VOCs elimination and health risk reduction in e-waste dismantling workshop using integrated techniques of electrostatic precipitation with advanced oxidation technologies

Jiangyao Chen[a], Yong Huang[a,b], Guiying Li[a], Taicheng An[a,*], Yunkun Hu[c], Yunlu Li[c]

[a] State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
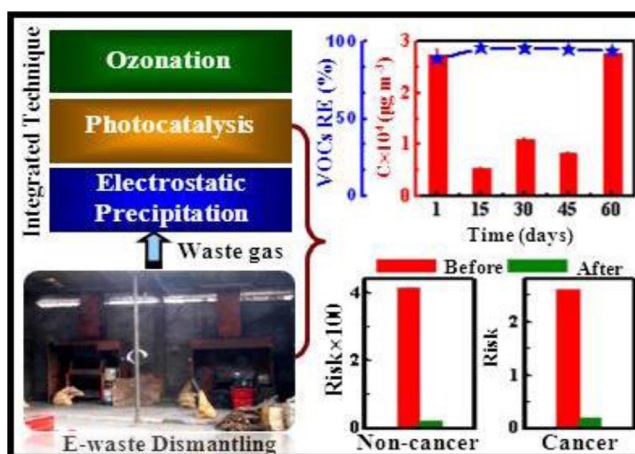[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Guangzhou Longest Environmental Science and Technology Co., Ltd., Guangzhou 510660, China

HIGHLIGHTS

- Pilot-scale investigation of VOCs removal during e-waste dismantling process.
- EP-PC-ozonation integrated reactor show high and stable removal ability to VOCs.
- Health risks of target VOCs decrease significantly after the treatment.

GRAPHICAL ABSTRACT

ABSTRACT

Volatile organic compounds (VOCs) emitted during the electronic waste dismantling process (EWDP) were treated at a pilot scale, using integrated electrostatic precipitation (EP)-advanced oxidation technologies (AOTs, subsequent photocatalysis (PC) and ozonation). Although no obvious alteration was seen in VOC concentration and composition, EP technology removed 47.2% of total suspended particles, greatly reducing the negative effect of particles on subsequent AOTs. After the AOT treatment, average removal efficiencies of 95.7%, 95.4%, 87.4%, and 97.5% were achieved for aromatic hydrocarbons, aliphatic hydrocarbons, halogenated hydrocarbons, as well as nitrogen- and oxygen-containing compounds, respectively, over 60-day treatment period. Furthermore, high elimination capacities were also seen using hybrid technique of PC with ozonation; this was due to the PC unit's high loading rates and excellent pre-treatment abilities, and the ozonation unit's high elimination capacity. In addition, the non-cancer and cancer risks, as well as the occupational exposure cancer risk, for workers exposed to emitted VOCs in workshop were reduced dramatically after the integrated technique treatment. Results demonstrated that the integrated technique led to highly efficient and stable VOC removal from EWDP emissions at a pilot scale. This study points to an efficient approach for atmospheric purification and improving human health in e-waste recycling regions.

© 2015 Elsevier B.V. All rights reserved.

Introduction

Electronic waste (e-waste) includes electrical and electronic products that are no longer used and have been discarded. Approximately 20–50 million tons of e-waste are generated each year worldwide, with an annual increase estimated at 4% [1,2]. Given high profit potential, millions of tons of e-waste are dismantled and recycled every year [3]; many volatile organic compounds (VOCs) are discharged into atmosphere as a result of these disposal processes [4,5]. It has been well documented that VOC inhalation and long-term exposure, both in work and residential environments, lead to chronic health effects such as non-cancer and cancer risks [6,7]. To address these concerns, new techniques are needed to efficiently reduce the concentration and risk of atmospheric VOCs near e-waste facilities.

Recently, advanced oxidation technologies (AOTs), including Fenton oxidation, photocatalytic oxidation, electrochemical oxidation, etc. have emerged as promising VOC abatement technologies [8–10]. Among these AOTs, photocatalysis (PC) has attracted considerable attention for degrading organics, given its generation of powerful and non-selective oxidant active species [11,12]. Furthermore, numbers of VOCs with small and large molecular weights can be successfully photocatalytically degraded under various conditions, indicating PC technology's excellent and non-selective ability to remove VOCs [13–15]. However, this single treatment technology has a significant drawback, in that photocatalyst deactivation may occur, resulting in a gradual decrease of PC activity [16–18].

To overcome this problem, researchers have successfully eliminated VOCs by combining biological approaches with PC technology (post or pretreatment) to maximize synergistic effects [19–21]. Nevertheless, a relatively long acclimation period is needed to use microorganisms in biological system [21,22]. As such, to achieve higher VOCs removal efficiencies and reduce health risks, alternative technologies with faster start-up times and high VOC removal capabilities should be further developed.

Ozonation is another promising AOT for effectively removing organic contaminants, because ozone is such a powerful oxidizing agent ($E^\theta = 2.07$ V) [23]; VOCs can be completely removed after ozonation in gas and water [24,25]. Thus, integrating PC with ozonation processes may increase VOC removal potential. First, both technologies have simple and quick responses. Second, both can produce strong oxidant species (such as h^+ and active oxygen species for PC, and ozone molecules and •OH for ozonation) to unselectively and efficiently decompose VOCs, and mineralize them into CO_2 and H_2O. Third, PC unit can significantly and stably degrade VOCs, due to its excellent regeneration ability after the utilization of vacuum ultraviolet lamps [26]. Meanwhile, ozone generated from PC unit can be directly used as an effective oxidation species in ozonation unit. Notably, the existence of adsorbent can further enrich the ozone and organics to extend the reaction time between them, which will promote the efficiency of ozonation to remove VOCs and minimize ozone pollution [27].

However, no publication to date has addressed VOC removal from e-waste dismantling processes using integrated PC and ozonation technologies. Such research would require exploring ways to eliminate waste gas particulate matter to avoid covering photocatalyst surface, as this particulate matter would decrease PC activity [20]. That is, particles must be removed from waste gas before VOC elimination using the integrated PC and ozonation technologies. Recently, electrostatic precipitation has been proved as an effective technology for the reduction of airborne dust [28].

As such, an integrated electrostatic precipitation-PC-ozonation (EP-PC-ozonation) pilot scale reactor was developed to eliminate VOCs emitted from the e-waste dismantling process inside a workshop at a pilot scale. To evaluate reactor performance, VOC removal efficiency (RE) and elimination capacity (EC) were compared between the single unit and the integrated reactor. Further, health risks to workers exposed to VOCs at the e-waste dismantling workshop (EWDW) was also evaluated before and after the integrated EP-PC-ozonation reactor treatment during the 60-day operation period.

