



## Using an integrated decontamination technique to remove VOCs and attenuate health risks from an e-waste dismantling workshop



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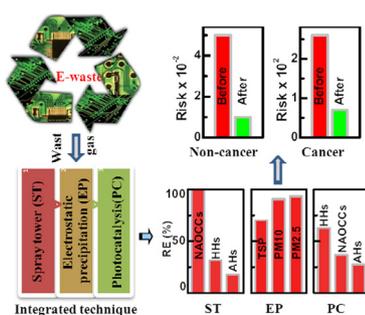
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### HIGHLIGHTS

- Pilot-scale removal of VOCs was carried out during electronic waste dismantling.
- Water-soluble VOCs and particles were pretreated before photocatalysis.
- Photocatalysis prefers degradation of VOCs with higher dielectric constant.
- Integrated reactor show high and stable removal ability to emitted VOCs.
- Health risks of individual and total VOCs decrease significantly after treatment.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Recycling e-waste is increasingly recognized as an important resource management strategy; however, the process emits different pollutants, including volatile organic compounds (VOCs). Sixteen dominant VOCs, with total concentrations ranging from  $1.6 \times 10^3$  to  $6.7 \times 10^3 \mu\text{g m}^{-3}$ , were presented during the manual process of dismantling television printed circuit boards using electric heating furnaces. An integrated treatment technique, involving a spray tower (ST), electrostatic precipitation (EP), and photocatalysis (PC), was used to eliminate these VOCs. The highest VOC removal efficiency during the 60-day treatment period was 69.5%. The removal efficiency was mainly due to the combined effect of preferential elimination of hydrosoluble VOCs and efficient interception of large-sized particles by ST; the enhanced capture efficiency of micro-sized particles by EP; and the dominant degradation of particle-free VOCs by PC. The PC treatment was able to remove more hydrocarbons (an average 62.7%) than nitrogen- and oxygen-containing and aromatic compounds (36.4% and 27.3% in average), due to the hydrocarbons' higher dielectric constants. Risk assessment revealed that the non-cancer and cancer risks associated with VOCs significantly decreased after the integrated technique was applied, indicating that the treatment is an efficient approach for purifying the atmosphere and protecting human health inside e-waste recycling workshops.

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## 1. Introduction

Increasing population growth and rapid industrialization have placed enormous pressure on traditional raw material sources and have produced large volumes of electronic waste (e-waste) [1,2]. A win-win situation for communities, governments, recyclers, and the environment can occur when e-waste is properly recycled, because e-waste recycling is an important form of resource recovery [3,4]. When the e-waste recycling process is not sufficiently regulated, large amounts of gaseous pollutants are emitted and released into air, severely polluting the atmosphere and threatening human health [5].

During e-waste dismantling processes, heavy metals and organic pollutants have been demonstrated as the main pollutants [6,7]. Generally, significant researches have been focused on the pollution profiles of heavy metals and semi-volatile organic compounds (SVOCs) in e-waste recycling environments [8–10]. There has been limited research, however, about contamination from volatile organic compounds (VOCs) from e-waste recycling, especially inside workshops [11]. These VOCs could pose health risks for workers, due to a lack of efficient environmental protection equipment in these workshops [12,13]. As such, efficient VOCs purification technologies are needed to mitigate health risks in these facilities.

As a first example of such a technology, photocatalysis (PC) has attracted considerable attention based on its ability to effectively degrade organic pollutants; this ability is driven by the generation of powerful and non-selective oxidant active species [14–16]. PC has been demonstrated to effectively degrade more than sixty kinds of individual VOCs [17–22], as well as mixed VOCs in laboratory settings [23,24]. However, unlike in lab environments, complex real-life situations can deactivate catalysts, primarily because of coexisting particulate matter in real waste gas treatment [25]. Therefore, to maintain the high efficiency and stability of PC technique, particle removal technologies must be sequenced properly.

Turning to a second kind of technology, previous studies have indicated [26,27] that electrostatic precipitation (EP) efficiently removes ultra-fine particles (e.g., micro- and nano-meter in size) from industrial waste gas. Recent work showed that total suspended particulates can be effectively trapped by the electrostatic precipitator, enhancing the ability of a subsequent PC system to remove VOCs at an on-site e-waste recycling workshop. Besides ultra-fine particles, particles with larger sizes (such as dust on aged e-waste surfaces) must be eliminated before reaching the EP unit. This is because larger particles could damage the EP unit's discharge electrodes, decreasing the EP unit's efficiency in removing ultra-fine particles.

A third technology is the spray tower (ST), which has emerged as a widely used and easily constructed and operated control device to remove different sized particles from industrial effluent gases [28,29]. This technology also removes some water-soluble atmospheric pollutants [30]. After this pretreatment, the PC reactor can then degrade and detoxify particle-free gaseous organics [19,31].

