, ketones, among others [5]. The continuous emission of VOCs result in the local large-scale pyrolysis of WPCB processes and may seriously harm to human health. Consequently, appropriate treatment measures should be taken in order to reduce VOC concentrations and minimize odors to acceptable levels.

Although conventional control methods such as photocatalytic destruction, wet scrubbing and incineration can be used to reduce VOCs emission, they are relatively expensive and generate undesirable byproducts [6-8]. Biofiltration has been successfully applied for the treatment of VOCs because it is cost-effective and environmentally friendly [9].

An increasing number of studies have demonstrated that biofiltration can remove not only the single compounds such as toluene, xylene and styrene, but also mixtures of VOCs effectively [10,11]. However, these studies were mainly confined to the laboratory level of testing and no pilot-scale or industrial research, to date, has been carried out for complex VOCs treatment during WPCB pyrolysis processes.

In this study, a pilot-scale biotrickling filter (BTF) was established for VOC treatment in a typical WPCB pyrolysis workshop. Before treatment, the components and concentrations of VOCs were analyzed to provide baseline data for subsequent VOC treatment in the WPCB pyrolysis workshop. To evaluate the performance of the BTF, the VOC removal efficiencies and total elimination capacity were examined for over 90 days. To reveal the dynamic changes of microbial community in response to different operation periods of the BTF, the V_3 region of 16S rDNA was analyzed by polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) and the resulting bands were sequenced. In addition, the health risk of the VOCs from the inlet and outlet of the BTF was predicted by calculation of a hazard ratio index (HRI).

2. Materials and Methods

2.1. Study site

The pilot-scale site was located at a typical WPCB pyrolysis workshop of Shantou city (Guangdong, china), which mainly engaged in pyrolysis of various WPCBs, such as mobile telephone circuit boards (MTCB), mobile telephone charger boards (MTC), telephone circuit boards (TCB), computer main boards (CMB), display card boards (DCB), router boards (RB), and sound card boards (SCB).

2.2. Experimental set-up

The pilot-scale BTF used in this study was made of fiberglass reinforced plastics consisting of a square circulating nutrient medium unit (50 × 50 × 20 cm) and a cylindrical biofiltration bed (inner diameter: 1.20 m, height: 2.20 m and effective packing volume: about 1.36 m^3) (Fig. 1). The utilized BTF packing material consisted of spheroidal ceramsites (Rong Xian Ceramic Factory, Guangdong, China). The particle size, porosity, bulk density and water holding capacity were 20.00 ± 2.00 mm, 41.25 ± 2.01%, 210.36 ± 14.62 kg/m^3 and 12.53 ± 0.12 g/g, respectively.

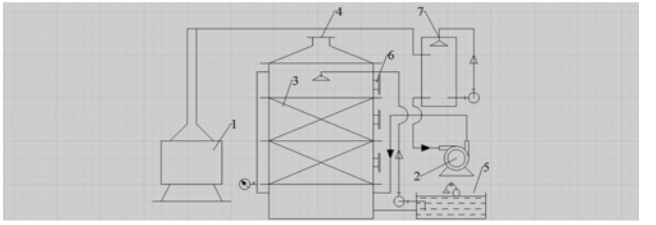

Fig. 1. Diagram of the biofiltration system: 1 pollutant evaporator; 2 blower; 3 packing material bed; 4 gas sampling ports; 5 recirculating water tank; 6 packing material sampling port; 7 spray tower.

2.3. Inoculum and BTF reactor startup

The inoculum acclimated from petroleum polluted soil was proved with the capability of degrading toluene, xylene and styrene. Before the BTF started, the TXS culture was incubated in 15 L of M9 medium (composed of: 2.000 g/L KNO_3, 0.600 g/L $Na_2HPO_4{\cdot}12H_2O$, 0.005 g/L NaH_2PO_4, 0.250 g/L $MgSO_4{\cdot}7H_2O$, 0.020 g/L $CaCl_2$, 0.005 g/L $FeSO_4{\cdot}7H_2O$, and pH value was adjusted from 7.0 to 7.5 by addition of 0.1 MNaOH) at 30ºC and 180 rpm for about 24 h, and then inoculated into the BTF. The medium circulated in the BTF at a flow velocity of 1.8 m/sec, 8 h and was refreshed daily.

