# Treatment of organic waste gas in a paint plant by combined technique of biotrickling filtration with photocatalytic oxidation

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## HIGHLIGHTS

▶ VOCs emissions in different paint production processes were analyzed.
▶ VOCs removal performance of single and combined BTF–PCO technology was evaluated.
▶ Potential risks for VOCs before and after treatment by BTF–PCO were predicted.
▶ Effect of technical parameters on the removal of mixture VOCs was investigated.

## ARTICLE INFO

## ABSTRACT

A pilot-scale system integrated with biotrickling filtration (BTF) and photocatalytic oxidation (PCO) for the treatment of organic waste gas in a paint plant was investigated in this study. The components of volatile organic compounds (VOCs) and their concentrations were measured by gas chromatography–mass spectrometry (GC–MS). Results showed that the main components of organic waste gas in the paint plant were ethyl acetate, toluene, ethylbenzene, xylene, ethyltoluene and trimethylbenzene. The removal efficiencies of these VOCs ranged from 79.4% to 99.8% by BTF–PCO treatment even after 90 days operation. After BTF–PCO treatment, hazard ratio index based on threshold limit value for time weighted average (TLV-TWA) and VOCs concentrations indicated that the non-cancer risk of VOCs was rapidly reduced. At steady state of the treatment system, total VOCs (TVOC) removal efficiencies maintained steadily within the range of 95.8–98.2% with the increase of inlet TVOC concentration from 6.69 to 129.00 mg/m$^3$, and increased from 95.8% to 99.5% with the flowrate decrease from 3000 to 1333 m$^3$/h. In addition, the maximum elimination capacities of different systems in this study followed the order: BTF (47.8 g m$^{-3}$ h$^{-1}$) > BTF–PCO (25.2 g m$^{-3}$ h$^{-1}$) > PCO (19.2 g m$^{-3}$ h$^{-1}$), while VOCs average removal efficiencies followed the order of BTF–PCO (95.6%) > PCO (88.7%) > BTF (73.7%). Overall, by the combination of BTF and PCO systems, the high concentration and multicomponent VOCs from paint plant were removed effectively and environmental friendly.

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## 1. Introduction

Volatile organic solvents including aromatics, such as benzene, xylene, toluene and esters, such as ethyl acetate, ethyl butyrate are commonly used to dissolve resin in the paint production, which is one of the most important volatile organic compounds (VOCs) sources. According to National Emission Trend database from United States Environmental Protection Agency (USEPA) in 1999, annual emissions of VOCs from paint and allied facilities were estimated to be 26,500 tonnes [1]. The massive VOCs discharge results in occupational disease in the workplaces [2]. This is because most of VOCs are toxic, and some of them, such as benzene are considered to be mutagenic, teratogenic, and carcinogenic [3]. Although toluene and xylene are not currently classified as carcinogens, an increase of oesophageal, rectal and colon cancer incidences in workers with long-term exposure to these compounds have been reported [4]. In addition, another most significant problem related to the emission of VOCs is focused on the possible production of photochemical oxidants. For example, ozone and peroxyacetyl nitrate which are formed in the presence of sunlight from NO$x$ and VOCs, are toxic to humans, damaging to crops and involve in the formation of acid rain [5].

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As a result of these environmental problems, VOCs pollution has drawn considerable attention in the last decade. Although conventional VOCs control technologies such as thermal incineration [6], catalytic combustion [7–9] and adsorption [10] could reduce VOCs emission, they would generate undesirable byproducts, are energy intensive and relatively expensive. Thus, biological and photocatalytic oxidation (PCO) have becoming attractive techniques for this purpose due to their low energy consumption, relatively moderate operating costs and minimal byproduct generation [11]. Moreover, these two techniques can decompose VOCs to nontoxic final products such as $CO_2$ and $H_2O$ at ambient temperatures [12–17]. Several researches have been found that a large number of VOCs, like benzene [18,19], toluene [20,21], xylene [1,22] and styrene [23,24] could be removed by single biological or PCO purification technology. However, some drawbacks still existed in the application of these single treatment methods. For biological treatment, slow biological oxidation of less biodegradation VOCs (i.e. recalcitrant of hydrophobic) made biofilters very large and uncompetitive [25]. Also, biological processes may not run consistently and were slow adaption to fluctuating VOCs concentrations, resulting in reducing VOCs elimination capacities [26]. An acclimation period with lower removal efficiency (RE) of VOCs was necessary for microorganisms according our previous study [14]. For PCO, photocatalyst deactivation could result in the gradual decrease of its photocatalytic activity as observed in many researches [17,27,28]. Therefore, it is considered that single biological or PCO is not so perfect for organic waste gas treatment.

Based on long-term stable VOCs biodegradation efficiency of biological treatment and broad selectivity for various VOCs of PCO [20,29], the integration of PCO and biological treatment have been attemped. For instance, with the combination of a photocatalytic reactor and a biofilter, Hinojosa-Reyes et al. [26] obtained an increase up to 36% additional ethylbenzene (EB) removal compared with the individual treatment. Palau et al. [30] found that the elimination capacity of biofiltration to toluene increased by more than $12\,g\,m^{-3}\,h^{-1}$ when combined with PCO reactor. From these studies, it can be seen that the integration of PCO and biological treatment showed an advantage to remove hydrophobic and recalcitrant air polluants, provide synergistic improvement in the removal of VOCs. However, these studies were mainly confined to laboratory level test and rare pilot-scale or industrial research has been carried out for complex VOCs treatment. Moreover, since PCO was used as the pretreatment in these studies, photocatalyst deactivation was still an insolvable problem since photocatalyst surface could be easily covered with particulate matters and refractory organics, resulting in the significant decrease of photocatalytic activity in the complex pilot-scale field. Furthermore, due to less convenient control of overall pressure drop, pH and nutrient, one of the shortcomings of a natural media biofilter was that it was less effective to facilitate more continuous operation than biotrickling filter (BTF) [31].