In this study, an integrated ST-EP-PC technique was applied to assess VOC elimination and risk reduction inside a waste printed circuit board (WPCB) recycling workshop, on a pilot scale. The abilities of ST, EP, and PC technologies to remove particles and VOCs were analyzed separately; the integrated technique was then evaluated for its ability to successfully eliminate atmospheric VOCs. Following this, the potential health risk from different VOCs was evaluated before and after the 60-day treatment operation. The goal of the study was to provide useful guidance for controlling VOC emissions from WPCB recycling processes.

## 2. Experimental design

### 2.1. Study site

The pilot scale experiments were conducted in a WPCB recycling workshop in Guangdong Province, China, where the WPCBs of television are manually recycled on electric heating furnaces (EHFs). The experiments lasted for 60 days, from November 2014 to January 2015.

### 2.2. Set-up

A pilot-scale integrated ST-EP-PC reactor (Fig. S1) was constructed to purify waste gas emissions. The waste gas was first fed into the ST unit (approximately 4500 mm high with a 3000 mm diameter), and then into the EP-PC integrated unit (2260 mm × 2500 mm × 3590 mm). Gas was fed using two centrifugal pumps mounted separately between the ST outlet, and the PC outlet to obtain a stable flow-rate of 10,000 m<sup>3</sup> h<sup>-1</sup>. Waste gas was introduced into the ST reactor from the bottom to top with residence time of 2.0 s and fed into the EP-PC integrated unit with the residence time of 7.3 s.

The ST unit mainly consists of a polypropylene ST and a water spraying and circulating unit (with a rate of 0.4 m<sup>3</sup> h<sup>-1</sup>). The former portion was divided into three equal-height layers, each packed with commercial rasching rings (12 mm × 12 mm × 3 mm; Bulk density: 0.69–0.73 g cm<sup>-3</sup>; S<sub>BET</sub>: 0.42–0.48 m<sup>2</sup> g<sup>-1</sup>; porosity ≥ 70%).

For the EP system, 16 electrostatic dust collectors were distributed symmetrically at the bottom of the EP-PC integrated reactor. The upper part of the reactor was divided into ten equal units using 20 pieces of foam nickel (1000 mm × 500 mm for each) coated TiO<sub>2</sub> (commercial Degussa P25; particle diameter: 300 nm; specific surface area: 50 m<sup>2</sup> g<sup>-1</sup>) and 44 vacuum ultraviolet lamps (30 W for each, maximum wavelength at 254 nm with a minimum <5% emission at 185 nm, ZY30S19 W, Guangdong Cnlight CO. Ltd., China). Details about the EP and PC units are provided in Supporting Information and previous papers [13,25].

### 2.3. Sample collection and analysis

VOC samples were collected at the inlet, ST outlet, and PC outlet, using 2.7-L stainless Summa canisters (ENTECH Instruments Inc, Silonite™), about every 10 days. The 10, 20, 30, 40, and 50-day samples were denoted as 1st, 2nd, 3rd, 4th, and 5th samples, respectively. Canisters were pre-cleaned five times with ultra-high-purity nitrogen, and then pre-evacuated before sampling. VOC analyses were conducted using an Entech 7100 pre-concentrator (Entech Instruments Inc., CA, USA), followed by gas chromatography–mass spectrometry (7890-5975 GC-MS, Agilent technologies, USA), using the U.S. Environmental Protection Agency (USEPA) TO-15 method [32]. The column was 60 m × 0.32 mm with 0.25 μm thick film (DB-5MS, Agilent Technology, USA).

Waste gas from the Summa canisters were highly concentrated by the pre-concentrator and swept into the column for separation after quickly desorbed at 120 °C min<sup>-1</sup>. The oven temperature was programmed as follows: the initial temperature of 40 °C was held for 5 min; the temperature was then increased to 150 °C at a rate of 5 °C per min; the temperature was then raised to 250 °C at a rate of 15 °C per min, and was then held for another 2 min. The temperature of the injector, transfer line and detector were: 200 °C, 290 °C and 230 °C, respectively. Ultra-high-purity helium was used as the carrier gas, at a constant flow of 1.2 mL per min; the MS was

operated in full scan mode, with  $m/z = 45\text{--}260$  and an injection volume of 50 mL.

Calibration standards with six points were prepared by diluting a certified standard sample TO-15 (Linde Spectra Environment Gases, USA) with ultra-high-purity nitrogen in an Entech 4600 dynamic dilution apparatus (Entech Instruments Inc., CA, USA). Target VOCs were identified by their retention times, and by consulting the National Institute of Standards and Technology (NIST) 05 mass spectral database. The calibration curve correlation coefficients for most VOCs exceeded 0.99 within the investigated concentration range. The detection limits of the methodology are provided in Table S2.