2.4. Experimental procedures

Different WPCBs were burnt in an incinerator at temperatures ranging from 200 to 500ºC for about three hours to completely separate electronic components and epoxy resin copper boards in batch mode. VOC-containing organic waste gas was introduced into the BTF through a 2.0 m PVC pipe and spray tower to maintain inlet gas temperature. The temperature difference of the inlet gas during the >90 days operation period was mainly attributed to weather changes. The inlet gas introduced into the BTF had a steady temperature maintained at about 30ºC to support the microorganisms' growth (Fig. S1). The inlet and outlet gases during different operation periods were collected by vacuum Summa canisters (2.7 L, Entech Instruments Inc., CA, USA), which were thoroughly cleaned by high purity nitrogen before use. Collected gases were

then analyzed by gas chromatography-mass spectrometry (GC-MS). Biofilm samples were collected with corresponding gas samples and stored at the -80°C freezer. The microbial communities composing the biofilm samples were analyzed by PCR-DGGE.

2.5. Analytical method

The VOC sample components were qualitatively and quantitatively detected by 7890A gas chromatography coupled with a 5975C mass spectrometer detector (GC-MSD, Agilent Technologies, USA) and an Entech 7100 preconcentrator (Entech Instruments Inc., CA,USA). The combined techniques and instruments were applied to the USEPA TO-15 method [12]. Firstly, 150 mL of waste gas from sampling Summa canisters were concentrated through a glass bead trap, which was maintained at 150ºC with liquid nitrogen. The trapped analytes were desorbed at 20ºC and transferred to a Tenax-TA trap maintained at -40ºC. The concentrated components were desorbed a second time at 190ºC and then focused at the cold top of the capillary column, which was cooled to -180ºC. After 2.5 min, the analytes were swept into the column for separation. The gas chromatography system was equipped with a flame ionization detector and a DB-1 column (60 m × 0.32 mm × 0.25 μm). The carrier gas used was ultrahigh purity helium. The operation parameters of the GC-MS were conducted as described by He *et al.* [13]. The concentrations of VOCs were quantified by external standard calibration using TO-15 (Linde Spectra Environment gases, USA) as a standard sample. Each target species was identified by its retention time and mass spectra by using the NIST 05 database (National Institute of Standards and Technology).

2.6. Microbial community structure analysis

PCR-DGGE of 16S rDNA V_3 region was used to analyze the BTF microbial community during different operation periods. At the end of each experiment, packing materials (50 g, wet weight) were collected from the BTF, mixed with 50 mL phosphate buffer (137 mM NaCl, 2.70 mM KCl, 4.30 mM Na_2HPO_4, and 1.40 mM KH_2PO_4; pH 7.3), and vortexed for 30 min. The packing materials were discarded after detachment, next the liquid phase containing the biofilm was centrifuged at 8,000 rpm for 10 min, and finally the genomic DNA was extracted as reference [14,15]. PCR was used to amplify a 177 base pair portion of the 16S rDNA using primers the 341F-GC and 518R. Amplification conditions were carried out as documented in the previous research [16,17]. Negative controls were included to verify the absence of contamination.

DGGE was performed with a D-Code Universal Mutation Detection System (Bio-Rad Lab-oratories Inc., USA), using 8% polyacrylamide gels prepared with a denaturing gradient ranging from 45 to 65% (where 100% denaturant contained 7 M urea and 40% (v/v) formamide) [14]. Approximately 500 ng of sample PCR products were loaded onto each gel. Electrophoresis was run at 60ºC and 80 V for 12 h [18,19]. The resulting gel was stained with Goldview (Company, City, Country) and visualized with ImageQuant 350 (GE Healthcare, USA). The relative abundance and densities of main bands in the DGGE image were calculated by the Quantity one version 4.4 software (Bio-Rad, USA). The obtained sequences were compared using the Basic Local Alignment Search Tool (BLAST) algorithm feature of the National Center for Biotechnology Information (NCBI) website, and the sequence in the database most similar to each clone was used as reference. The ClustalW alignment tool was used in Mega 5.0 to align the sequences. Phylogenetic trees were constructed with parsimony.