Therefore, in this study, a pilot-scale combined BTF–PCO reactor, consisting of a BTF pretreatment system and a PCO system, was established for organic waste gas treatment in the paint plant. To evaluate the performance of BTF–PCO, the comparative VOCs REs and the elimination capacities (ECs) between single and combined reactors were conducted during whole 90 days operation. In addition, the effect of technical parameters including inlet concentration of total VOCs (TVOC) and flowrate were evaluated on the REs of TVOC after 45 days operation. Before treatment, VOCs emissions characteristics of different paint product processes were firstly analyzed to provide basic data for subsequent VOCs treatment in the paint plant. Additionally, the possible risk of the VOCs from inlet and outlet of BTF–PCO reactor was predicted by calculation of hazard ratio index (HRI).

## 2. Experimental

### 2.1. Study site

The pilot-scale site was selected at a fine chemical company of Foshan city (Guangdong, China), which mainly engaged in products of paints, pigment and synthetic resin. The study was carried out in the paint workshop which produced amino paint, insulating paint, alkyd paint and other related products. With the output of about 10 tons per day, massive organic compounds which are used as organic solvent can emit from the products into the air.

The paint manufacturing industry contains four processes which are generally followed by predispersing, grinding, tinting and packaging (Fig. S1). The process of predispersing includes combining the raw materials, solvents, resins, pigments, and other ingredients, and then blending them with a high-speed mixer. After predispersing, the batches are transferred to a mill for additional grinding and uniformly distributing by grinding machine. Tinting consists of comparing colors between the different batches, then adding pigments and solvents or thinner in order to match the shade. Finally, the paint is filtered and packed into cans. Overall, the workshops of these four processes were selected as the sampling sites.

### 2.2. Microorganism inoculation and photocatalyst prepared

The microbial consortium that used to inoculate biotrickling filter was originally enriched from the activated sludge of a on-site wastewater treatment station [32]. Before system started up, 150 L of the consortium culture were sprayed at the top of BTF. The leachate was collected in a tank and then recirculated continuously for the next 8 h to ensure microorganisms attachment. Meanwhile, waste gases containing VOCs were introduced into the system to acclimate the microorganisms. The base nutrient medium for the growth of microorganisms contained (g/L): 2.000 $KNO_3$, 0.600 $Na_2HPO_4 \cdot 12H_2O$, 0.200 $NaH_2PO_4$, 0.005 $FeSO_4 \cdot 7H_2O$, 0.250 $MgSO_4 \cdot 7H_2O$, 0.002 $CaCl_2 \cdot 2H_2O$. The initial pH was adjusted to 7.0–7.5 with 1 M NaOH.

The supported photocatalyst was prepared by spray coating method. The procedure was described as follows: $TiO_2$ (Degussa P25) was dispersed into distilled water (1 g in 100 ml) under vigorous stirring for 30 min until uniform $TiO_2$ suspension was formed. Eight pieces (1 m × 1 m) of porous foam nickel (thickness: 1.6 ± 0.2 mm; porosity ⩾ 95%; Ni ⩾ 99.99%; pore density: 80–100 ppi; Brunauer–Emmett–Tellrt surface area ($S_{BET}$): 1.2 $m^2/g$; Guangzhou Nonferrous Metal Research Institute, China) were used as substrate due to their high-opened porous structure and excellent hydrodynamics properties which can reduce the air-resistance and the loss of photocatalyst at high flow velocities. After cleaned by ethanol to remove grease, the foam nickels were coated by spaying prepared $TiO_2$ suspension using a laboratory spay gun (F-2, Taiwan Color CO., Ltd.). The coatings were dried naturally at room temperature for 24 h. The $TiO_2$ film coated on the foam nickel with the weight of 5.19 $g/m^2$ was used as the photocatalyst in the following photocatalytic reactor.

### 2.3. Experimental set-up

All experiments were performed in a mid-scale custom-made integrated BTF–PCO stainless steel system (Fig. 1). The waste gas from paint packaging plant was collected into the reactor by an exhaust fan mounted at the end of the reactor at a rate of 3000 $m^3$/h. The waste gas was firstly introduced into the BTF (up-flow counter-current mode) and then to the photocalatytic reactor (downflow mode).
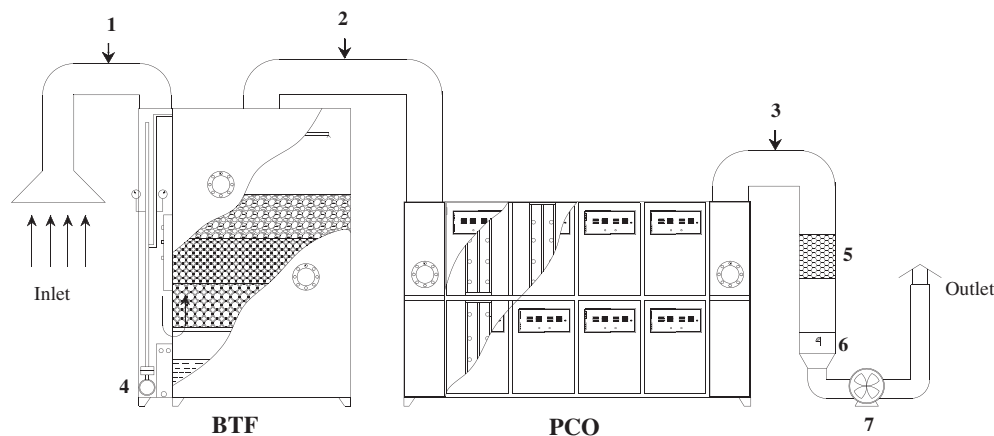
**Fig. 1.** Schematic diagram of BTF–PCO equipment. (1–3: Sampling point of inlet, outlet of BTF and outlet of PCO reactor, respectively; 4: Peristaltic pump; 5: Active carbon; 6: Flow controller; 7: Exhaust fan).