Total suspended particulate (TSP) and particulate matter ( $PM_{10}$  and  $PM_{2.5}$ ) samples were collected on glass fiber filters (GFFs) ( $10.2\text{ cm} \times 12.7\text{ cm}$ , MUNKTE, Sweden) using three high-volume samplers ( $300\text{ L min}^{-1}$ , Guangzhou Mingye environmental protection technology CO., Ltd., China). Air sample with volumes of  $94.5\text{--}146.1\text{ m}^3$  were drawn at  $0.3\text{ m}^3\text{ min}^{-1}$  for approximately 8 h. Prior to sampling, GFFs were baked at  $450\text{ }^\circ\text{C}$  for 6 h, then balanced for 24 h in a desiccator (BD115, binder, Germany) at a temperature of  $25\text{ }^\circ\text{C}$  and humidity of 50%. After sampling, loaded GFFs were wrapped with  $450\text{ }^\circ\text{C}$  pre-baked aluminum foil sheets, sealed with double-layer polyethylene bags, then transported into the laboratory and stored at  $-20\text{ }^\circ\text{C}$  until analysis. Concentrations of TSP,  $PM_{10}$  and  $PM_{2.5}$  were determined by weighing filters before and after sampling.

## 2.4. Risk assessment

### 2.4.1. Occupational exposure cancer risk

Occupational exposure limit ( $E_i$ ) estimates were generated by comparing the target compound  $i$  concentration ( $C_i$ ,  $\mu\text{g m}^{-3}$ ) with its time-weighted average value ( $TLV\text{-}TWA_i$ ,  $\mu\text{g m}^{-3}$ ) obtained from previous studies [13,33] (Eq. (1)). The  $TLV\text{-}TWA_i$  value was defined using a 8 h workday, with a 5 day workweek. The total risk ( $\sum E_i$ ) was assessed using Eq. (2).

$$E_i = \sum_{i=0}^n \frac{C_i}{TLV - TWA_i} \quad (1)$$

$$\sum E = \sum E_i \quad (2)$$

It was assumed that a compound with an attributable risk exceeding 1.0 could pose a cancer threat to workers [12]; an  $E_i$  value below 0.1 indicated no harmful risks.

### 2.4.2. Non-cancer and cancer risk

Adverse effects may impact neighborhood resident health, because e-waste recycling is generally carried out near residential areas. Thus, the non-cancer risk ( $HR$ ) associated with VOC exposure was assessed before and after the treatment. The non-cancer risk of each compound was defined as the ratio of its chronic daily concentration ( $C_i$ ,  $\mu\text{g m}^{-3}$ ) to its corresponding reference concentration ( $RfC_i$ ,  $\mu\text{g m}^{-3}$ ) provided by USEPA (<http://www.epa.gov/iris/>) (Eq. (3)). Based on references [33,34], VOCs levels with an  $HR$  above 1.0 were considered to pose a human health concern; a range of 0.1 to 1.0 indicated a potential concern.

$$HR_i = \frac{C_i}{RfC_i} \quad (3)$$

Lifetime cancer risk ( $LCR$ ) was also calculated, using the equation  $LCR = C_i \times UR_i$ , where each compound's unit risk ( $UR_i$ ) was obtained from the USEPA (<http://www.epa.gov/iris/>). A compound with a  $LCR$  greater than  $10^{-4}$ , between  $10^{-5}$  and  $10^{-4}$ , and between  $10^{-6}$  and  $10^{-5}$  were labeled as "definite risk," "probable risk," and "possible risk," respectively [35,36].

## 3. Results and discussion

### 3.1. VOC pollution profiles

First, the components and concentrations of VOCs emitted during the dismantling processes of television WPCBs using EHF were investigated. As Table S1 shows, 16 VOCs were most prevalent, categorized into the following three groups: halogenated hydrocarbons (HHs), aromatic hydrocarbons (AHs), and ethyl acetate.

Fig. 1 shows that the total VOC (TVOC) concentrations ranged from  $1.6 \times 10^3$  to  $6.7 \times 10^3\text{ }\mu\text{g m}^{-3}$ . HHs was the most dominant group (average percentage of 67.4% and concentration of  $2.3 \times 10^3\text{ }\mu\text{g m}^{-3}$ ). AHs contributed approximately 30.5% to the TVOC with an average concentration of  $6.9 \times 10^2\text{ }\mu\text{g m}^{-3}$ ; the lowest percentage was obtained for ethyl acetate (2.1%, average concentration of  $45\text{ }\mu\text{g m}^{-3}$ ). The percentage of dominant HHs in this study was 16.9% higher than in a reference study (50.5%) [12], in which EHF were also used to dismantle television WPCBs. The increase in HHs suggests an increased amount of chlorinated organics, such as Dechlorane Plus [37,38], often used as flame retardants during WPCB production.