2.7. Calculation of the performance of the BTF and VOC risk assessment

In terms of the *IL* (g/m^3 h), *RE* (%) and *EC* (g/m^3 h), the performance of the BTF was evaluated, which were calculated by the following equalities.

$$IL = \frac{C_{in} Q}{V} \quad \text{(Eq. 1)}$$

$$EC = \frac{Q(C_{in} - C_{out})}{V} \quad \text{(Eq. 2)}$$

$$RE = \frac{(C_{in} - C_{out})}{C_{in}} \times 100 \quad \text{(Eq. 3)}$$

Though the target VOCs in this study have not been classified as carcinogenic agents by the International Agency for Research on Cancer (IARC), they still have non-carcinogenic toxins that can affect workers in the workshop. Hence, a model of non-carcinogenic risk assessment based on the HRI of the occupational exposure limit is characterized in terms of non-carcinogenic toxins for workers in the WPCB pyrolysis workshop, which is defined as [20]:

$$HRI_i = \frac{C_i}{TLV - TWA_i} \quad \text{(Eq. 4)}$$

Where $TLV\text{-}TWA_i$ is the threshold limit value for time weighted average of compound i (see Table S1) and C_i is the concentration of compound i. In the workshop, VOCs with HRI above 1.0 are deemed a potential human health

concern. Hence, it is required that HRI and the sum of HRI_i (see Eq. 5 below) should not exceed the value 1.0.

$$HRI = \sum_i HRI_i \quad \text{(Eq. 5)}$$

3. Results and Discussion

3.1. VOC concentrations during different WPCB pyrolysis processes

In this study, more than twenty VOCs which contained aromatic hydrocarbons, alkanes, ketones and aldehydes, were identified by GC-MS from the waste gas of seven WPCBs during pyrolysis processes. The dominant VOCs were benzene (Ben), toluene (Tol), chlorobenzene (CB), ethyl-benzene (EB), (m-/o-/p-)xylene (Xyl), styrene (Sty), benzaldehyde (BZD), and (1,2,3-/1,2,4-/1,3,5-) trimethyl-benzene (TMB). The VOC species and concentrations had significant differences during different WPCB pyrolysis processes (Table 1). The highest Ben concentration was 5.41 ± 0.16 mg/m^3 in in the MTC pyrolysis process and the lowest was 2.51 ± 0.13 mg/m^3 in in the SCB pyrolysis process. The Tol concentration had significant fluctuation during different printed circuit board (PCB) pyrolysis processes where the highest concentration was 16.83 ± 0.50 mg/m^3 in for the MTCB pyrolysis process and the lowest was 0.84 ± 0.03 mg/m^{3}in in the TCB pyrolysis process. The other VOCs ranged from 0.05 ± 0.002 to 5.31 ± 0.16 mg/m^3 in in different WPCB pyrolysis processes. Total VOC (TVOC) concentration was in the range of 5.43 ± 0.23-40.33 ± 1.38 mg/m^3, in which the highest and the lowest concentrations were in pyrolysis MTC and TCB procedures respectively, suggesting that the concentration was significantly irregular during different WPCB pyrolysis processes. In addition, according to the HRI evaluation standard, the HRI values for TVOC were larger than 1.0 in different WPCB pyrolysis processes, which would damage workers' health (Table S2). Hence, appropriate treatment measures should be taken to reduce the risk in WPCB pyrolysis workshop.

3.2. Removal efficiencies (RE) of VOCs

The *RE*s of individual VOCs increased gradually with inlet concentrations by the BTF with 9.80 sec of the empty bed residence time (*EBRT*) except on the 60th day within 3 months of the operation period during the different WPCB pyrolysis processes (Fig. 2). For example, the *RE*s of Ben and Tol reached 38.8 and 69.1% with the highest inlet concentrations of 4.55 and 11.95 mg/m^3 on the 15th day and more than 90% *RE*s of individual VOCs were obtained by the BTF on the 45th day with the exception of CB (Figs. 2A, 2C, and 2F). Reasons for above results could be due to the BTF inoculum being domesticated by only carbon source contained Sty, Xyl and Tol at a lab scale over 2 years and Ben, EB, BZD and TMB were similar in chemical structure and matebolic pathways to Xyl and Tol, which the carbon atom of side-chain is between C2 and C7. Several studies have proven that when a substituent group(s) joins onto the benzene ring opens up the possibility of alternative modes of biodegradation under aerobic conditions: either ring attack or side-chain attack. All of n-alkylbenzenes (C2-C7) were catabolised *via* ring attack, rather than side chain attack, proceeding *via* initial mono-oxygenase or 1,2/2,3-dioxygenase activity resulting in the corresponding intermediate metabolites. All n-alkylbenzenes (C2-C7) were ultimately catabolised through the TCA cycle and degraded to H_2O, CO_2 and cellular components [21-23].