2. Experimental

2.1. Experimental setup

The pilot-scale experiment was conducted in an EWDW from April to June 2013. In this EWDW, various printed circuit board assemblies (PCBAs) were continuously dismantled in rotary incinerators (detail description was supplied in Supporting information and Fig. S1), where VOC pollution is the heaviest compared to other dismantling techniques [4]. Pilot-scale experiments were performed in a mid-scale custom-made integrated reactor (rated power: 1.5 kW, size: 3300 mm × 1200 mm × 1200 mm, Guangzhou Longest Environmental Science & Technology Co., Ltd.) (Fig. S2), averagely divided into three adjacent units: EP, PC, and ozonation. The EP unit included three electrostatic dust collectors (720 mm × 360 mm × 850 mm), arranged side by side. Each collector was consisted of 4 × 11 electrostatic fields and the discharge voltage for each electrostatic field was in the range of 6000–14,000 kV with the discharge current of ca. 0.8 A. The size of each electrostatic field was 50 mm in diameter and 265 mm in length. The PC unit consisted of three pieces of foam nickel coated with TiO_2 (detailed coating procedure is provided in Supporting information and our previous works [20,21,29]) and eight 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., which could produce ozone [30]), fixed on each side of foam nickel in parallel. The distance between the foam nickel and lamp was ca. 50 mm with a light intensity of 2.5 mW cm^{-2}. An ozone generator (350 mm × 320 mm × 600 mm, ozone generation capacity: 15 g h^{-1}) and a honeycomb activated carbon bed (1100 mm × 250 mm × 800 mm, surface area: 800 m^2 g^{-1}, volume density: 0.40–0.48 g mL^{-1}, Guangzhou Hanyan Activated Carbon Manufacturing Co., Ltd.) were laid in the ozonation unit one behind the other, with a distance of ca. 300 mm. The waste gas emitted from rotary incinerators was collected using an exhaust fan mounted at the ozonation unit's outlet, and routed through a hood linked to the EP unit inlet. The flow rate was 1000 m^3 h^{-1}.

2.2. Sample collection and analysis

Samples were collected at continuously five time points, day 1, 15, 30, 45, and 60, to accurately evaluate the pollutant levels and stability of the integrated technique to remove waste gas emitted from dismantling different PCBAs. Total suspended particles (TSP) were collected before and after treatment using an intelligent high volume air sampler (TH-1000CH, Wuhan Tianhong Instrument Factory Co., Ltd., China) at the EP unit's inlet and outlet; there was a total air volume of approximate 140 m^3 over 8 h. TSP were blocked by glass fiber filters. After sampling, the loaded filters were wrapped in pre-baked aluminum foil and stored at −20 °C. TSP mass was determined by weighing equilibrated filters before and after sampling.

* Corresponding author. Fax: +86 20 85290706.
E-mail address: antc99@gig.ac.cn (T. An).

VOC samples were collected at EP unit's inlet and outlet, as well as PC and ozonation unit outlets, using 2.7-L stainless steel canisters (ENTECH Instruments Inc., SiloniteTM). Canisters were pre-cleaned five times using high-purity nitrogen and were pre-evacuated using a canister cleaner before sampling. Collected samples were qualitatively and quantitatively analyzed using a Entech 7100 preconcentrator (Entech Instruments Inc., CA, USA) and gas chromatography–mass spectrometer (7890A GC-5975C MS, Agilent technologies, USA), along with combined techniques using the U.S. Environmental Protection Agency [31] TO-15 method [20]. A HP-5MS capillary column (60 m × 0.32 mm × 0.25 μm, Agilent Technology, USA) was used with helium as carrier gas at a rate of 1.2 mL min^{-1}. The injector and detector temperatures were 200 and 230 °C, respectively. GC oven temperature was initially programmed at a temperature of 40 °C for 5 min, then increased to 150 °C at a rate of 5 °C min^{-1}, and then increased to 250 °C at a rate of 15 °C min^{-1} and holding for 2 min. The MS detector was run in full scan mode with m/z = 45–260; the injection volume was 150 mL. VOC concentrations were quantified using external standard calibration, determined using a standard sample (TO-15, Linde Spectra Environment gases, USA). Each target species was identified by its retention time and mass spectra using the NIST05 database.

2.3. Quality assurance and quality control

Triplicate VOC samples were collected at each sampling time point; all samples were analyzed within 24 h after collection. Experimental instruments were calibrated prior to measurements; blank sample (ultra-nitrogen) analyses indicated that no target analytes were present in the system. Quality assurance and quality control measures included method detection limits, field blanks, retention time, accuracy, precision duplications, and reference sample analyses; all were performed using USEPA Compendium Method TO-15 [31].

2.4. Calculations of RE, loading rate (LR), EC, and VOC risk assessment

Reactor performance was evaluated in terms of RE (%), LR (g m^{-3} h^{-1}) and EC (g m^{-3} h^{-1}). Cancer and non-cancer VOC exposure risks were assessed using USEPA standard methods, and focused on the risks caused by worker inhalation of VOCs in the EWDW before and after treatment. Detail calculations were provided in Supporting information.

3. Results and discussion

3.1. Alteration of VOCs pollution profiles treated by EP technology

During this study, a total of 43 VOCs are detected during PCBA dismantling using rotary incinerators. These VOCs are categorized into four groups, listed in Table S1: aromatic hydrocarbons (AHs), aliphatic hydrocarbons (AlHs), halogenated hydrocarbons (HHs), and nitrogen- and oxygen-containing compounds (NAOCCs). First, the EP unit's removal of these four groups of VOCs is explored (Fig. 1). Before EP treatment, at all five sampling times, AHs have the highest concentrations (ranging from $1.7 \times 10^3 \pm 57$ to $2.5 \times 10^4 \pm 8.4 \times 10^2$ μg m^{-3}), followed by NAOCCs (ranging from $1.3 \pm 0.13 \times 10^3$ to $3.4 \pm 0.13 \times 10^3$ μg m^{-3}) and HHs (ranging from $1.2 \pm 0.32 \times 10^2$ to $2.3 \pm 0.86 \times 10^3$ μg m^{-3}), with AlHs at the lowest concentrations (ranging from 55 ± 4.8 to $8.4 \pm 0.20 \times 10^2$ μg m^{-3}).

The significantly different VOC concentrations are due to the nature of e-waste. As well known, PCBAs are manufactured mainly with epoxy or phenol resin containing a fire retardant, such as tetrabromobisphenol-A (TBBPA) [32]. At a high combustion temperature (>400 °C in the rotary incinerator), the single bond between carbon atom and benzene ring in TBBPA may be broken or substituted by other radicals during the heating, releasing a large amount of AHs [33]. Although AlHs are also released [34], they are more apt to be oxidized (and possibly transformed into NAOCCs), leading to higher concentrations of AHs and NAOCCs than AlHs. When these VOCs flow through the EP unit, there are no obvious decreases in concentrations and components. This suggests that EP technology has poor VOC removal efficiency. However, EP can efficiently remove waste gas particles [35], protecting the subsequent PC unit's photocatalyst from exposure to these particles, leading to high and stable VOC elimination capability.

As Fig. S3 shows, the inlet TSP concentration is very high (ranging from 3.8×10^3 to 1.3×10^4 μg m^{-3}), far higher than the second grade value of China's current ambient air quality standards (300 μg m^{-3}, GB3095-2012). However, a great decrease in TSP concentration is seen after EP treatment; the average RE reaches 47.2% during the 60-day period. Meanwhile, pollutants such as heavy metals [36] and semi-volatile organic compounds [29] adsorbed onto the TSP may also be efficiently and simultaneously removed. In addition, VOC compositions are also compared before and after EP unit treatment (Figs. S3–S6). While slight changes in single VOC percentages are observed, VOC group components remain the same. For example, with AHs (Fig. S4), styrene accounts for 51.8% and 45.6% on days 1 and 60, while benzene accounts for 52.8%, 31.5% and 36.2% on days 15, 30 and 45 before EP unit treatment. And negligible changes are observed after EP unit treatment that styrene accounts for 50.8% and 42.6% on days 1 and 60, while benzene accounts for 62.4%, 32.9% and 36.1% on days 15, 30 and 45. Similar results are seen with the other three VOC groups (Figs. S5–S7).