The BTF reactor (2000 mm × 2000 mm × 4500 mm) mainly contained a biofiltration bed and a circulating nutrient unit. The former portion consisted of biofilm-carriers including the ceramic particles ($\Phi$: 6–8 mm; Bulk density: 0.75–1.10 g/cm$^3$; $S_{BET}$: 2–5 m$^2$/g; Porosity $\geqslant$ 36%; Transing Chemical Packing Co., Ltd., Jiang-xi, China), hollow plastic balls ($\Phi$: 35 mm; Bulk density: 0.12–0.14 g/cm$^3$; $S_{BET}$: 2–4 m$^2$/g; Porosity $\geqslant$ 87%; Shengfeng Chemical Packing Co., Ltd., Jiangxi, China) and rasching ring (12 mm × 12 mm × 3 mm; Bulk density: 0.69–0.73 g/cm$^3$; $S_{BET}$: 0.42–0.48 m$^2$/g; Porosity $\geqslant$ 70%; Shengfeng Chemical Packing Co., Ltd., Jiangxi, China), with the mass ratio of 1:1:1. And the effective volume of the biofilm-carriers was 6 m$^3$. The volume of the circulating nutrient liquid containing mineral salt in the latter unit was maintained at 2 m$^3$ by adding dechlorinated water and 1 L nutrient liquid at the bottom of BTF reactor everyday. The nutrient liquid was firstly introduced into the top of the biotrickling filter by a peristaltic pump at a rate of 13 m$^3$/h, which passed through the biofilm-carriers and then returned to the bottom. During the whole operation period, the pH value of circulating liquid was aperiodically adjusted to neutral with 0.1 M NaOH.

The PCO reactor (3060 mm × 1255 mm × 2350 mm) consisted of eight parallel-connected units. Each unit contained a piece of foam nickel coated with TiO$_2$ at the center and four 30 W low-pressure vacuum ultraviolet lamps (with a maximum at 254 nm and a minimum (<5%) emission at 185 nm, ZY30S19 W, Guangdong Cnlight CO., Ltd., China) which were fixed on each side of foam nickel in parallel. And the distance between the foam nickel and UV lamps was about 50 mm with light intensity of about 2.5 mW/cm$^2$.

### 2.4. Experimental procedures

The combined BTF–PCO reactor was operated for more than 3 months under the different operational conditions including temperature and relative humidity which were summarized in Table 1. The great difference of the temperature and relative humidity at the gas inlet during the 90 days operation period was mainly attributed to the changeable weather, which did not affect the temperature or relative humidity so greatly at the gas outlet. The waste gas stream was firstly introduced into the BTF with the temperature maintained at about 30 °C which is in favor of the microorganisms' growth [32]. Initially, no bacteria grew on the packing materials. The attached bacteria increased gradually with an increase in the start-up time. For instance, on the day 10, 50 and 80, the biomass increased to 5.42, 15.35 and 38.46 mg/g dry weight. By passing through the BTF reactor with the residence time

**Table 1**
Summary of the experimental operational conditions.

| Operation time (day) | Gas inlet | | Gas outlet | |
|---|---|---|---|---|
| | Temperature (°C) | RH[a] (%) | Temperature (°C) | RH[a] (%) |
| 0–30th | 29.3 ± 2.2 | 75.0 ± 5.3 | 30.4 ± 0.3 | 77.8 ± 1.0 |
| 30th–60th | 32.0 ± 3.0 | 68.8 ± 4.4 | 30.5 ± 0.5 | 79.4 ± 2.1 |
| 60th–90th | 24.5 ± 1.1 | 48.4 ± 7.2 | 31.2 ± 0.1 | 84.0 ± 2.8 |

[a] RH: relative humidity.

of 7.2 s, the VOCs in the waste gas were partially removed and humidified for the PCO reactor. The foam nickels coated with TiO$_2$ were pretreated or regenerated by irradiation of vacuum UV lamps for 1 h to remove the deposit on the photocatalyst surface before waste gas stream passing. As the waste gas was introduced into the PCO reactor with residence time of 10.8 s, a slightly higher temperature (30.4–31.2 °C) was found during operation. The relative humidity increased approximately from 60% to 80%. Also, about 20 ppmv of O$_3$ was formed by photochemical dissociation of O$_2$ with irradiation of 185 nm light (detected with on-site ozone meter, LIMICEN Ozone R&D Center, Guangzhou, China) (shown in Fig. S2). After the operation of the BTF–PCO reactor for 3 h, the gaseous samples were collected by vacuum Summa canisters (2.7 L, Entech Instruments Inc., CA, USA), which were thoroughly cleaned by high purity nitrogen before use, from inlet, outlet of BTF and outlet of PCO reactor, respectively. Then the waste gas was qualitatively and quantitatively analyzed. The flowrates were varied by flow controller to investigate the effects on the removal efficiency of VOCs. At the end of the PCO reactor, the ozone concentration was below detection (0.1 ppmv) after active carbon treatment.

### 2.5. Analytical methods

Six VOCs were detected as the target contaminants whose physical–chemical properties and threshold limit values for time weighted average (TLV-TWA) concentrations were listed in Table S1. They were qualitatively and quantitatively detected by a Entech 7100 preconcentrator (Entech Instruments Inc., CA, USA) and GC–MS (7890A GC-5975C MS, Agilent technologies, USA) combined techniques with the USEPA TO-15 method [33]. Firstly, 150 mL of the waste gas from sampling Summa canisters were concentrated at the glass beads trap (module 1), which was maintained at 150 °C with liquid nitrogen. The trapped analytes

were then desorbed at 20 °C and transferred to a Tenax-TA trap (module 2) maintained at −40 °C. The concentrated components were again desorbed at 190 °C and then focused at the cold top of the capillary column, which was cooled to −180 °C. After 2.5 min, the highly focused VOCs were quickly desorbed at 120 °C/min and swept into the column for separation.

A DB-1 column (60 m × 0.32 mm × 0.25 μm, Agilent Technologies, USA) was used with GC oven temperature program: initially 35 °C for 5 min, programmed to 150 °C at a rate of 5 °C/min, and then to 250 °C at a rate of 15 °C/min which was held for 2 min. The carrier gas was ultrahigh purity helium at a constant flow rate of 1.2 mL/min. Mass spectrometer conditions were as follows: temperature of the transfer line: 290 °C; ionizing energy: 70 eV; scan range: 45–260 me$^{-1}$. The concentrations of VOCs were quantified by external standard calibration which was determined by standard sample (TO-15, Linde Spectra Environment gases, USA). Each target species was identified by its retention time, mass spectra by using the NIST 05 database (National Institute of Standards and Technology).