CB was more difficult to be removed by the BTF. For example, it could be found that only 81.1% of *RE* for CB was obtained with the lowest inlet concentration of 0.17 mg/m^3 after 90 days operation of the BTF (Fig. 2C). This was due to CB being the only halogenated aromatic of the VOCs in the study and its degradation pathway in

Table 1. VOC concentrations of different WPCB pyrolysis processes in a typical workshop

Compounds	Concentration(mg/m^3)*						
	TCB	MTCB	DCB	SCB	MTC	RB	CMB
Tol	0.84 ± 0.03	16.83 ± 0.50	1.12 ± 0.07	3.37 ± 0.13	15.98 ± 0.64	3.06 ± 0.09	4.17 ± 0.21
EB	0.26 ± 0.01	1.79 ± 0.07	0.23 ± 0.01	0.41 ± 0.02	4.11 ± 0.08	0.72 ± 0.04	0.24 ± 0.01
Xyl	0.23 ± 0.01	0.36 ± 0.01	0.27 ± 0.01	2.01 ± 0.08	4.23 ± 0.17	0.46 ± 0.01	2.46 ± 0.07
Ben	2.81 ± 0.11	4.69 ± 0.14	5.10 ± 0.20	2.51 ± 0.13	5.41 ± 0.16	4.76 ± 0.19	2.72 ± 0.09
CB	0.05 ± 0.00	0.08 ± 0.01	0.12 ± 0.01	0.32 ± 0.02	0.35 ± 0.02	0.17 ± 0.01	0.16 ± 0.01
Sty	0.54 ± 0.03	0.71 ± 0.02	1.79 ± 0.05	0.91 ± 0.04	5.31 ± 0.16	2.01 ± 0.06	0.85 ± 0.03
BZD	0.57 ± 0.03	0.72 ± 0.03	1.03 ± 0.04	2.19 ± 0.09	4.78 ± 0.14	3.11 ± 0.09	4.86 ± 0.15
TMB	0.13 ± 0.01	0.22 ± 0.01	0.38 ± 0.02	0.59 ± 0.03	0.16 ± 0.01	0.28 ± 0.01	0.61 ± 0.03
TVOC	5.43 ± 0.23	25.40 ± 0.77	9.99 ± 0.41	12.31 ± 0.54	40.33 ± 1.38	14.57 ± 0.51	16.07 ± 0.60

*TCB: telephone circuit boards; MTCB: mobile telephone circuit boards; DCB: display card boards; SCB: sound circuit boards; MTC: mobile telephone charger boards; RB: router boards; CMB: computer main boards.