3.2. VOC decomposition using advanced oxidation technologies

As noted previously and illustrated in Fig. S8, the EP unit on its own cannot efficiently remove VOCs emitted from e-waste dismantling process. However, rapid decreases in VOC peaks on the total ion chromatograms are seen after PC and ozonation treatment, indicating efficient VOC removal using these advanced oxidation technologies. Figs. 2, S9–S11 provide detailed results for VOC REs using PC and ozonation unit. Fig. 2 shows that PC-ozonation combination techniques display very high REs across the four VOC groups, with average REs of 95.7%, 95.4%, 87.4%, and 97.5% for AHs, AlHs, HHs, and NAOCCs (without benzaldehyde, to be discussed later), respectively.

Further observation reveals that the PC unit has a different function and contribution to the total REs. Only 33.0% of HHs on average is removed by the PC unit (Fig. 2c); this increases to 45.2% for AHs (Fig. 2a) and 57.6% for NAOCCs (Fig. 2d). The PC unit exhibits the highest RE toward AlHs (with the average RE of 74.0%) (Fig. 2b), which is possibly due to their lowest concentration among the four VOC groups (Fig. 1).

Before the organics are photocatalytically degraded, they must be first adsorbed onto photocatalyst surface sites; the efficient adsorption of substances onto photocatalyst is an important step in determining degradation at very low concentrations [15,37]. For typical compounds in each VOC group, PC unit shows the highest RE toward α-pinene in AlHs (average RE: 99.7%), followed by styrene in AHs (average RE: 80.7%), and methyl methacrylate in NAOCCs (average RE: 66.8%) (Figs. S9 and S10). However, even if PC unit has a limited ability to remove other organics, such as toluene (average RE: 31.2%), chlorobenzene (average RE: 37.5%) and acrylonitrile (average RE: 40.1%), then ozonation unit may make up for these disadvantages in PC treatment. The average total REs of these three VOCs increase to ≥92.1% when PC and ozonation technologies are combined (Figs. S9 and S10). Since PCBAs are manufactured mainly with epoxy or phenol resin containing bromine flame retardant, the removal of the emitted bromine VOCs is also investigated.
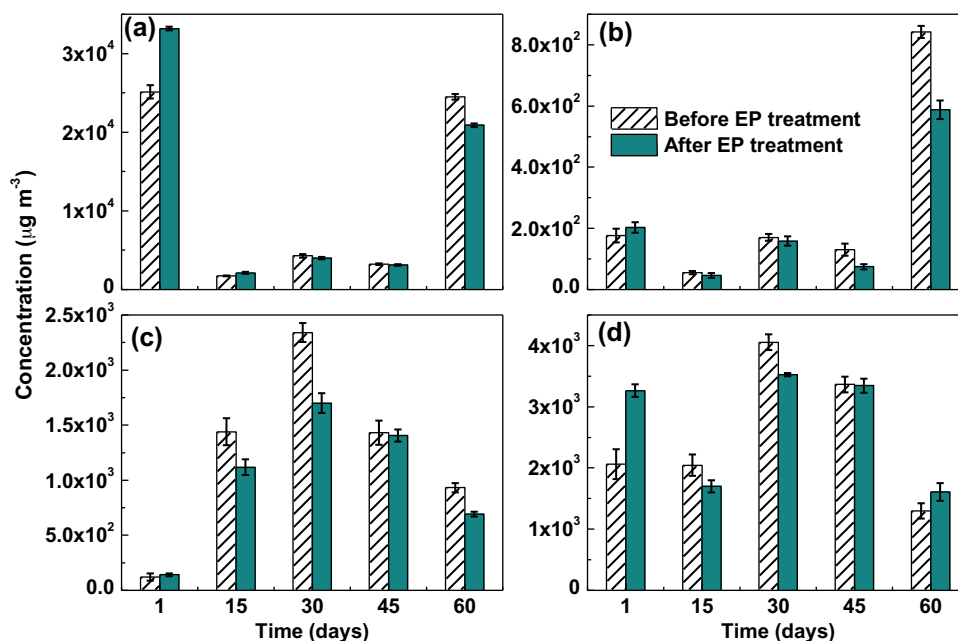
Fig. 1. Concentrations of VOCs before and after EP treatment. (a) AHs; (b) AlHs; (c) HHs; (d) NAOCCs.
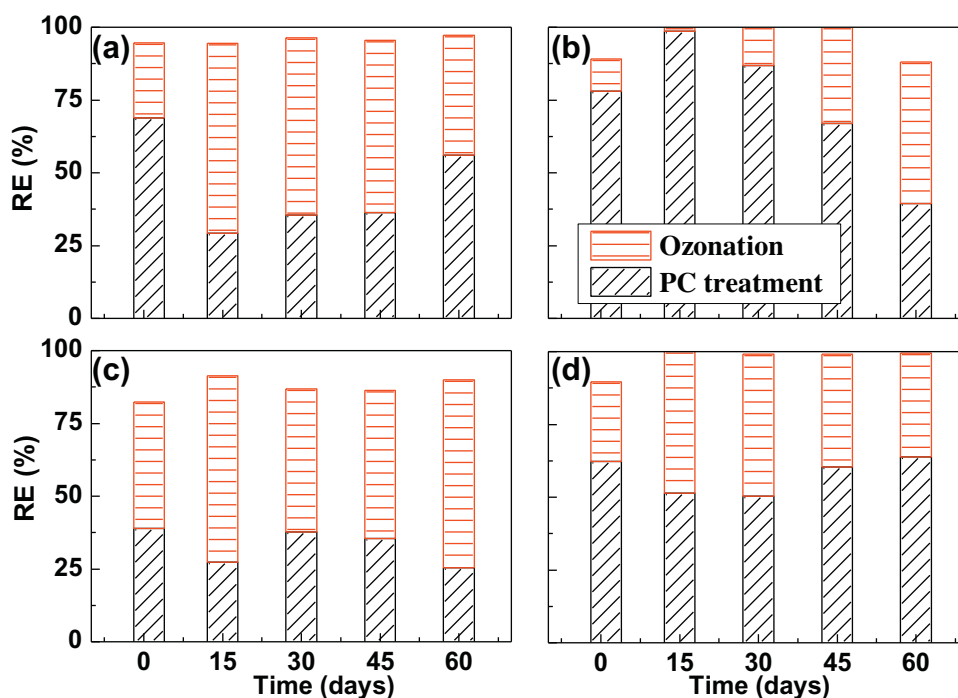

Fig. 2. Removal efficiencies of VOCs using integrated PC-ozonation techniques. (a) AHs; (b) AlHs; (c) HHs; (d) NAOCCs.