There were also more emitted chlorinated VOCs (chloromethane, chloroethane, 1,3-dichloro-1-propene, 1,2-dichloroethane, and methylene chloride) in this study than in the reference study, which found chloromethane and chloroform [12]. This result also supports the above hypothesis (Figs. S2 and S3). Among the six kinds of HHs detected, 1,2-dichloropropane contributed the most, at 40.1%; this is significantly higher than the contribution of bromomethane at 27.3% (Fig. S3a). Conversely, bromomethane was the dominant compound (88.5%) among HHs in a previous study [12]; in that setting, they may have resulted from the brominated flame retardant decomposition in the WPCBs during high temperature treatment.

The significant differences in the dominant HH compound between studies (from bromomethane to 1,2-dichloropropane) suggests that the percentage of chlorinated flame retardants used in the recycled WPCBs in this study was higher than in the brominated ones. Nevertheless, the fire retardant type appears to have only a negligible impact on the percentage of formed AHs observed. As Fig. S3b shows, toluene was present at the highest percentage (74.4%) among AHs, similar to the previous result (76.7%) [12]. However, for NAOCCs, only ethyl acetate was seen in this study (Fig. S3c), which is different from the reference, where only methyl isobutyl ketone was seen [12].

Esters or ketones are generally used as solvents for resins or paints in the printed circuit board manufacturing process; the substances are easily released from the products during high temperature treatment processes [25,39]. As such, either ethyl acetate or methyl isobutyl ketone may have been used to produce the printed circuit boards, resulting in different emission profiles when dismantling WPCBs in these two different studies.

### 3.2. Removal of particles by the integrated technique

In a PC system, particle related catalyst poisoning significantly decreases catalyst activity. Therefore, to ensure the PC's efficient and stable removal of VOCs, pre-elimination of particles in waste gas is needed. Fig. 2 shows TSP,  $PM_{10}$  and  $PM_{2.5}$  concentrations before and after the integrated treatment. As expected, dismantling television WPCBs generated highly concentrated particles ( $3.2 \times 10^3\text{ }\mu\text{g m}^{-3}$  of TSP,  $2.8 \times 10^3\text{ }\mu\text{g m}^{-3}$  of  $PM_{10}$  and  $2.8 \times 10^3\text{ }\mu\text{g m}^{-3}$  of  $PM_{2.5}$ ). After ST treatment, concentrations significantly increased to  $7.1 \times 10^3$ ,  $9.0 \times 10^3$  and  $1.6 \times 10^4\text{ }\mu\text{g m}^{-3}$ , respectively. This indicates that the ST technology lacked the ability to eliminate micron-size particles, possibly due to the slower water

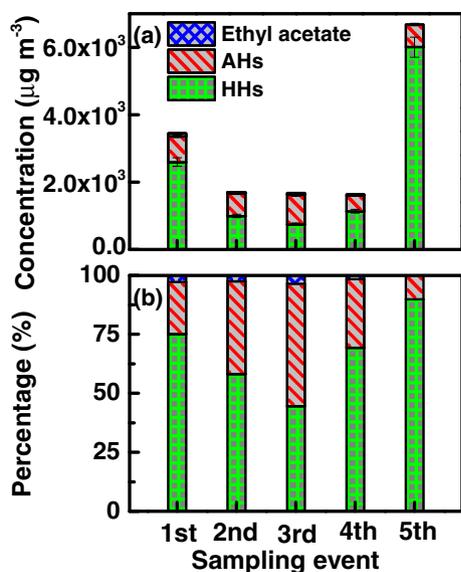


Fig. 1. Concentrations (a) and percentages (b) of three VOC groups emitted during the WPCB dismantling process.

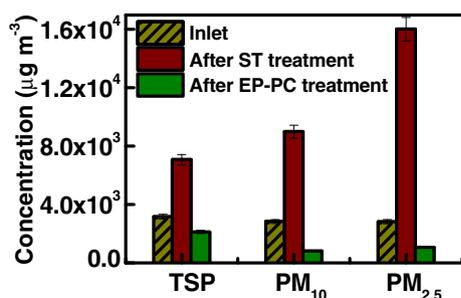


Fig. 2. TSP,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  concentrations before and after the integrated treatment.

spraying and circulation rate in the ST system ( $0.4 \text{ m}^3 \text{ h}^{-1}$ ) when compared to the waste gas inlet ( $10,000 \text{ m}^3 \text{ h}^{-1}$ ).