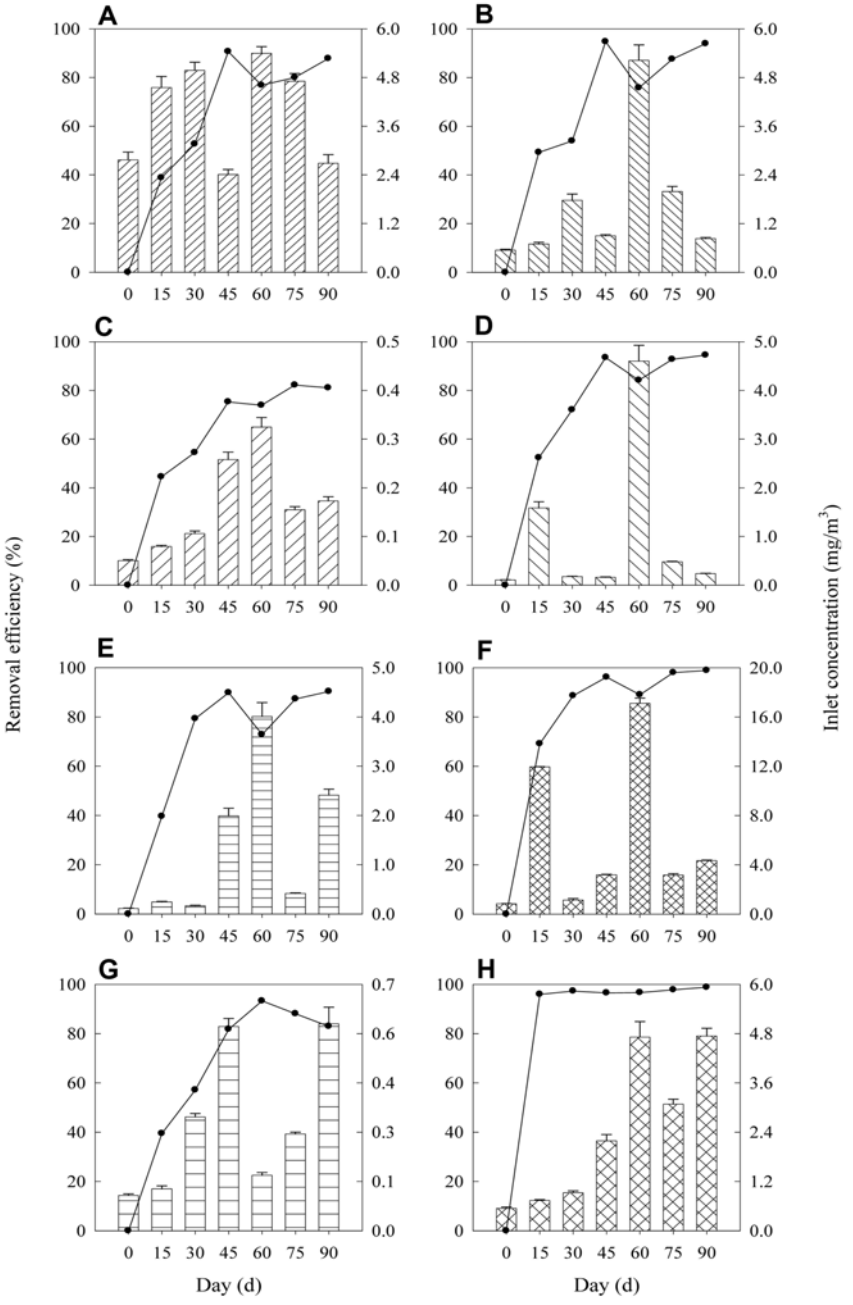

Fig. 2. Removal efficiencies (line+symbol) under biotrickling filtration (BTF) over 90 days continue to degrade together with the inlet concentrations (column) of (A) Ben, (B) Sty, (C) CB, (D) EB, (E) Xyl, (F) Tol, (G) TMB, and (H) BZD.

bacteria resembles mono-alkybenzenes when undergoing ring or chlorine atom attack. Moreover, the electron density of CB was reduced by introduction of the chlorine atom due to strongly absorbing electronics capability and oxidation enzymes hardly obtain electrons in the benzene ring under aerobic conditions [24,25].

The *RE* of BZD was highest of all the other VOCs filtered by the BTF during the study and stabilized above 95% after the 15th day operation (Fig. 2H). The result indicated that a shorter acclimation period and a higher biodegradation rate were needed for oxygenated compounds than for aromatic VOCs. Several researchers also found similar results for the degradation of oxygenated and aromatic compounds [26,27]. It was reported that pollutants with high Henry's constant were more difficult to be eliminated by BTF, because these pollutants had an unfavorable gas-liquid proportion and the pollutant's concentrations in the biofilm were too low to sustain a high biodegradation rate [28]. The Henry's constant of BZD was significantly lower than the aromatic VOCs which could

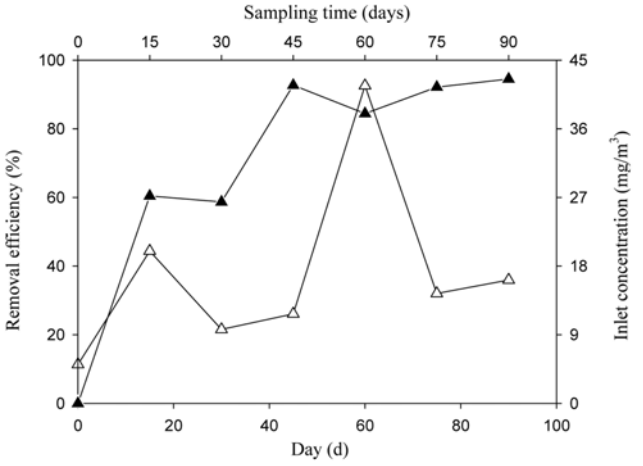

Fig. 3. TVOC inlet concentration (hollow triangle) versus removal efficiency of the BTF (solid triangle) in different sampling time.

result in the higher *RE* and shorter acclimation period of BZD than the aromatic VOCs (Table S1). Biofiltration of hydrophobic VOCs was also intrinsically limited by poor transfer of the pollutants from the gaseous to the liquid biotic phase, where biodegradation occurred. In addition, BZD was an intermediate metabolite of other benzene series which also could result in helping biodegradation due to a common biochemical enzyme system [21].