As shown in Fig. S11, the bromomethane is detected on day 15 to 60, while 21.1% and 69.6% of which in average are removed by the PC and ozonation units, respectively, leading to the total average RE of ca. 90.7% by the integrated PC-ozonation techniques. This results reveals that during the studied e-waste dismantling process, limited bromine VOCs are generated and also can be efficiently removed by the integrated AOTs technique.

The PC technology shows the lowest RE with benzene (average RE: 18.5%), which may be because benzene is a produced intermediate from other large molecular weight AHs [38,39]. However, after subsequent ozonation treatment, an average 93.8% of benzene is removed (Fig. S9). An increase of benzaldehyde concentration is

also observed at the PC unit's outlet (Fig. S12), which may be due to extra benzaldehyde being generated as an intermediate from large molecular weight AHs during PC treatment [14,40]. A similar result was reported by Kim et al. concerning PC treatment of toluene in the laboratory [41]. However, after subsequent ozonation treatment, benzaldehyde concentration rapidly decreases, with lower outlet concentrations than inlet concentrations after PC-ozonation combination treatment. This result again highlights high removal efficiency of the integrated PC-ozonation AOTs for all investigated VOCs (Fig. S12). The possible mechanism for the high and stable removal ability of the integrated AOTs may be as follows: photocatalysis originated from the oxygen reactive species has
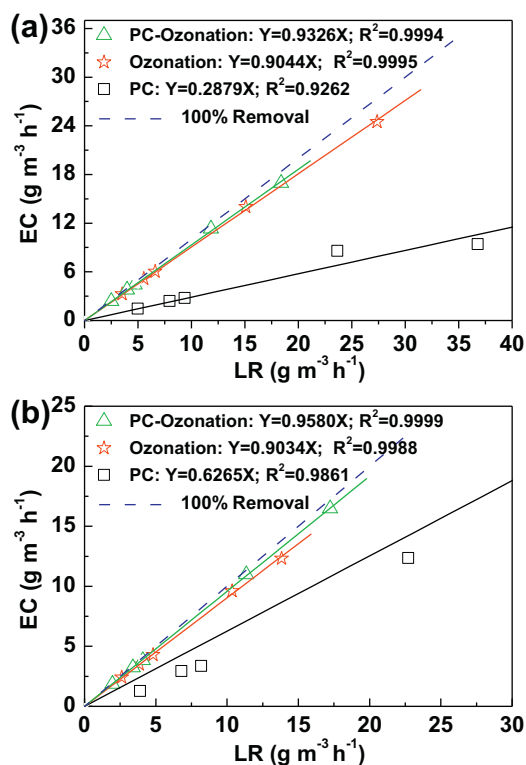
Fig. 3. Comparing elimination capacities of PC, ozonation and PC-ozonation against different VOC loading rates. (a) With benzaldehyde; (b) without benzaldehyde.

been already confirmed for the effectively degradation of gaseous organic pollutants [10,42]. Meanwhile, due to the utilization of ozone-producing lamps, another strong oxidant specie—ozone can also be generated during photocatalytic process, and the synergetic effect of photocatalysis and ozonation can lead to the higher efficient removal of a certain amount of VOCs [43]. Notably, the high photoactivity of the photocatalyst can be preserved, due to its excellent regeneration ability after the utilization of vacuum ultraviolet lamps [26]. The residual VOCs are then brought into the ozonation unit and easily be adsorbed by the activated carbon bed, which can also efficiently trap the residual ozone from PC unit as well as newly generated ozone from ozone generator ahead. Subsequently, the ozonation catalytic degradation of low concentration residual VOCs happens in situ on the activated carbon bed, leading to the almost complete removal of VOCs and the prevention of emission of formed ozone to the atmospheric environment.

Besides RE, the comparative performance of advanced oxidation units are evaluated using elimination capacity (EC, the amount of VOCs degraded per unit of the reactor volume and time for different loading rates (LR)) [44]. Fig. 3a shows the relationships between LRs and ECs during PC-ozonation combination treatment toward all VOCs. The slopes of the dashed and solid lines represent theoretical 100% REs and total average VOCs REs, respectively. The EC increases linearly with LR increase ($R^2 \geq 0.9262$), indicating that the inlet LR increase does not appear to inhibit VOCs removal in either the single or integrated unit; the maximum EC (EC_{max}) mainly depends on inlet LR.

For PC and ozonation unit, ECs_{max} are 9.4 and 24.5 g m^{-3} h^{-1} at the maximum LRs of 36.8 and 27.4 g m^{-3} h^{-1}, respectively. The EC_{max} of the integrated PC-ozonation reactor is not high (16.9 g m^{-3} h^{-1}), mainly due to larger reactor volume (twice as large as the volume of PC or ozonation unit). The EC_{max} is greatest with the ozonation alone, followed by the PC-ozonation treatment and the PC treatment alone. Although this result cannot be defined

as the actual EC_{max} because higher LRs were not tested in this study, it can be concluded that ozonation contributes more than PC in the integrated AOTs under the studied conditions.

Furthermore, the fitted curve slopes show that the average VOC REs of 28.8%, 90.4% and 93.3% are achieved by the PC unit, ozonation unit, and PC-ozonation combined unit, respectively, with the PC-ozonation combination exceeding ozonation alone, which exceeds PC alone. The average VOC RE using the PC unit is far smaller than with the ozonation unit, possibly due to much higher LRs of the PC technology and the production of the highly concentrated intermediate, benzaldehyde.

Given this result, the relationships between LRs and ECs of the PC-ozonation combination technique toward other VOCs, except benzaldehyde, are examined (Fig. 3b). Compared with the results in Fig. 3a, the maximum LR decreases slightly (from 36.8 to 34.5 g m^{-3} h^{-1}) for the PC unit and decreases greatly for the ozonation unit (from 27.4 to 10.8 g m^{-3} h^{-1}), leading to an opposite EC_{max} (increasing from 9.4 to 23.6 g m^{-3} h^{-1} for the PC unit and decreasing from 24.5 to 9.3 g m^{-3} h^{-1} for ozonation unit), with the PC unit being greater than the PC-ozonation unit, which is greater than the ozonation unit alone. Moreover, the average VOC REs increase to 62.7% and 95.8% for the PC and PC-ozonation units, respectively, while slightly decreasing (90.3%) for the ozonation unit. The PC-ozonation unit remains greater than the ozonation unit, which is greater than with the PC unit alone. These results show that in a hybrid PC-ozonation system, with high LR excellent PC unit pre-treatment, and high EC in the ozonation unit, the PC-ozonation combination technique effectively eliminates the VOCs in this pilot-scale study.

3.3. Non-cancer and cancer risks assessment of VOCs before and after treatment

Because of the ubiquitous presence of VOCs in the EWDW atmosphere, the potential chronic health effects (non-cancer and cancer risks) caused by VOC exposure through inhalation are assessed using USEPA risk assessment methods [4]. In this study, for all detected and quantified VOCs, 19 VOCs (in following description, *m,p*-xylene and *o*-xylene call xylene, and 1,3,5-, 1,2,4-, 1,2,3-trimethylbenzene call trimethylbenzene (the HR of each individual trimethylbenzene or xylene is calculated and then added), so total of 16 VOCs are calculated) were selected to assess non-cancer risks and 6 VOCs are selected to assess cancer risks, respectively. Selections were based on available reference concentrations and unit risk values, as shown in Table S2.