Because the nearly complete removal of micron-size particles by ST is only seen under optimal operating conditions [40,41], increasing the efficiency of ST in removing micron-size particles in the waste gas based on the incoming rate requires further study and optimization. As Fig. 2 shows, the larger the particle size, the more effective the ST is, which is consistent with previous reports [28,29]. After the combined EP-PC, approximately 70.1%, 90.9% and 93.3% of TSP,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were removed, respectively. Most of this removal was due to the EP technology, as EP showed a clear ability to trap TSP (the highest removal efficiency of 87.7%) during the on-site e-waste dismantling process [13].

The relatively high ability of EP to remove ultra-fine particles in this study may have been due to the efficient pre-treatment of large particles by ST; this protected the EP discharge electrodes from damage by large particles. However, approximately 6.7–29.9% of ultra-fine particles still entered the atmospheric environment, threatening worker health. This suggests that the particle elimination technique used in this study should be further improved for future applications.

### 3.3. VOC elimination using the integrated technique

After particle removal, VOC elimination using the integrated technique was further investigated. As Fig. 3 shows, VOC peaks (concentrations) generally decreased gradually using the

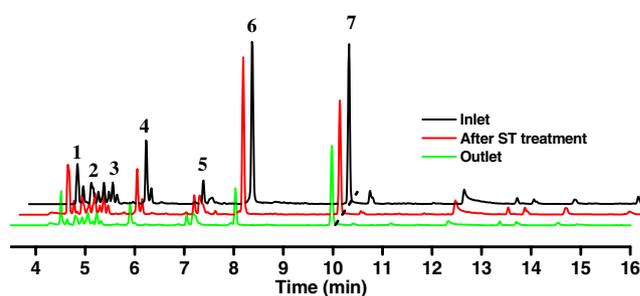


Fig. 3. Total ion chromatograms of VOCs detected before and after the integrated treatment at the first sampling event. (1: bromomethane; 2: chloroethane; 3: bromoethane; 4: ethyl acetate; 5: benzene; 6: 1,2-dichloro propane; 7: toluene).

integrated ST-EP-PC technique, indicating the efficient removal of different VOCs. Fig. 4 provides a detailed view of TVOCs by each unit. ST demonstrated a limited ability to remove TVOCs; the highest removal efficiency was only 19.8%, mainly attributable to the removal of relatively hydrophilic VOCs. In fact, during some sampling events, the outlet TVOC concentration after ST treatment was higher than the inlet VOC concentration. This is probably due to that some VOCs species may be scattered into the water while amount of waste gas passed. However, the water would be vigorously disturbed as the exhaust gas passed with high flow rate, leading to the release of VOCs from the water to the air.

There were significant VOC concentration fluctuations at different intervals during the dismantling process. This may be due to differences in the technical skill of individual workers, as well as WPCB volume at different intervals. As expected, a higher VOC removal efficiency (an increase from 31.9% to 82.0%) was seen after the EP-PC treatment, despite fluctuating inlet VOC concentrations. The efficient and stable VOC elimination is the result of all three ST, EP and PC technologies.

As discussed above, ST and EP were able to efficiently trap particles (with a removal efficiency exceeding 70.1%) to protect the sequent catalysts from continuous staining. The synergetic effect of porous foam nickel  $\text{TiO}_2$  film and the vacuum ultraviolet lamp led to the PC system's high and stable particle-free VOC decomposition and degradation (60.8% removal efficiency on average). Other research confirms the PC technique's effective degradation of gaseous VOCs, because the generated oxygen reactive species have a high oxidation capability [42,43]. Meanwhile, the ozone-producing lamps used in this study also simultaneously generated another strong oxidant species, ozone, during the photocatalytic process. The synergetic effect of photocatalysis and ozonation could facilitate VOC removal. More importantly, the high photoactivity of the catalyst could also be preserved, due to its excellent regeneration ability after using vacuum ultraviolet lamps.

This study also evaluated the removal of HHs, AHs, and ethyl acetate using the integrated technique. As Fig. 5 shows, ST did not efficiently remove HHs and AHs, with maximum removal efficiencies of only 31.2% and 17.3%, respectively. Much higher removal levels were achieved for ethyl acetate, reaching 100% removal by the fourth sampling event. Ethyl acetate was also at their lowest concentrations at this event at  $27 \mu\text{g m}^{-3}$ .