After 45 days of operation, stable biodegradation *RE*s of VOCs was reached. For example, the *RE* of TVOC was 60.4 and 92.7% by the BTF on the 15th and 45th day, and was maintained at 94.5% on the 90th day with the inlet concentrations of 19.97, 11.73 and 16.18 mg/m^3, respectively (Fig. 3). The biomass shift has positive correlation to the increase and stabilization of *RE*. For instance, the biomass increased to 1.55, 9.58 and 9.69 mg/g dry weight on the 15th, 45th, and 90th days (Fig. S2). It is worth noting that the *RE* of TVOC dropped on both the 30th and 60th day compared with the 15th and 45th day. For example, the *RE* of TVOC was slightly down from 60.4 to 58.7% on the 15th and 30th day. This was due to the inlet concentration of Ben was relatively higher (4.98 mg/m^3) and accounted for 51.3% of TVOC concentration. Ben was chemically stable due to absence of constituents which result in a low *RE* (Fig. 2A) [21]. The *RE*s of individual and TVOCs dropped on the 60th day with the exception of (1,2,3-/1,2,4-/1,3,5-) TMB. The main reason was that the TVOC concentrations were much higher than individual ones on the 45th day. Further, they surpassed the *EC*s of biomass which resulted in restriction of the biological degradation process. However, the TMB concentration was lower than others which resulted in a higher *RE* with the inlet concentrations of 0.58 and 0.16 mg/m^3 on the 45th and 60th day, respectively (Fig. 2G).

Based on VOC concentrations (Fig. 2), the HRI values of individual and TVOCs in the inlet and outlet of the BTF was calculated (Table 2). The HRI values for the inlet Ben and TVOC were larger than 1.0 and the maximum reached was 3.102 and 3.225, respectively, on the 60th day, indicating that it was harmful to workers' health. After the BTF treatment, the HRI values reduced greatly and were less than 1.0 after 45 of days operation. For example, the HRI value of TVOC for the outlet was 0.545, which was far lower than 2.774 for the inlet on the 75th day. These results suggest that the non-carcinogenic risk was effectively reduced after the BTF treatment.

3.3. Elimination capacity of the BTF

The performance of the BTF was additionally evaluated by the *EC* and the *RE* because of the different inlet TVOC concentrations. The relationship between *IL* and *EC* of the BTF was shown in the Fig. 4. The slopes of black and red lines represent theoretical 100% and average TVOC *RE*s, respectively. Obviously, the *EC* linearly increased with increasing TVOC *IL*, indicating that the increase of inlet *IL* appeared to have no inhibition on VOCs removal and the

Table 2. HRI value for VOCs in the inlet and outlet of the BTF over 90 days of operation

Compounds	HRI											
	15th day		30th day		45th day		60th day		75th day		90th day	
	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet
Tol	0.032	0.0010	0.003	0.001	0.009	0.000	0.046	0.005	0.008	0.000	0.012	0.000
EB	0.004	0.002	0.000	0.000	0.000	0.000	0.011	0.002	0.035	0.000	0.013	0.000
Xyl	0.001	0.000	0.000	0.000	0.005	0.001	0.009	0.003	0.001	0.000	0.006	0.001
Ben	2.616	1.601	2.860	1.354	1.386	0.130	3.102	0.719	2.706	0.542	1.543	0.189
CB	-	-	-	-	-	-	-	-	-	-	-	-
Sty	0.008	0.004	0.019	0.013	0.010	0.001	0.056	0.014	0.022	0.003	0.009	0.001
BZD	-	-	-	-	-	-	-	-	-	-	-	-
TMB	0.001	0.001	0.003	0.001	0.005	0.001	0.001	0.00	0.002	0.000	0.005	0.001
HRI	2.661	1.617	2.885	1.368	1.414	0.132	3.225	0.742	2.774	0.545	1.587	0.190

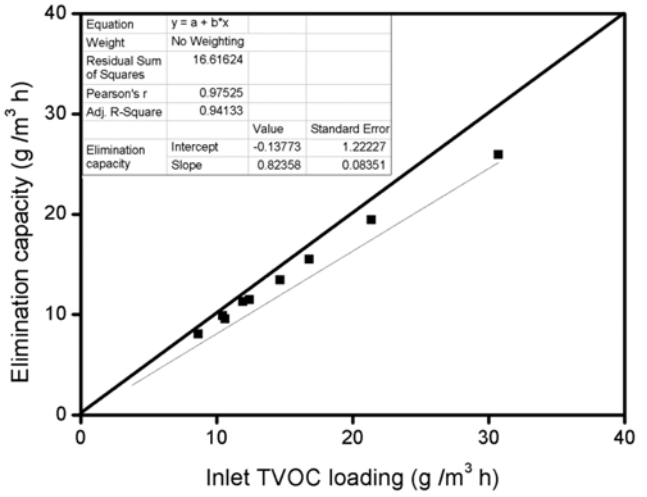

Fig. 4. The elimination capacity of the BTF versus different inlet loading of TVOCs at a fixed *EBRT* of 9.80 sec.