The non-cancer risk of detected VOCs in the EWDW is assessed first before treatment. As Fig. 4 shows, the HRs of n-propylbenzene on day 1; toluene and ethylbenzene on day 15; methyl isobutyl ketone on days 30 and 45; *i*-propylbenzene and chlorobenzene on days 1, 15, 30, and 45; and 1,2-dichloroethane on day 60 are all less than 0.1, below the level of concern [7]. However, the HRs are higher than 0.1 for other VOCs, indicating concentrations above the level of potential concern [45]. For example, HRs are in the range of 0.1–1 (exceeding the level of potential concern) for chloromethane on day 45 (0.88); chlorobenzene on day 60 (0.13); styrene on day 15 (0.29) and 45 (0.72); ethylbenzene on day 30 (0.26) and 45 (0.19); chloroform on day 30 (0.36) and 45 (0.37); toluene on day 1 (0.34), 30 (0.22), 45 (0.18) and 60 (0.68).

HRs exceed 1 (the level of concern) for ethylbenzene on day 1 (1.94); chloromethane on day 30 (1.10); methyl methacrylate on days 15 (26.35), 30 (2.91), 45 (2.66), and 60 (1.03); and xylene and styrene on days 1 (29.89 and 13.01), 30 (3.84 and 1.19) and 60 (36.93 and 11.16). Selected VOCs show high HRs well above the level of concern, such as bromomethane (from 96.04 to 383.07), acrylonitrile (from 26.35 to 171.40), benzene (from 30.70 to 168.37), and treimethylbenzene (from 2.62 to 86.80) [45].
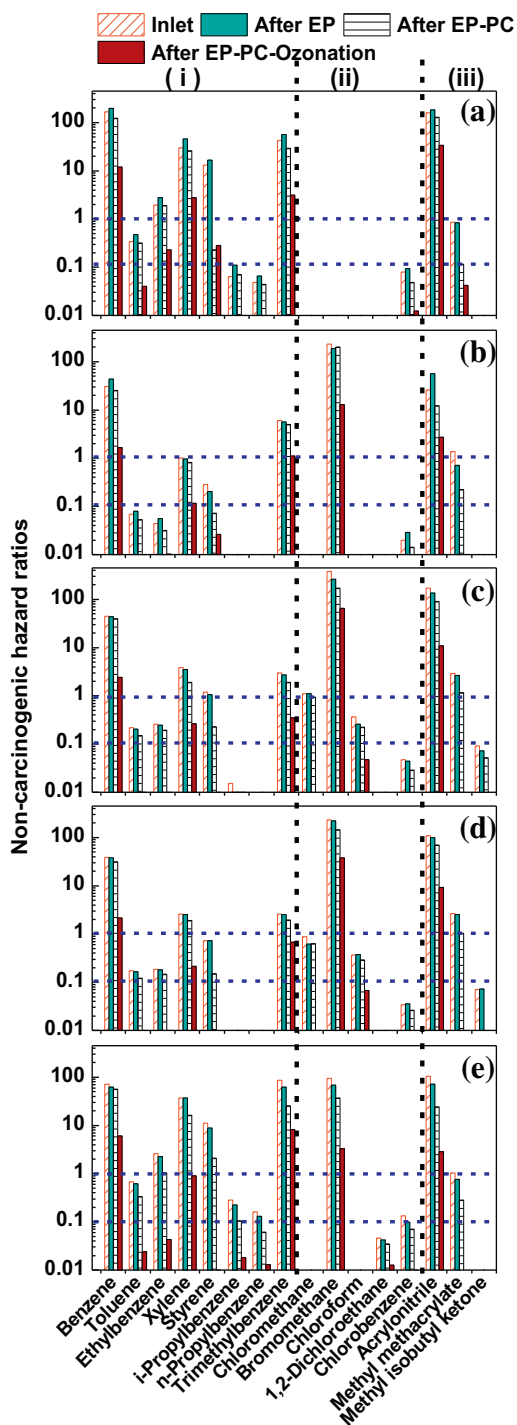
Fig. 4. Non-cancer risk from VOCs before and after treatment at day 1 (a), 15 (b), 30 (c), 45 (d) and 60 (e); (i) AHs; (ii) HHs; (iii) NAOCCs.
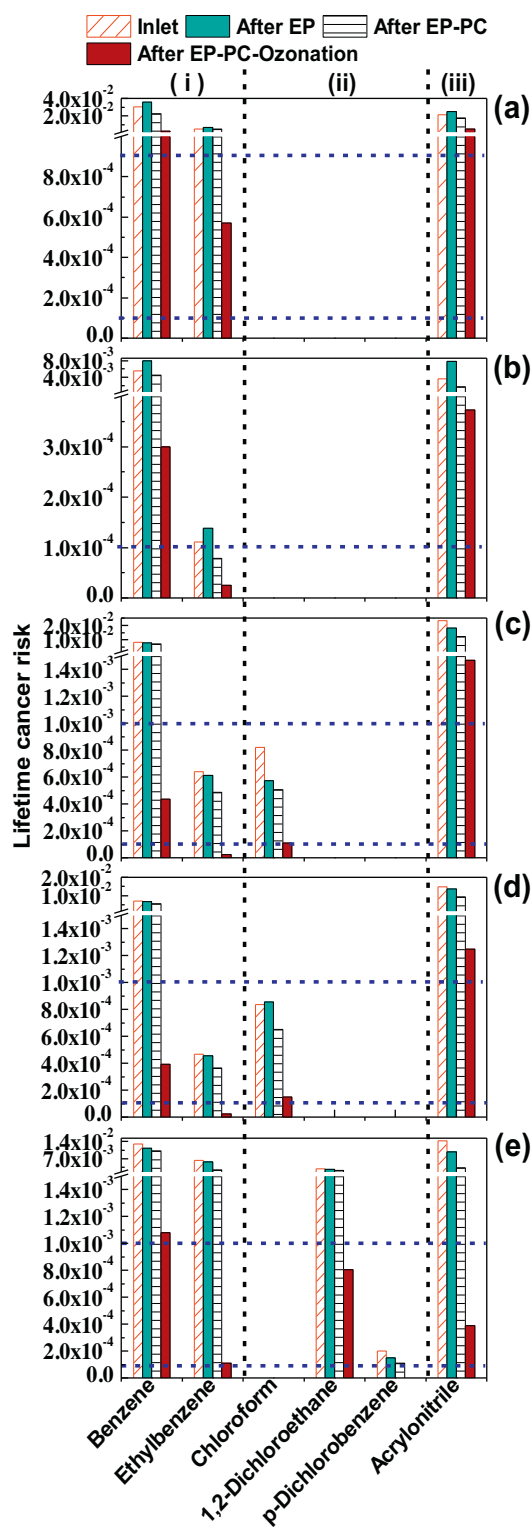

Fig. 5. Lifetime cancer risk from VOCs before and after treatment at day 1 (a), 15 (b), 30 (c), 45 (d) and 60 (e); (i) AHs; (ii) HHs; (iii) NAOCCs.