### 2.6. Calculation of the removal efficiency, loading rate and elimination capacity and VOCs risk assessment

The performance of the reactor was evaluated in terms of the RE (%), loading rate (LR, g m$^{-3}$ h$^{-1}$) and EC (g m$^{-3}$ h$^{-1}$), which were calculated by the following Eqs. (1–5) (see the Supporting Information).

Though the target VOCs in this study have not been classified as carcinogen agents by the International Agency for Research on Cancer (IARC), while they have important non-carcinogenic toxic for workers in the workshop. Hence, a simple model of assessment non-carcinogenic risk based on occupational exposure limit is characterized in terms of a HRI, which is defined as [34]:

$$HRI_i = \frac{C_i}{TLV - TWA_i} \tag{1}$$

where TLV-TWA$_i$ is the threshold limit value for time weighted average of compound $i$, which is list in Table S1; $C_i$ is the concentration of compound $i$. In the workshop, VOCs with HRI above 1.0 are deemed to pose a potential human health concern [35]. Hence, it is require that HRI, the sum of HRI$_i$, should not exceed the value 1.0.

$$HRI = \sum_i HRI_i \tag{2}$$

## 3. Results and discussion

### 3.1. VOCs concentrations during different paint producing processes

The components and concentrations of VOCs during different paint-producing processes were investigated by GC–MS (Fig. S3). It was observed that the grinding process resulted in the most abundant VOCs with more than forty-five species identified. These compounds could be divided into four groups: aromatic hydrocarbons, alkanes, esters and alcohols. Since some VOCs in other processes were under detection limit, only six prevailing compounds including ethyl acetate (EA), toluene (Tol), EB, (m-/o-/p-)xylene (Xyl), (2-/3-/4-)ethyltoluene (ET) and (1,2,3-/1,2,4-/1,3,5-)trimethylbenzene (TMB) were mainly focused on as the performance of VOCs emission in paint-producing.

The average concentrations of total and individual VOCs at the background (a place in Guangzhou city without any chemical company around) and paint workshop were obtained from experiments replicated in triplicate (Table 2). Results showed that the TVOC concentrations of different processes were far higher than those at background, followed the order: grinding (432.47 ± 53.40 mg/m$^3$) > predispersing (321.99 ± 59.48 mg/m$^3$) > tinting (242.14 ± 71.03 mg/m$^3$) > packaging (69.19 ± 22.42 mg/m$^3$). The highest TVOC concentration in grinding may be attributed to the highest environmental temperature resulted from the greatly intense friction between dispersion plate and glass beads of the grinding machines, leading to a strong evaporation of solvent and then high TVOC concentration. And the emission was dominated by EB and Xyl with concentrations of 124.30 and 211.31 mg/m$^3$ in this process, accounting for 28.7% and 48.8% of TVOC concentration, followed by ET (13.3%), TMB (7.3%), Tol (1.1%) and EA (0.6%) (Fig. S4), indicating that the mainly used solvents, Xyl and EB, can be easily emitted in this process. Although the TVOC concentration at predispersing process was less than that at grinding process in respect of using different mix machine, the proportions of individual VOCs were similar to grinding, suggesting that the dominant emission source from the former two processes was the same raw solvents. As for tinting, it was noted that the concentrations of EA and Tol increased swiftly from 2.78 and 4.91 mg/m$^3$ in grinding process to 66.61 and 40.56 mg/m$^3$, respectively. This was due to that the solvent with higher content of EA and Tol was added as assistant agents for special function in tinting. Without any mix machine, the VOCs emission from packaging was the lowest among the paint-producing processes. In addition, according to the HRI values of individual VOCs and TVOCs calculated and listed in Table S2, it was worthwhile to note that the HRI value for TVOC was 1.041 in grinding process which was lager than 1.0, indicating that it would be harmful to workers' health. Hence, some measures must be taken to reduce the risk in the grinding workshop. However, the operation of the gringding process mainly relied on the grinding machines, while the paint was packaged only by workers. The number of workers in packaging workshop was much more than any other workshops. Therefore, the packaging workshop was chosen as the target workshop to remove the pollutants at a pilot-scale.

### 3.2. Removal efficiencies of VOCs

The REs of individual VOCs under single and combined techniques together with inlet concentrations during 3 months are presented in Fig. 2. It was observed that the concentrations of

**Table 2**
VOCs Concentrations of different processes in paint product.

| Compounds | Backgroud[a] concentration (mg/m$^3$) | Processes concentration (mg/m$^3$) | | | |
|---|---|---|---|---|---|
| | | Predispersing | Grinding | Tinting | Packaging |
| EA | 0.045 ± 0.002 | 2.621 ± 0.153 | 2.779 ± 0.228 | 66.611 ± 20.100 | 13.876 ± 10.902 |
| Tol | 0.037 ± 0.003 | 8.141 ± 2.738 | 4.914 ± 0.581 | 40.564 ± 23.369 | 2.443 ± 2.362 |
| EB | 0.046 ± 0.002 | 107.480 ± 19.762 | 124.302 ± 26.386 | 46.599 ± 8.203 | 20.814 ± 7.903 |
| Xyl | 0.021 ± 0.005 | 145.307 ± 20.489 | 211.306 ± 21.729 | 66.539 ± 15.173 | 29.822 ± 8.495 |
| ET | 0.009 ± 0.001 | 48.392 ± 13.556 | 57.456 ± 3.701 | 16.002 ± 2.889 | 1.071 ± 1.025 |
| TMB | 0.004 ± 0.001 | 10.050 ± 2.800 | 31.712 ± 0.772 | 5.823 ± 1.294 | 1.174 ± 0.556 |
| TVOC | 0.162 ± 0.014 | 321.990 ± 59.482 | 432.470 ± 53.398 | 242.140 ± 71.030 | 69.190 ± 22.417 |