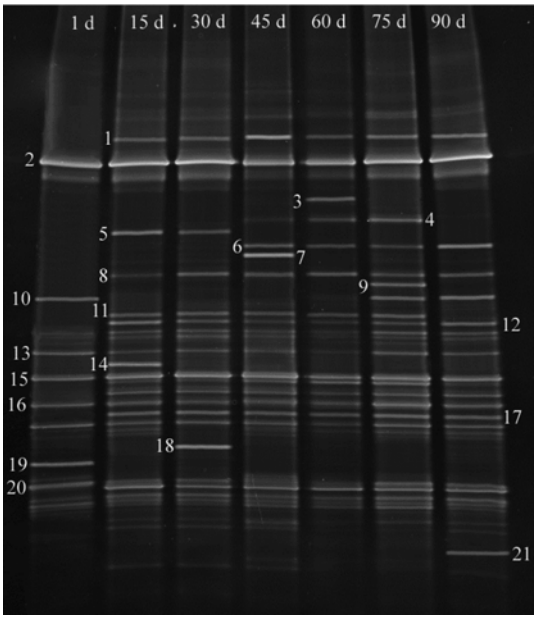

Fig. 5. DGGE profiles of the V3 region of 16S rDNA in the BTF during different operation times.

maximum VOCs *EC* mainly relayed on the *IL*. The maximum VOC elimination capacity of 25.94 g/m^{3}h was achieved with the maximum *IL* of 30.72 g/m^{3}h at the fixed *EBRT* of 9.80 s in this study. This result cannot be defined as the actual EC_{max} because different PCBs had different VOC concentrations and higher *IL*s were not tested. In addition, it was difficult to compare our *EC* findings with those in the literature due to the differences in components, fluctuant concentrations, and operation conditions. For example, Sempere *et al.* applied a pilot-scale BTF in treating VOC emissions from a painting and wood manufacturing facility. When the *EBRT* increased from 10 to 35 sec, TVOC *EC* dropped from 32.80 to 12.70 g/m^{3}h, but TVOC *RE* increased from 49 to 70% [29]. Furthermore, it was observed that VOC average *RE* of 82.4% from the slope of the fitting curve. Overall, the pilot-scale BTF with a high *EC* and *RE* could be successfully applied in treating VOC emissions from a typical WPCB pyrolysis workshop.

3.4. Microbial community structure analysis

The BTF inoculum enriched from petroleum polluted soil and domesticated by the carbon sources contained only Tol, Xyl and Sty at a lab scale. The DGGE profile showed that the BTF bacterial community shifts contained inoculation, domestication and stabilization were significantly related to the various VOCs sourced from different WPCB pyrolysis processes (Fig. 5). Many bands (such as bands 2, 13, 15, 16, 20; Fig. 5) consistently appeared with higher intensity. Band 2 was the most dominant strain in the bacterial communities over the entire operation time. These results indicate that the microbial consortium may be suitable as initial inoculums and were essential for maintaining high VOC REs and stability of the BTF during the operation. Band 19 was observed on the first day but disappeared during the subsequent operation period. This indicates that the bacteria was not suitable for VOCs produced by pyrolysis in all kinds of PCBs processes. In contrast, bands 1,3,4,5,6,7,8,9,11,12,14,17,18 and 21 were not observed on the first day but were present in most of the samples collected from different operation periods. Bands 1,8,12, and 17 appeared consistently after their absence on the first day. This may be due to the multicomponent and changed concentration of VOCs resulting in the accumulation of metabolic products and stimulation of heterotrophic microorganisms during the operation process. Moreover, it was interesting that band 10 was not observed from the 15th and 60th day but reappeared on the 75th and 90th day. This seems to indicate that the bacteria are very sensitive to specific conditions.