The great differences in removal efficiencies across these VOC groups may be due to different inlet concentrations and solubility properties. As Fig. 1 shows, ethyl acetate were present at the lowest average inlet concentration ( $45 \mu\text{g m}^{-3}$ ), followed by AHs ( $6.9 \times 10^2 \mu\text{g m}^{-3}$ ), and HHs ( $2.3 \times 10^3 \mu\text{g m}^{-3}$ ). Moreover, ethyl acetate solubility (eg.,  $83 \text{ g L}^{-1}$  for ethyl acetate) was much higher than for HHs (eg.,  $2.6 \text{ g L}^{-1}$  for 1,2-dichloro propane) and AHs (eg.,  $0.53 \text{ g L}^{-1}$  for toluene) [25]. As a result, ST is most efficient in removing ethyl acetate, followed by HHs and then AHs.

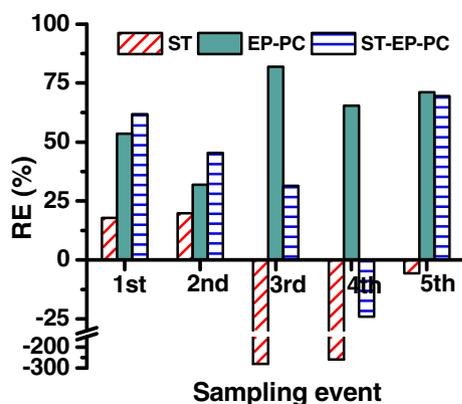


Fig. 4. Removal of TVOCs emitted during the WPCB dismantling process using the integrated technique.

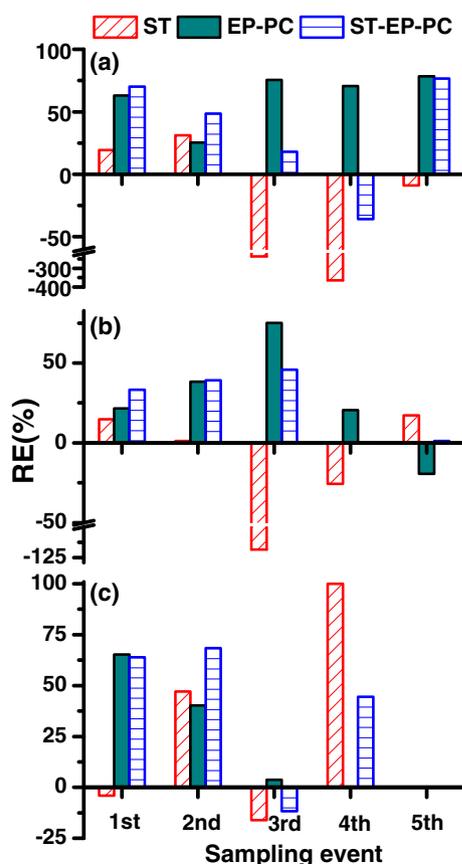


Fig. 5. Removal of HHs (a), AHs (b), and ethyl acetate (c) using the integrated technique.

The EP-PC system achieved the highest efficiency in removing HHs (average: 62.7%), followed by ethyl acetate (average: 36.4%), and AHs (average: 27.3%). The PC was primarily responsible for the efficient removal levels, due to poor ability of EP to eliminate these three groups [13]. PC degradation of organic pollutants depends largely on the efficient adsorption of VOCs onto the catalyst surface [23,24,31,44]. Previous work demonstrated that VOCs with a higher dielectric constant had a better affinity for hydrophilic photocatalysts, resulting in more efficient photocatalytic degradation [23,45]. In this study, the PC reaction occurred onto the TiO<sub>2</sub> surface, which was prepared in a solution and easily enriched hydroxyl groups to achieve hydrophilic properties. Thus, the

photocatalyst with the hydrophilic surface should more easily adsorb VOCs with higher dielectric constant.

Fig. S5 further confirms the hypothesis that the three dominant HHs, ethyl acetate, and AHs were removed at the following efficiency levels: 1,2-dichloropropane (76.3%), ethyl acetate (65.2%) and toluene (19.4%). This order is consistent with the order of their dielectric constants: 1,2-dichloropropane (8.93) is greater than ethyl acetate (6.02), which is greater than toluene (2.44) [46].

### 3.4. Health risk attenuation

#### 3.4.1. The attenuation of occupational exposure cancer risk

Generally, risk assessments are used to evaluate the health impact of hazardous substances or processes to people, compared to a healthy baseline. First, the occupational exposure cancer risks associated with VOCs were evaluated before and after the treatment. Table S3 shows the threshold limit value time-weighted average of selected VOCs. Figs. 6 and S6 show that the  $E_i$  values of individual VOCs or TVOC at the inlet were all below 1. This suggests that VOCs at this concentration level pose little cancer threat to the workers during the WPCBs dismantling process. However, bromomethane and benzene showed the top two highest  $E_i$  values across sampling events, causing potential concern about cancer risks, particularly for benzene (considered as a definite human carcinogen).