Fig. 5 also shows the individual LCRs for six quantified VOCs. Based on reference [46], compounds with an attributable cancer risk of $>10^{-4}$ are labeled as "definite risk;" compounds with a risk between 10^{-5} and 10^{-4} are labeled as "probable risk;" and compounds with a risk between 10^{-5} and 10^{-6} are labeled as "possible risk." In this study, the cancer risk from VOCs in the selected EWDW is very high; acrylonitrile ($>3.58 \times 10^{-3}$), benzene ($>5.53 \times 10^{-3}$), ethylbenzene ($>1.11 \times 10^{-4}$), 1,2-dichloroethane (2.95×10^{-3}), chloroform ($>8.21 \times 10^{-4}$) and *p*-dichlorobenzene (2.02×10^{-4}) are all regarded as posing definite risk, consistent with our previous research [4].

These results show that non-cancer and cancer risks attributable to VOC exposure are not negligible and must be taken seriously when considering treatment approaches. As such, it is also necessary to consider the non-cancer and cancer risk from these VOCs after treatment using the integrated techniques. Figs. 4 and 5 show that after EP unit treatment, there are no obvious decreases in non-cancer and cancer risks across sampling periods, suggesting that

the EP technology offers poor VOCs risk reduction ability. In contrast, the hybrid AOTs show excellent risk reduction ability. After PC treatment, there is a great reduction in both non-cancer and cancer risks for all investigated VOCs, especial for styrene (from 16.84, 0.20, 1.05, 0.72, and 8.90 to 0.23, 0.07, 0.23, 0.15, and 2.08 on days 1, 15, 30, 45, and 60) and acrylonitrile (from 182.86, 57.13, 134.15, 99.97, and 72.11 to 130.69, 12.27, 91.09, 69.74, and 24.44 on days 1, 15, 30, 45, and 60) for non-cancer risk, and benzene (from 3.58×10^{-2} and 7.94×10^{-3} to 2.22×10^{-2} and 4.53×10^{-3} on days 1 and 15) and acrylonitrile (from 7.73×10^{-3} and 9.81×10^{-3} to 1.63×10^{-3} and 3.23×10^{-3} on days 15 and 60) for cancer risk. Because the VOC concentrations before PC treatment are so high, even with the significant risk reductions, the HRs and LCRs for most VOCs after PC treatment are still higher than 0.1 except for styrene (0.07 at day 15), and 10^{-4} except for ethylbenzene (7.87×10^{-5} at day 15), respectively.

After subsequent ozonation treatment, the non-cancer and cancer risks from these VOCs are further reduced, mostly to below 0.1 and 10^{-4}, respectively, indicating high VOC risk reduction capability using the integrated AOTs. Even after integrated PC-ozonation treatment, the HRs and LCRs for some VOCs still exceed 1 (benzene (11.92, 1.67, 2.41, 2.17, and 5.98 on days 1, 15, 30, 45, and 60), bromomethane (12.91, 65.79, 37.82, and 3.29 on days 15, 30, 45, and 60) and acrylonitrile (33.79, 2.74, 10.81, 9.20, and 2.86 on days 1, 15, 30, 45, and 60)), and above 10^{-4} (benzene (2.2×10^{-3}, 3.0×10^{-4}, 4.3×10^{-4}, 3.9×10^{-4}, and 1.1×10^{-3} on days 1, 15, 30, 45, and 60) and acrylonitrile (4.6×10^{-3}, 3.7×10^{-4}, 1.5×10^{-3}, 1.3×10^{-3}, and 3.9×10^{-4} on days 1, 15, 30, 45, and 60)), suggesting that VOC levels may pose both non-cancer and cancer risks to EWDW workers. Therefore, to ensure EWDW worker security, the airtightness of rotary incinerators should be further developed.

3.4. Occupational exposure cancer risk assessment of VOCs before and after treatment

Occupational exposure cancer risk is also evaluated using ACGIH and E_i values of 17 VOCs from TWA (Table S3). As Fig. 6 shows, before EP treatment, the E_i values of benzene (categorized into A1-definite human carcinogens) are calculated as 4.74, 1.27, 1.10, and 2.04 on days 1, 30, 45, and 60. All of these exceed 1, suggesting that benzene poses a cancer threat to EWDW employees [47]. The E_i values of other major pollutants such as bromomethane (0.45, 0.74, 0.45, and 0.19 on days 15, 30, 45, and 60), acrylonitrile (0.11 and 0.12 on days 1 and 30) and styrene (0.23 and 0.20 on days 1 and 60) falling into groups A3 or A4 (cannot be regarded as carcinogens), have risk levels above 0.1, pointing to possible harmful effects for EWDW employees.

Like the non-cancer and cancer risk assessment results, there is no obvious decrease in occupational exposure cancer risk after EP treatment; risk levels decrease significantly after hybrid PC-ozonation treatment. Among the selected VOCs, the PC unit shows excellent risk reduction ability against styrene; E_i values for styrene are all lower than 0.1 after PC treatment. However, the E_i values for benzene still exceed 1 after PC treatment, decreasing dramatically after subsequent ozonation treatment (<0.1 on days 15, 30, and 45). This suggests there is no obvious cancer threat posed by benzene after PC-ozonation treatment, and a strong ability for integrated AOTs to reduce risks caused by VOCs.

4. Conclusion

In summary, a pilot-scale investigation was conducted in a real e-waste dismantling workshop, using an integrated EP-PC-ozonation technique to assess VOC removal and health risk reduction. The results indicated that the EP unit could efficiently
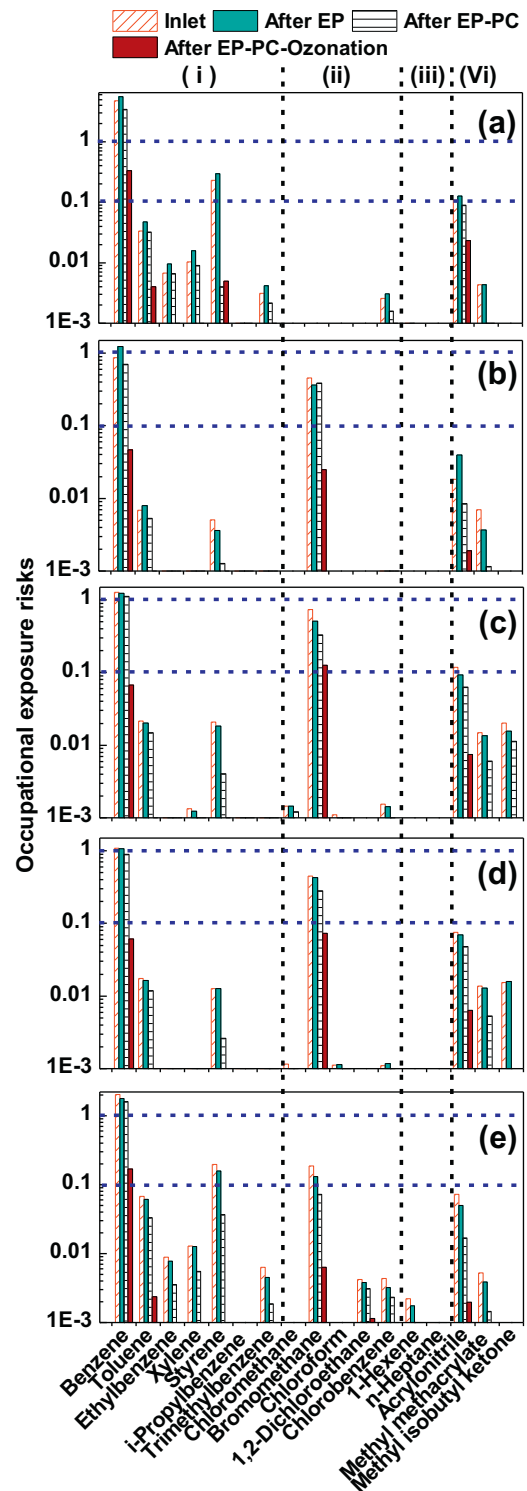