[a] The background sampling site was a place in Guangzhou city without any chemical company around.
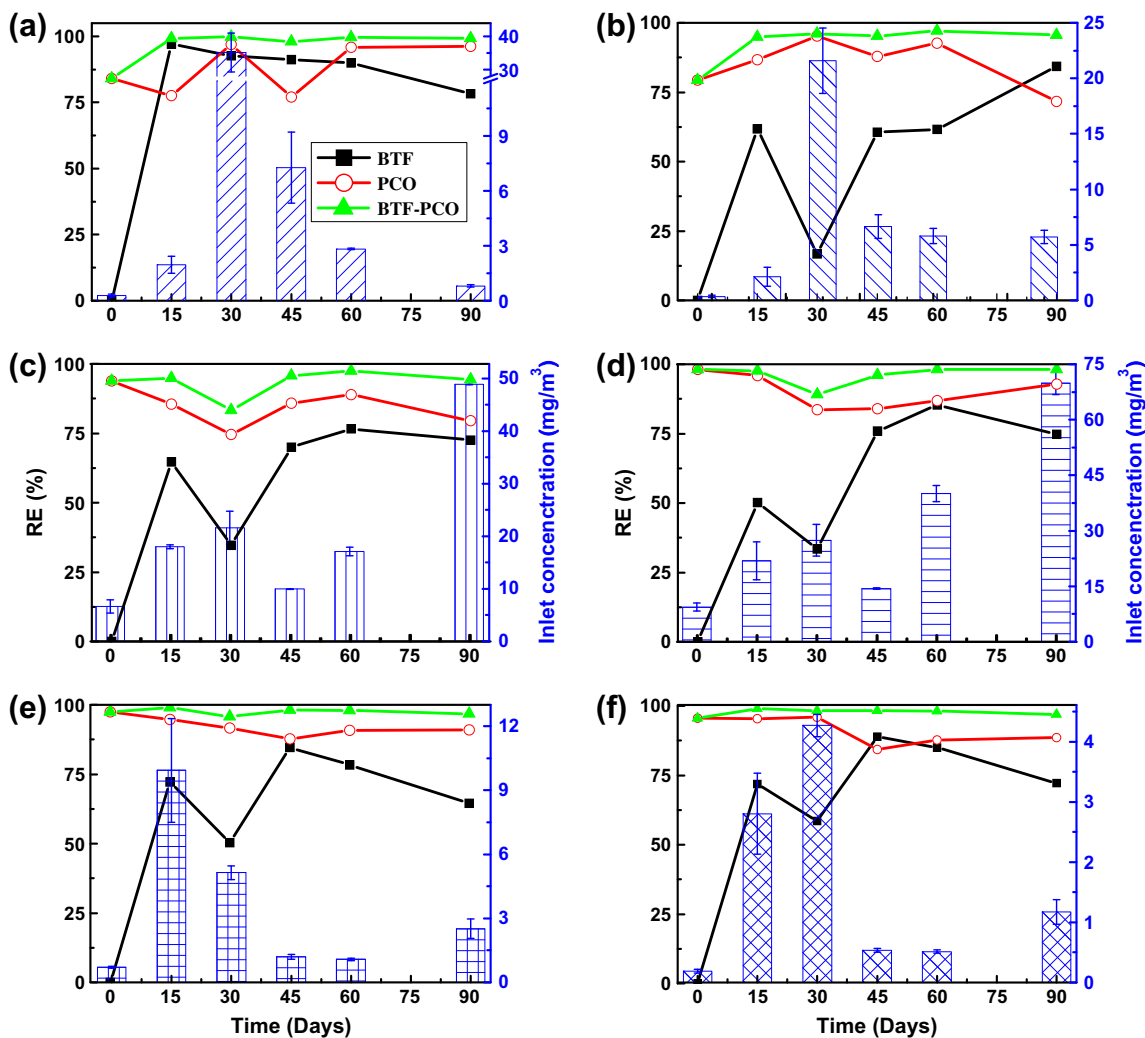
**Fig. 2.** Removal efficiencies under single and combined techniques during 90 days continue degradation together with the inlet concentrations (bar) of (a) EA, (b) Tol, (c) EB, (d) Xyl, (e) ET and (f) TMB.

individual VOCs were irregular and variable. For instance, high-level emission of 35.10 mg/m$^3$ of EA on 30th day but low concentration emission of 0.28 mg/m$^3$ on 1st day (Fig. 2a). This is probably due to that different paint products are packaged in the packaging workshop every day. Therefore, the various concentrations of individual VOCs in packaging workshop on different operating days might affect the removal efficiency under same degradation techniques employed.

For the single BTF, the biodegradation REs of EB and Xyl (Fig. 2c–d) reached 64.7% and 50.2% with the inlet concentrations of 18.00 and 21.92 mg/m$^3$ on the 15th day, suggesting that biofilm began to form. However, a significant decrease in REs of EB and Xyl was observed by the values of 30.1% and 16.7% on the 30th day. Similar decreasing tendency of biodegradation REs for Tol, ET and TMB was also found (Fig. 2e–f). This should be because that the process of biofilm formation was not completely yet [14] or the microorganisms of the formed biofilm could not adapt to the sudden increase of the other inlet VOCs concentrations, such as the increase of EA and Tol inlet concentrations from 1.96 and 2.13 mg/m$^3$ (on the 15th day) to 35.12 and 21.60 mg/m$^3$ (on the 30th day) (Figs. 2a and b), respectively. In addition, the solubility and octanol/water partition coefficient values of EA were far higher than aromatic VOCs as shown in Table S1, indicating that the EA was more hydrophilic than aromatic compounds. It was considered