The  $E_i$  values associated with TVOC at the inlet on the 1st, 2nd and 5th sampling events all exceeded 0.1, suggesting possible adverse effects for workers at these VOC concentrations. After ST treatment, the  $E_i$  values associated with some individual VOCs and TVOCs decreased slightly, whereas the  $E_i$  values associated with other VOCs increased. These decreases and increases were consistent with the individual substance concentrations.

For example,  $E_i$  values of bromomethane and TVOC decreased from 0.11 to 0.06 and 0.13 to 0.08, respectively, during the 1st sampling event (Fig. 6). In contrast, they increased from 0.07 to 0.29 and 0.09 to 0.35, respectively, during the 3rd sampling event (Fig. S6). Overall, however, after EP-PC treatment, the  $E_i$  values associated with the TVOC for most sampling events (except the 5th) were below 0.1. This suggests that the combination treatment effectively reduced occupational cancer risk, with the PC technology being particularly useful. These results should, however, be viewed with some caution, as the highest VOC constituent generated by the WPBCs dismantling process, 1,2-dichloropropane, lacks a definite TWA. This may lead to an underestimate of the  $\sum E_i$  value.

#### 3.4.2. The attenuation of non-cancer and cancer risks

Based on the available reference concentrations and unit risk values (Table S3), thirteen and four quantified VOCs were selected as the basis for assessing non-cancer and cancer risks, respectively (Fig. 7, S7 and 8). For non-cancer risk, the HRs of some VOCs (e.g., from 0.02 to 0.04 for styrene) were less than 0.1 across all sampling events, indicating negligible non-cancer risk concern associated with these VOCs. However, m/p-xylene (0.32, 0.31, 0.62, 0.26 and 0.26 at sampling events 1–5) and benzene (1.05, 2.01, 0.86, 0.35 and 1.21 at sampling events 1–5) presented much higher HR values (>0.1) across all sampling periods, revealing potential concerns associated with these constituents based on the assessment standard [34]. The HRs of 1,2-dichloropropane (from 9.3 to 1148.6) and bromomethane (from 36.6 to 124.5) significantly exceeded 1, indicating that they may pose non-cancer threats to the people based on the assessment standard [35].

This study also evaluated the LCRs associated with the VOCs from the WPCBs dismantling processes [47]. Fig. 8 presents the individual and total LCRs of four quantified VOCs. The LCRs of three out of the four selected VOCs (all except methylene chloride) at the

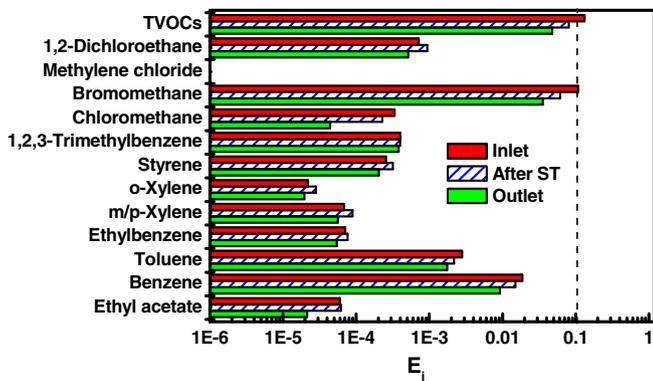


Fig. 6. Occupational exposure indexes associated with VOCs before and after the integrated technique at the first sampling event.

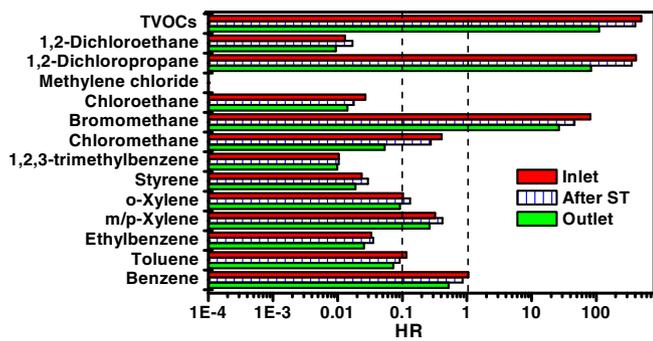


Fig. 7. Non-cancer risks associated with VOCs before and after the integrated technique at the first sampling event.

inlet exceeded  $10^{-5}$ , indicating probable cancer risk. For the 1st, 2nd, 3rd and 5th sampling events, benzene and 1,2-dichloroethane were associated with a definite risk, given that their LCRs were by far higher than  $10^{-4}$  ( $2.0 \times 10^{-4}$ – $4.7 \times 10^{-4}$  for benzene and  $8.1 \times 10^{-4}$ – $2.3 \times 10^{-3}$  for 1,2-dichloroethane).