Fig. 6. Occupational exposure risk from VOCs before and after treatment at day 1 (a), 15 (b), 30 (c), 45 (d) and 60 (e); (i) AHs; (ii) HHs; (iii) AlHs; (iv) NAOCCs.

remove TSP from emitted waste gas without altering VOC concentration and composition. Of the four VOC types, AHs were the most dominant group, followed by NAOCCs and HHs, with AlHs having the least concentrations. Styrene and benzene were the major components of the dominant AHs. When VOCs flowed through the subsequent integrated PC-ozonation AOTs, average REs of 95.7%, 95.4%, 87.4%, and 97.5% were obtained for AHs, AlHs, HHs, and NAOCCs during 60-day treatment period. This demonstrates that

the integrated technique achieved stable and effective VOC removal capacity. The linear increase of ECs with increasing VOCs LRs in this pilot study also suggest that the integrated PC-ozonation techniques could remove VOCs efficiently in the EWDW over a long period. In addition, risk assessment results showed non-cancer and cancer risks, as well as the occupational exposure cancer risk, from emitted VOCs to EWDW workers were dramatically reduced after treatment using the integrated techniques.

Acknowledgments

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.jhazmat.2015.10.006.

References

[1] J.J. Fu, Y.W. Wang, L.J. Zhou, A.Q. Zhang, G.B. Jiang, Pollution status and perspectives of persistent toxic substances in e-waste dismantling area in China, Prog. Chem. 23 (2011) 1755–1768.

[2] K. Breivik, J.M. Armitage, F. Wania, K.C. Jones, Tracking the global generation and exports of e-waste. Do existing estimates add up? Environ. Sci. Technol. 48 (2014) 8735–8743.

[3] M.H. Wong, S.C. Wu, W.J. Deng, X.Z. Yu, Q. Luo, A.O.W. Leung, C.S.C. Wong, W.J. Luksemburg, A.S. Wong, Export of toxic chemicals—a review of the case of uncontrolled electronic-waste recycling, Environ. Pollut. 149 (2007) 131–140.

[4] T.C. An, Y. Huang, G.Y. Li, Z.G. He, J.Y. Chen, C.S. Zhang, Pollution profiles and health risk assessment of VOCs emitted during e-waste dismantling processes associated with different dismantling methods, Environ. Int. 73 (2014) 186–194.

[5] J. Guo, Y. Jiang, X.F. Hu, Z.M. Xu, Volatile organic compounds and metal leaching from composite products made from fiberglass-resin portion of printed circuit board waste, Environ. Sci. Technol. 46 (2012) 1028–1034.

[6] J.E.C. Lerner, E.Y. Sanchez, J.E. Sambeth, A.A. Porta, Characterization and health risk assessment of VOCs in occupational environments in Buenos Aires, Argentina, Atmos. Environ. 55 (2012) 440–447.

[7] N. Ramirez, A. Cuadras, E. Rovira, F. Borrull, R.M. Marce, Chronic risk assessment of exposure to volatile organic compounds in the atmosphere near the largest Mediterranean industrial site, Environ. Int. 39 (2012) 200–209.

[8] B.B. Huang, C. Lei, C.H. Wei, G.M. Zeng, Chlorinated volatile organic compounds (Cl-VOCs) in environment-sources, potential human health impacts, and current remediation technologies, Environ. Int. 71 (2014) 118–138.

[9] T.C. An, M.L. Zhang, X.M. Wang, G.Y. Sheng, J.M. Fu, Photocatalytic degradation of gaseous trichloroethene using immobilized ZnO/SnO$_2$ coupled oxide in a flow-through photocatalytic reactor, J. Chem. Technol. Biotechnol. 80 (2005) 251–258.

[10] J.Y. Chen, G.Y. Li, H.M. Zhang, P.R. Liu, H.J. Zhao, T.C. An, Anatase TiO$_2$ mesocrystals with exposed (0 0 1) surface for enhanced photocatalytic decomposition capability toward gaseous styrene, Catal. Today 224 (2014) 216–224.

[11] D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, Photocatalysis. A multi-faceted concept for green chemistry, Chem. Soc. Rev. 38 (2009) 1999–2011.

[12] S.B. Wang, H.M. Ang, M.O. Tade, Volatile organic compounds in indoor environment and photocatalytic oxidation: state of the art, Environ. Int. 33 (2007) 694–705.

[13] T.C. An, L. Sun, G.Y. Li, Y.P. Gao, G.G. Ying, Photocatalytic degradation and detoxification of o-chloroaniline in the gas phase: mechanistic consideration and mutagenicity assessment of its decomposed gaseous intermediate mixture, Appl. Catal. B: Environ. 102 (2011) 140–146.

[14] L. Sun, G.Y. Li, S.G. Wan, T.C. An, Mechanistic study and mutagenicity assessment of intermediates in photocatalytic degradation of gaseous toluene, Chemosphere 78 (2010) 313–318.

[15] J.Y. Chen, G.Y. Li, Z.G. He, T.C. An, Adsorption and degradation of model volatile organic compounds by a combined titania–montmorillonite–silica photocatalyst, J. Hazard. Mater. 190 (2011) 416–423.

[16] J.H. Mo, Y.P. Zhang, Q.J. Xu, J.J. Lamson, R.Y. Zhao, Photocatalytic purification of volatile organic compounds in indoor air: a literature review, Atmos. Environ. 43 (2009) 2229–2246.

[17] H. Einaga, S. Futamura, T. Ibusuki, Heterogeneous photocatalytic oxidation of benzene, toluene, cyclohexene and cyclohexane in humidified air: comparison of decomposition behavior on photoirradiated TiO$_2$ catalyst, Appl. Catal. B: Environ. 38 (2002) 215–225.

[18] T.C. An, J.Y. Chen, X. Nie, G.Y. Li, H.M. Zhang, X.L. Liu, H.J. Zhao, Synthesis of carbon nanotube-anatase TiO$_2$ sub-micrometer-sized sphere composite photocatalyst for synergistic degradation of gaseous styrene, ACS Appl. Mater. Interfaces 4 (2012) 5988–5996.

[19] M. Hinojosa-Reyes, V. Rodriguez-Gonzalez, S. Arriaga, Enhancing ethylbenzene vapors degradation in a hybrid system based on photocatalytic oxidation UV/TiO$_2$–In and a biofiltration process, J. Hazard. Mater. 209 (2012) 365–371.

[20] Z.G. He, J.J. Li, J.Y. Chen, Z.P. Chen, G.Y. Li, G.P. Sun, T.C. An, Treatment of organic waste gas in a paint plant by combined technique of biotrickling filtration with photocatalytic oxidation, Chem. Eng. J. 200 (2012) 645–653.