Twenty-one discernable bands were excised and used for sequence analysis to better understand the dynamic changes in the bacterial community during the operation. The closest relative, phylogeny, and relative abundance of the DGGE bands are listed in Table 3. According to the GenBank database, most bands were individually identified as different members of the phylum Proteobacteria, with the exception of bands (7, 12 and 21). Bands 5, 8, and 17 belonged to the α-Proteobacteria class. Bands 2, 3, 6, 11, 13, 15, 16, 18, 19 and 20 grouped with the β-Proteobacteria class, while bands 1, 4, 9, 10 and 14 clustered within the γ-Proteobacteria class. These results suggest that the Proteobacteria phylum,

Table 3. Sequences of 16S rDNA DGGE fragments and relative abundance of DGGE bands

Band[a]	Accession	Closest genera[b]	Phylogeny	Relative abundance.	Band	Accession	Closest genera[b]	Phylogeny	Relative abundance.
1	AB426189	Unidentified bacterium	γ-Proteobacteria	3.73%	2	KC462881	*Burkholderia* sp. *T3*	β-Proteobacteria	14.62%
3	EU770267	*Pseudomonas* sp. *A15*	β-Proteobacteria	4.86%	4	KC887931	*Proteobacterium K12*	γ-Proteobacteria	4.27%
5	KC462882	*Ochrobactrum* sp. *DX2*	α-Proteobacteria	4.12%	6	JX010988	*Burkholderia* sp. *C5*	β-Proteobacteria	4.73%
7	AB298731	*Propioniciclavatarda*	Actinobacterium	7.14%	8	JX100249	Uncultured bacterium	α-Proteobacteria	1.56%
9	AY639376	*Acinetobacter* sp.	γ-Proteobacteria	4.02%	10	AY830897	*Acidithiobacillussp*	γ-Proteobacteria	4.57%
11	AB504647	Unidentified bacterium	β-Proteobacteria	2.51%	12	GQ406184	*Chloroflexi bacterium*	Chloroflexi	3.78%
13	EU684748	*Burkholderia* sp. *ME59-2*	β-Proteobacteria	2.94%	14	AJ318161	Unidentified bacterium	γ-Proteobacteria	4.89%
15	KF460558	*Pseudomonas aeruginosa*	β-Proteobacteria	7.87%	16	KF450811	*Pseudomonas* sp. *GS35395*	β-Proteobacteria	6.62%
17	HM159984	*Ochrobactrum* sp. *OTU29*	α-Proteobacteria	4.55%	18	AF502222	Unidentified bacterium	β-Proteobacteria	7.82%
19	AF170281	*Thaueraaromatica*	β-Proteobacteria	5.37%	20	GU206550	*Pseudomonas*	β-Proteobacteria	4.54%
21	AB693055	*Propioniferaxsp*	Actinobacterium	5.38%	-	-		-	-

[a]The bands are designated as shown in Fig. 5.
[b]The closest genus were determined by both sequence match in Blast and phylogenetic analysis shown in Supplementary data.

which widely exists in polluted environment, was dominant in the BTF. Analysis of the DGGE profile using the Quantity One software and phylogenetic tree, bands 2 (14.62%), 15 (7.87%), and 16 (6.62%), resulting from inoculum had higher relative abundance during the operation of the BTF. The bands were clustered within the *Burkholderia* and *Pseudomonas* genus, respectively (Fig. S3). Several publications have demonstrated the aromatic degrading capacity and genes involved in aromatic degrading enzymes in some species of the *Burkholderia* and *Pseudomonas* genus, such as the *tmoA* and *tod*C1 gene [30,31].

4. Conclusion

In this study, the main components of VOCs emitted during pyrolysis of different WPCB processes included Ben, Tol, CB, EB, Xyl, Sty, BZD, and TMB which were eliminated effectively by the BTF over 90 days of operation. The results showed excellent degrading performance for both aromatic and aldehyde VOCs was achieved by the BTF. After treatment, the HRI values for the outlet VOCs were rapidly reduced and of non-carcinogenic risk. The linear increase of *EC*s with increasing VOC *IL*s showed that the BTF could remove the VOCs efficiently. Further investigation of the resulting microbial community revealed initial inoculum and some emerging bacteria played crucial roles in the improvement of the BTF performance with the biodegradation of VOCs. Overall, the BTF can be used as an environmental-friendly solution for treatment of VOCs from a typical WPCB pyrolysis workshop.

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Nomenclature

BTF : Biotrickling filter
VOC : Volatile organic compound
C : VOC concentration in the air (mg/m^3)
Q : Gas flow rate (m^3/h)
V : Packed volume (m^3)
EBRT : Empty bed residence time (sec)
IL : Inlet loading in biotrickling filter (g/m^{3}h)
EC : Elimination capacity (g/m^{3}h)
RE : Removal efficiency (%)
TLV-TWA : Threshold limit value for time weighted average (mg/m^3)
in : Inlet gas
out : Outlet gas
i : Compound
max : Maximum value

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