that, in a mixture of VOCs, the higher concentrations of hydrophilic VOCs were introduced, the lower removal rates for hydrophobic VOCs (e.g. aromatic VOCs) were obtained [36]. Hence, the REs of aromatic VOCs decreased dramatically on 30th day. After 45 days acclimation, stable biodegradation REs of aromatic VOCs were achieved. For instance, the REs of EB and Xyl were 70.0% and 76.0% by BTF on the 45th day, which were maintained at 72.6% and 74.6% even with the inlet concentrations of 69.90 and 48.84 mg/m$^3$ on the 90th day for EB and Xyl, respectively. As for oxygenated compounds, EA, the highest RE reached 97.1% after 15 days operation and trended to be stable (Fig. 2a) in the whole 90 days, indicating that a shorter acclimation period was needed for oxygenated compounds than for aromatic VOCs. It was found that the conditions were more favorable for EA biodegradation than aromatic VOCs. Similar conclusions were also obtained for the mixtures of oxygenated and aromatic VOCs by other researchers [36–38]. It was considered that pollutants with high Henry's constant were more difficult to eliminate in BTF, because these pollutants had an unfavorable gas–liquid partition and the pollutants concentrations in the biofilm were too low to sustain a high biodegradation rate [13]. As listed in Table S1, the Henry's constants of aromatic VOCs were about 40 times higher than that of EA, which might result in the lower REs and longer acclimation period of aromatic VOCs than EA. Moreover, biofiltration of hydrophobic

volatile pollutants was intrinsically limited by poor transfer of the pollutants from the gaseous to the liquid biotic phase, where biodegradation occurred [39]. Nevertheless, when the BTF went into stable state, stable REs above 70% of all the individual VOCs were obtained.

After biodegradation, the waste gas was introduced into PCO reactor for further treatment. Therefore, the inlet VOCs concentrations of PCO reactor corresponded to the outlet concentrations of BTF reactor, which were listed in Table S3. From Fig. 2 and Table S3, on the 1st day, it was found that the highest photocatalytic REs was Xyl (98.2%) with the inlet concentration of 9.39 mg/m$^3$, followed by ET (97.4%), TMB (95.5%), EB (93.9%), EA (84.1%) and Tol (79.4%), indicating that the photocatalytic oxidation efficiencies of target components were very high, though no VOCs were degraded in BTF reactor. On the 15th day, however, the PCO RE of EB dropped to 85.9% with the similar inlet concentrations (6.36 mg/m$^3$) of 1st day (Fig. 2c). And similar trendy was also found for the REs of other VOCs except Tol, which is likely due to the increase of relative humidity of waste gas after passing through the BTF reactor, resulting in lower adsorption capacity of VOCs than that of $H_2O$ on the photocatalyst surface [40,41], and then lower PCO REs. On the 30th day, it was worthwhile to point out that although the inlet concentrations of EA and Tol were 44 and 22 times higher than those of 15 days ago, the PCO REs increased from 77.6% to 96.9% and 86.6% to 96.2% for EA and Tol from the 15th day to 30th day. As for other VOCs, the REs obtained were lower than before, suggesting that a negative effect occurred as the sudden increase of EA and Tol. It was considered that the inhibition may be a consequence of competition reaction onto the catalyst [29] and the mutual inhibition effect on the removal efficiencies of individual compound by the other components for multi-component degradation [42]. Despite slightly fluctuating of the concentrations of TVOC between on the 45th and 90th day, TVOC PCO REs still high which ranged from 71.6% to 96.2%, suggesting that long-term high photocatalytic activity of $TiO_2$ film under $UV_{254+185nm}$ irradiation to remove of VOCs could be achieved in this pilot-scale study. In contrast, Wei et al. fould that only 53.0% to 58.2% of toluene could be removed for the first 14 days and then greatly reduced to 22.2% on day 17 while PCO was employed as pretreatment [43]. $UV_{254+185nm}$ light was also found to be effective PCO removal of Tol, benzene [44], formaldehyde [45], or other VOCs even at ppbv-level [46]. It was considered that strong oxidative effect of abundant reactive species, such as $O_3$, $O(^1D)$ and OH·, could be generated additionally by photodecomposition of $O_2$ and $H_2O$ under $UV_{254+185nm}$. Besides, with the irradiation of $UV_{254+185nm}$, deactivated photocatalysts could be effectively regenerated in the absence of waste gas [47].

Since various conditions may lead to instability and even low removal efficiencies for individual VOCs during BTF or PCO process alone as discussed above, a combined technique with BTF and PCO reactor was also employed. As shown in Fig. 2, a stable REs of EA, Tol, ET and TMB which were above 94.9% were obtained by BTF–PCO during the whole operation period. Although lower REs of EB and Xyl corresponding to 83.3% and 89.1% were observed on 30th day due to similar reasons on BTF reactor as mention above, the REs on other days were more than 90%. Moreover, these REs were very stable during the 90 days operation. It was noted that combined BTF–PCO technique could ameliorate flaws of single technique, such as hydrophobicity for BTF and competition adsorption for PCO, which reduce the individual VOCs removal as mentioned above. The overall performance of single and combined techniques for TVOC removal was also investigated as listed in Table 3. The results showed clearly that highest TVOC removal efficiency was obtained by combined BTF–PCO (95.3–97.8%), followed by PCO (85.2–95.3%) and BTF (50.3–79.7%), suggesting that the combined BTF–PCO techniques was more suitable to re-

**Table 3**
Overall performance of single and combined technique in TVOC REs.

| Operation time (day) | TVOC REs (%) | | |
|---|---|---|---|
| | BTF | PCO | BTF–PCO |
| 0 | 0.0 | 95.3 | 95.3 |
| 15th | 61.7 | 92.2 | 97.0 |
| 30th | 50.3 | 86.3 | 93.2 |
| 45th | 75.1 | 85.2 | 96.3 |
| 60th | 79.7 | 89.3 | 97.8 |
| 90th | 74.1 | 86.8 | 96.6 |

move the organic waste gas with multi-component and changed concentration. Comparatively, only 83% of ethylbenzene could be removed by using combined photocatalytic and biological system [26], which was lower than those in this study. Wei et al. reported that 96.7% of toluene could be removed, however, the residence time was 60.6 s which was more than 3 times longer than that in our study [43]. Moreover, no reaction byproducts were detected or under detection limitions in the outlet gas stream in this work as illustrated in Fig. 3, even on the 30th day with the lowest VOCs REs and 90th day treatment. The formation of unstable intermediates cannot be ruled out and most VOCs appeared to be mineralized to $CO_2$ and $H_2O$ by combined BTF–PCO system, although the measurement of $CO_2$ was not carried out in this work.