[21] G.Y. Li, Z.Y. Zhang, H.W. Sun, J.Y. Chen, T.C. An, B. Li, Pollution profiles, health risk of VOCs and biohazards emitted from municipal solid waste transfer station and elimination by an integrated biological-photocatalytic flow system: a pilot-scale investigation, J. Hazard. Mater. 250 (2013) 147–154.

[22] T.C. An, S.G. Wan, G.Y. Li, L. Sun, B. Guo, Comparison of the removal of ethanethiol in twin-biotrickling filters inoculated with strain RG-1 and B350 mixed microorganisms, J. Hazard. Mater. 183 (2010) 372–380.

[23] D.L. Wu, Z.Z. Yang, W. Wang, G.M. Tian, S.N. Xu, A. Sims, Ozonation as an advanced oxidant in treatment of bamboo industry wastewater, Chemosphere 88 (2012) 1108–1113.

[24] M.E. Alcantara-Garduno, T. Okuda, W. Nishijima, M. Okada, Ozonation of trichloroethylene in acetic acid solution with soluble and solid humic acid, J. Hazard. Mater. 160 (2008) 662–667.

[25] N.E. Strokova, T.V. Yagodovskaya, S.V. Savilov, E.E. Lukhovitskaya, E.S. Vasil'ev, I.I. Morozov, V.V. Lunin, Modeling the interaction of ozone with chloroform and bromoform under conditions close to stratospheric, Russ. J. Phys. Chem. A 87 (2013) 170–176.

[26] W.R. Zhao, Q.M. Shi, Y. Liu, Performance, deactivation and regeneration of SnO$_2$/TiO$_2$ nanotube composite photocatalysts, Acta Phys.: Chim. Sin. 30 (2014) 1318–1324.

[27] C.Y.H. Chao, C.W. Kwong, K.S. Hui, Potential use of a combined ozone and zeolite system for gaseous toluene elimination, J. Hazard. Mater. 143 (2007) 118–127.

[28] B. Croxford, K.W. Tham, A. Young, T. Oreszczyn, D. Wyon, A study of local electrostatic filtration and main pre-filtration on airborne and surface dust levels in air-conditioned office premises, Indoor Air 10 (2000) 170–177.

[29] G.Y. Li, H.W. Sun, Z.Y. Zhang, T.C. An, J.F. Fu, Distribution profile, health risk and elimination of model atmospheric SVOCs associated with a typical municipal garbage compressing station in Guangzhou, South China, Atmos. Environ. 76 (2013) 173–180.

[30] L.X. Zhong, F. Haghighat, C.S. Lee, N. Lakdawala, Performance of ultraviolet photocatalytic oxidation for indoor air applications: systematic experimental evaluation, J. Hazard. Mater. 261 (2013) 130–138.

[31] USEPA, Determination of volatile organic compounds (VOCs). Air collected in speciallyprepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS), (1999).

[32] Y.M. Kim, S. Kim, J.Y. Lee, Y.K. Park, Pyrolysis reaction pathways of waste epoxy-printed circuit board, Environ. Eng. Sci. 30 (2013) 706–712.

[33] G. Grause, M. Furusawa, A. Okuwaki, T. Yoshioka, Pyrolysis of tetrabromobisphenol-A containing paper laminated printed circuit boards, Chemosphere 71 (2008) 872–878.

[34] M. Blazso, Z. Czegeny, C. Csoma, Pyrolysis and debromination of flame retarded polymers of electronic scrap studied by analytical pyrolysis, J. Anal. Appl. Pyrol. 64 (2002) 249–261.

[35] H.J. Kim, B. Han, Y.J. Kim, T. Oda, H. Won, Submicrometer particle removal indoors by a novel electrostatic precipitator with high clean air delivery rate, low ozone emissions, and carbon fiber ionizer, Indoor Air 23 (2013) 369–378.

[36] W.J. Deng, P.K.K. Louie, W.K. Liu, X.H. Bi, J.M. Fu, M.H. Wong, Atmospheric levels and cytotoxicity of PAHs and heavy metals in TSP and PM2.5 at an electronic waste recycling site in southeast China, Atmos. Environ. 40 (2006) 6945–6955.

[37] M.L. Zhang, T.C. An, J.M. Fu, G.Y. Sheng, X.M. Wang, X.H. Hu, X.J. Ding, Photocatalytic degradation of mixed gaseous carbonyl compounds at low level on adsorptive TiO$_2$/SiO$_2$ photocatalyst using a fluidized bed reactor, Chemosphere 64 (2006) 423–431.

[38] K. Demeestere, J. Dewulf, H. Van Langenhove, Heterogeneous photocatalysis as an advanced oxidation process for the abatement of chlorinated, monocyclic aromatic and sulfurous volatile organic compounds in air: state of the art, Crit. Rev. Env. Sci. Technol. 37 (2007) 489–538.

[39] J.H. Mo, Y.P. Zhang, Q.J. Xu, Effect of water vapor on the by-products and decomposition rate of ppb-level toluene by photocatalytic oxidation, Appl. Catal. B: Environ. 132 (2013) 212–218.

[40] T. Guo, Z.P. Bai, C. Wu, T. Zhu, Influence of relative humidity on the photocatalytic oxidation (PCO) of toluene by TiO$_2$ loaded on activated carbon fibers: PCO rate and intermediates accumulation, Appl. Catal. B: Environ. 79 (2008) 171–178.

[41] J. Kim, P.Y. Zhang, J.G. Li, J.L. Wang, P.F. Fu, Photocatalytic degradation of gaseous toluene and ozone under UV254 + 185 (nm) irradiation using a Pd-deposited TiO$_2$ film, Chem. Eng. J. 252 (2014) 337–345.

[42] J. Jeong, K. Sekiguchi, K. Sakamoto, Photochemical and photocatalytic degradation of gaseous toluene using short-wavelength UV irradiation with TiO$_2$ catalyst: comparison of three UV sources, Chemosphere 57 (2004) 663–671.

[43] H.B. Huang, D.Y.C. Leung, G.S. Li, M.K.H. Leung, X.L. Fu, Photocatalytic destruction of air pollutants with vacuum ultraviolet (VUV) irradiation, Catal. Today 175 (2011) 310–315.

[44] J. Paca, E. Klapkova, M. Halecky, K. Jones, T.S. Webster, Interactions of hydrophobic and hydrophilic solvent component degradation in an air-phase biotrickling filter reactor, Environ. Prog. 25 (2006) 365–372.

[45] M.C. McCarthy, T.E. O'Brien, J.G. Charrier, H.R. Hather, Characterization of the chronic risk and hazard of hazardous air pollutants in the united states using ambient monitoring data, Environ. Health Perspect. 117 (2009) 790–796.

[46] K. Sexton, S.H. Linder, D. Marko, H. Bethel, P.J. Lupo, Comparative assessment of air pollution-related health risks in Houston, Environ. Health Perspect. 115 (2007) 1388–1393.

[47] ACGIH, Threshold limit values for chemical substances in workplaces laid down by American Conference of Industrial Hygienists in 2010, Occup. Health Emerg. Rescue 28 (2010) 289–292.