Due to the ubiquitous presence of VOCs in the atmosphere, the total LCRs is a more suitable tool than individual LCR to illustrate the real effect of VOCs on human health. There were high LCRs associated with TVOC throughout the sampling period, ranging from  $1.6 \times 10^{-4}$  to  $2.6 \times 10^{-3}$  from the 1st to 5th sampling events, respectively. The average LCR value was  $1.3 \times 10^{-3}$ , an order of magnitude higher than the definite risk ( $10^{-4}$ ). All these results

indicate that the non-cancer and cancer risks associated with the VOCs produced in this workshop deserve attention.

After the ST treatment, there was no obvious decrease in the HRs and LCRs for most VOCs across the entire sampling period. This is consistent with the degradation results. Compared with ST alone, the combined EP-PC technique reduced risks better, especially for the HRs and non-cancer risk from the 1st, 3rd, 4th and 5th sampling events associated with chloromethane and 1,2-dichloropropane (chloromethane: HRs dropped from 0.28, 0.36, 0.85 and 1.31 to 0.05, 0.01, 0.28 and 0.14; 1,2-dichloropropane: HRs dropped from 352.2, 110.8, 1052.4 and 1247.7 to 83.5, 9.3, 243.2 and 56.1). For the LCRs, the cancer risk associated with 1,2-dichloroethane dropped from  $1.1 \times 10^{-3}$  and  $3.1 \times 10^{-4}$  to  $5.9 \times 10^{-4}$  and  $2.8 \times 10^{-5}$  on the 1st and 4th sampling events, respectively. Despite these decrease, risks remained from most VOCs based on the high concentrations, particularly with respect to the non-cancer risk associated with 1,2-dichloropropane and the cancer risk associated with benzene. Therefore, more effective waste gas collection systems and personal protective devices are needed to further reduce exposure levels.

#### 4. Conclusions

A pilot-scale integrated ST-EP-PC reactor was used to study the degradation and risks associated with VOCs in a real WPCBs dismantling workshop. HHCs were found as the dominant group of pollutants, followed by AHs and ethyl acetate. The substances 1,2-dichloropropane, toluene, and ethyl acetate were present at the highest concentrations in each of these three groups.

The ST component of the treatment system was able to significantly reduce water-soluble VOCs and large sized particles; EP was able to effectively reduce ultra-fine particles; and PC was most effective in degrading other VOCs. The integrated ST-EP-PC technique had the highest overall VOC removal efficiency, removing of 69.5% of contaminants studied during the 60-day treatment period. The PC technology was most beneficial in removing HHCs (62.7% in average), followed by ethyl acetate (36.4% in average) and AHs (27.3% in average). This was expected given the alignment of the substances' physical properties with the treatment method.

Additionally, occupationally-associated cancer risks, as well as non-cancer and cancer risks from the emitted VOCs, were greatly reduced using the ST-EP-PC integrated technique. Successfully applying the integrated ST-EP-PC system to degrade different VOCs on a pilot-scale provides an important data to support larger-scale air purification and improve human health in e-waste recycling workshops.

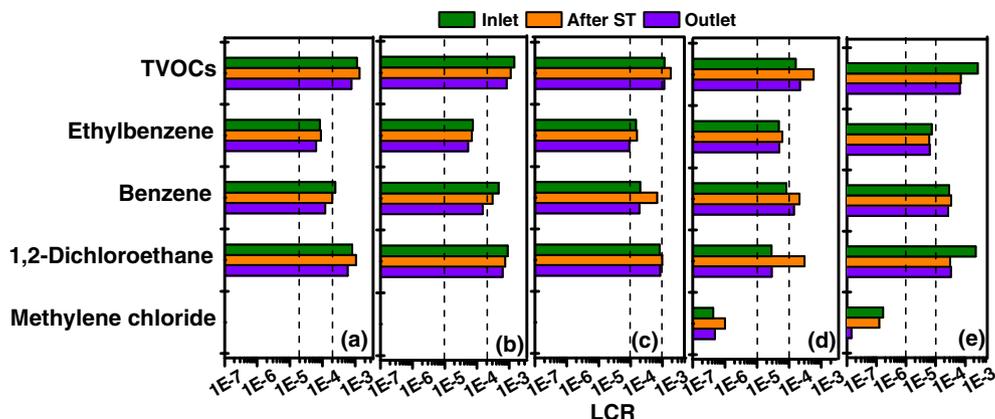


Fig. 8. Cancer risks associated with VOCs before and after the integrated technique at the first sampling event.

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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.cej.2016.05.004>.

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