Based on the concentrations of VOCs (Fig. 2 and Table S4), the HRI values of individual and total VOCs in the inlet and outlet of combined BTF–PCO reactor were calculated and listed in Table 4. During whole 90 days' operation, the maximum HRI values for the inlet EA, Tol, EB, Xyl, and TMB were $25.07 \times 10^{-3}$,
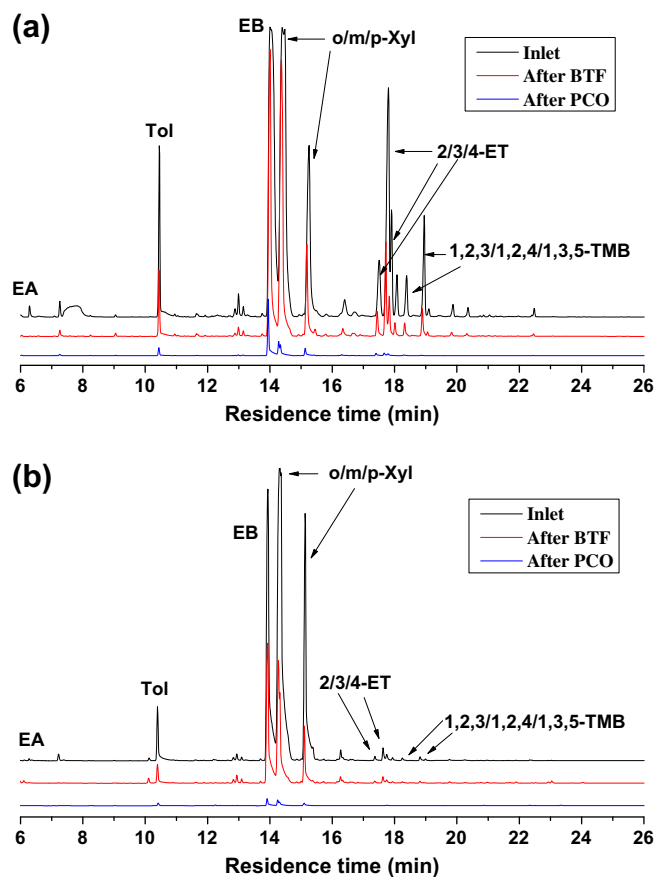


**Fig. 3.** Total ion current profiles of VOCs detected by preconcentration and GC–MS under combined technique on the (a) 30th d and (b) 90th d operation.

**Table 4**
HRI values for VOCs in the inlet and outlet of combined BTF–PCO reactor during 90 days operation.

| Compounds | HRI ($\times 10^{-3}$) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1st day | | 15th day | | 30th day | | 45th day | | 60th day | | 90th day | |
| | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet |
| EA | 0.197 | 0.031 | 1.400 | 0.009 | 25.071 | 0.057 | 5.187 | 0.104 | 2.019 | 0.008 | 0.577 | 0.005 |
| Tol | 0.960 | 0.198 | 5.680 | 0.290 | 57.600 | 2.292 | 17.779 | 0.850 | 15.463 | 0.436 | 15.236 | 0.675 |
| EB | 15.310 | 0.934 | 41.379 | 2.123 | 49.655 | 8.277 | 22.880 | 0.975 | 39.348 | 1.017 | 112.282 | 6.325 |
| Xyl | 21.586 | 0.389 | 50.391 | 1.164 | 63.103 | 6.884 | 33.041 | 1.272 | 92.142 | 1.781 | 160.699 | 2.952 |
| ET | – | – | – | – | – | – | – | – | – | – | – | – |
| TMB | 1.536 | 0.069 | 22.440 | 0.221 | 34.160 | 0.583 | 4.277 | 0.074 | 4.118 | 0.076 | 9.378 | 0.296 |
| $\sum$HRI | 39.590 | 1.621 | 121.290 | 3.807 | 229.590 | 18.093 | 83.165 | 3.276 | 153.090 | 3.318 | 298.172 | 10.253 |

$57.60 \times 10^{-3}$, $112.28 \times 10^{-3}$, $160.70 \times 10^{-3}$ and $34.16 \times 10^{-3}$, respectively. After the BTF–PCO treatment, the maximum HRI values reduced greatly, and corresponding to these VOCs were $5.70 \times 10^{-4}$, $2.29 \times 10^{-3}$, $8.28 \times 10^{-3}$, $6.88 \times 10^{-3}$ and $5.83 \times 10^{-4}$, respectively. The HRI values of TVOC for the outlet were in the range of $1.62 \times 10^{-3} - 18.09 \times 10^{-3}$, which was far lower than those for the inlet ($39.59 \times 10^{-3} - 298.18 \times 10^{-3}$), suggesting that the non-carcinogenic risk was effectively reduced after BTF–PCO treatment.

### 3.3. Effect factors of VOCs removal under combined BTF–PCO system

Following the successful start-up of BTF after 45 days operation, the effect of inlet TVOC concentrations on the REs by single and combined techniques were investigated with the fixed outlet velocity of 18.8 m/s (corresponds to flowrate 3000 m³/h). As shown in Fig. 4a, by employing combined BTF–PCO technique, the TVOC REs maintained steadily within the range of 95.8–98.2% with the increase of inlet TVOC concentration from 6.69 to 129.00 mg/m³, suggesting that TVOC could be effectively removed by the integrated technique and seemed not to be affected by the changes of the inlet concentration. However, considerable fluctuation of TVOC REs under single BTF (71.4–82.3%) and PCO (85.8–90.3%) was observed. It was likely that different contents of antiaromatic and aromatic led to different TVOC REs by single technique in some concentration ranges as mentioned at Section 3.2. Therefore, the BTF–PCO was more suitable than single techniques in purifying the waste gases with concentrations ranged from 6.69 to 129.00 mg/m³.

The effect of outlet velocity within the range of 8.0–18.8 m/s (corresponds to flowrate 1333–3000 m³/h) on the TVOC REs by single and combined techniques was also investigated with the inlet TVOC concentrations in the range of 30.72–39.22 mg/m³ which hardly affected the VOCs removal as mentioned above (Fig. 4b). It could be seen that as the flowrates decreased from 3000 to 1333 m³/h, TVOC REs by single BTF increased greatly from 70.4% to 89.3%, whereas those by single PCO increased from 85.8% to 95.1%. However, only slight fluctuation of RE was observed by using combined technique which increased from 95.8% to 99.5%. All these results indicated that lower flowrate was benefit for the removal of VOCs. This is because that lower flowrate can lead to larger empty bed residence time (EBRT) which can provide longer adsorption and contact time of VOCs on the biofilm or on the photocatalyst in the reactors [14,48]. However, lower flowrate would also result in less amount of waste gas to be treated, which would increase the operating costs in the industrial application.

### 3.4. Elimination capacity of single and combined techniques

Based on the different inlet TVOC concentrations and reactors volume, it was considered that the comparative performances of
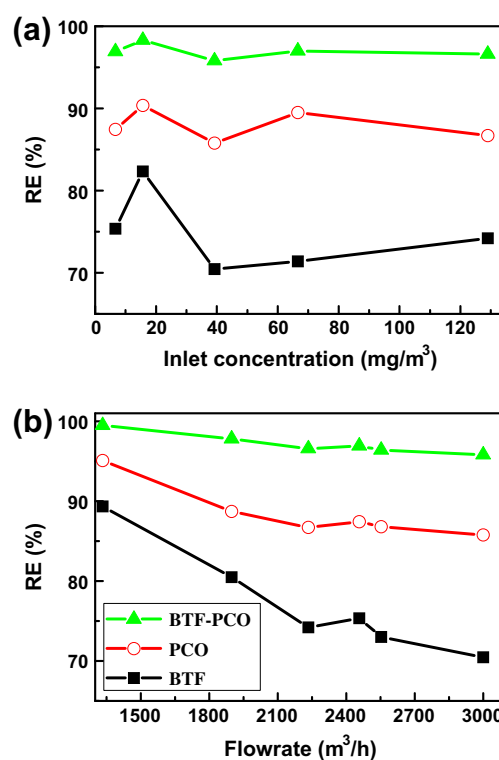


**Fig. 4.** Effect of (a) inlet TVOC concentration and (b) outlet flowrate on the removal efficiencies by single and combined techniques.

reactors should also be evaluated by the EC besides the RE [36]. The EC, which was defined as the amount of VOCs degraded per unit of the reactor volume and time for various LRs, reflected the degrading capacity for treatment systems. For all runs, the performance evaluation was carried out at steady state at the fixed EBRTs of 7.2, 10.8 and 18.0 s corresponding to BTF, PCO and BTF–PCO, respectively.

The relationship between LR and EC of different treatment systems is shown in Fig. 5. The slopes of dashed and solid lines represent theoretical 100% and average TVOC REs, respectively. Obviously, the EC linearly increased with increasing TVOC LR ($R^2 > 0.9869$) for each reactor, indicating that the increase of inlet LR appeared to have no inhibition effect on VOCs removal for either single or combined reactor, and the maximum EC ($EC_{max}$) mainly depended on the inlet LR. For BTF, the maximum VOCs elimination capacity of 47.8 g m⁻³ h⁻¹ was achieved at the maximum LR of 64.5 g m⁻³ h⁻¹. For PCO, due to the smaller LR of 19.2 g m⁻³ h⁻¹, the $EC_{max}$ was only 16.5 g m⁻³ h⁻¹. It is worthy to note that the $EC_{max}$ of 25.2 g m⁻³ h⁻¹ was attributed to larger volume on
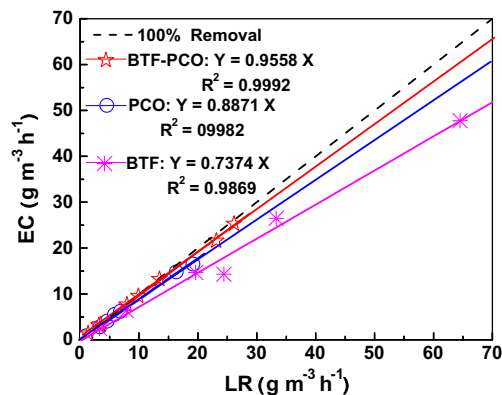
**Fig. 5.** Comparative elimination capacities of BTF, PCO and combined BTF–PCO at fixed EBRTs (BTF: 7.2 s; PCO: 10.8 s: BTF–PCO: 18.0 s) versus different loading rates (LRs) of TVOC.

combined BTF–PCO reactor. As a result, the $EC_{max}$ in this study followed the order of BTF > BTF–PCO > PCO. Although this result cannot be defined as the actual $EC_{max}$ because higher LRs were not tested in this study, it was noted that greater contribution of BTF than that of PCO in the combined technique was studied in the present conditions. Furthermore, from the slopes of fitting curves, it was observed that VOCs average REs of 73.7%, 88.7% and 95.6% were achieved by single BTF, PCO and combined BTF–PCO reactors, respectively, and followed the order: BTF–PCO > P-CO > BTF. Overall, with the highest BTF elimination capacity and the highest PCO removal efficiency, the combined technique could successfully remove the VOCs effectively in this pilot-scale study.

## 4. Conclusions

The main components in the waste gas emitted during paint producing process included ethyl acetate, toluene, ethylbenzene, xylene, ethyltoluene and trimethylbenzene which could be removed effectively by combined BTF–PCO techniques during 90 days operation. The results showed that excellent degrading performance for both aromatic and ester VOCs was found by the combined BTF–PCO. After treatment, the HRI values for the outlet VOCs were significantly reduced. With the combination of BTF and PCO technique, the VOCs removal efficiencies were slightly affected by TVOC concentrations and flowrates, respectively. The linear increase of ECs with increasing VOCs LRs indicated that the techniques can remove the waste VOCs efficiently from the packaging plant in any conditions in a long-term period (90 d) in this pilot-scale study.

## Acknowledgements

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2012.06.117.

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