



Preferential purification of oxygenated volatile organic compounds than monoaromatics emitted from paint spray booth and risk attenuation by the integrated decontamination technique



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ABSTRACT

Purification and risk attenuation of mixed oxygenated volatile organic compounds (OVOCs) and monoaromatics (total concentration: 5.8×10^5 – $1.2 \times 10^6 \mu\text{g m}^{-3}$) from a paint spray booth of auto 4S shop were investigated. The applied integrated technique of spray tower (ST) with photocatalysis (PC) displayed 2.5 times higher elimination capacity (EC) to OVOCs ($309.9 \text{ g m}^{-3} \text{ h}^{-1}$) than monoaromatics ($124.5 \text{ g m}^{-3} \text{ h}^{-1}$), due to higher synergetic elimination of these two techniques. Specifically, approximately 4.3 times higher amount of OVOCs than monoaromatics was removed by ST, contributing to their two orders of magnitude higher Henry's law constants. Similar EC trend was also observed on PC ($774.5 \text{ g m}^{-3} \text{ h}^{-1} > 518.5 \text{ g m}^{-3} \text{ h}^{-1}$). The corresponding quantum chemical calculation revealed more negative adsorption energy of OVOCs ($-40.29 \text{ kcal mol}^{-1}$) than monoaromatics ($-33.32 \text{ kcal mol}^{-1}$) onto the catalyst, resulting in more spontaneous and easy adsorption, enrichment and later degradation. Furthermore, the integrated technique displayed preferential and efficient reduction ability to both acute inhalation and chronic occupational exposure risks of OVOCs than monoaromatics. This study provided an efficient and pertinent approach to atmospheric purification and human health protection in motorvehicle repair business.

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1. Introduction

Since the beginning of the automotive industry from 1890s, the global production of motorvehicles significantly increased from 54 million in 1997 to 91 million in 2015 (from The International Organization of Motor Vehicle Manufacturers). Consequently, motorvehicle repair business accordingly expands rapidly during last few decades. Generally, most of repair items have to receive surface coatings for damaged vehicle shell redecoration, while a mixture of binder, organic solvent, pigment and additives has been inevitably applied (Viguri and Irabien, 2005). More than 70% of the used solvent end up as gaseous pollutant emissions (mainly of volatile organic compounds (VOCs)), resulting in severe atmospheric pollution and human health threat (Pierucci et al., 2005).

Although the constituent of emitted VOCs varies with the type of paint utilized, dominant composition was clarified from a mixture of monoaromatics and oxygenated VOCs (OVOCs) (Mathur and Majumder, 2008). Notably, these two groups of VOCs showed very different physical and chemical properties, including solubility and polarity. As such, to design a general control technology that can efficiently and specially eliminate these two groups of VOCs emitted from motorvehicle repair process based on their physico-chemical property disparities should be highly meaningful for our environment protection.

Given its generation of powerful oxidant active species, photocatalysis (PC) technology has attracted considerable attention recently for gaseous pollutants elimination (An et al., 2012; Ananpattarachai and Kajitvichyanukul, 2016; Chen et al., 2011b, 2013; Chen and Chu, 2011). PC has been proved to possess excellent degradation ability toward monoaromatics, OVOCs (Aghighi and Haghghat, 2015; Blanco et al., 1996; Lim et al., 2009; Moulis

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and Krysa, 2013), and the mixture of them (Lichtin et al., 1996; Palau et al., 2012) in laboratory. Notably, high degradation activity order of ethyl acetate > toluene (Chen et al., 2011a) or butyl acetate > m-xylene (Palau et al., 2011) onto TiO₂ based photocatalyst was obtained within their mixture under the different initial concentration, consistent with the order of their dielectric constants. Obviously, PC prefers degrading OVOCs to monoaromatics on TiO₂ based photocatalyst, due to the polar nature of the catalyst and much higher polar properties of OVOCs. However, the direct and overwhelming evidence to prove the more positive effect of polarity on the adsorption and degradation activities of OVOCs than monoaromatics onto the catalyst is still rare. Furthermore, all available data were obtained under ideal lab environment, and only two kinds of VOCs have been separately investigated. Whether and how does the property of VOCs influence the adsorption and degradation efficiencies in real? The questions are still unanswered yet. In our recent work, higher PC removal activity to ethyl acetate than toluene from the real electronic waste recycling process was obtained, which, however, was mainly due to significantly lower inlet concentration of ethyl acetate ($45 \mu\text{g m}^{-3}$) than toluene ($513 \mu\text{g m}^{-3}$) (Liu et al., 2016). Different from the dominant amount of monoaromatics from electronic waste recycling process, surface coating operation of car inside paint spray booth (PSB) using organic solvents would generate equal and even higher level of OVOCs than monoaromatics (Bratveit et al., 2004; Pierucci et al., 2005). Thus, the investigation of whether and why the PC preferentially eliminates OVOCs than monoaromatics in PSB is meaningfully and credibly, which will then give a solid answer to the above questions. However, up to date, such kind of works was not attempted yet.

In addition, complex real-situations would deactivate the catalyst during the long-term operation of photocatalytic technology, mainly due to the coexisted particulate matters within waste gas, such as the mists from paint spray process. Therefore, to maintain the high efficiency and stability of PC technique, and reduce the adverse effects of them on human health, the particle should be pretreated ahead of this technology. Spray tower (ST) with water is one of the most widely used control devices to remove the oil mist or particles from industrial effluent gases, mainly due to its easy operation, simple construction and high efficiency (Almuhanna et al., 2009; Mohan et al., 2008). For instance, nearly all the micron-size particles could be removed by ST technology under optimal operating conditions (Darcovich et al., 1997). Besides, this technology also showed its preference to remove hydrosoluble gaseous organics (Kim et al., 2000).

Therefore, in this study, these two efficient and selective techniques were contrapuntally united to develop an integrated ST-PC technique for OVOCs and monoaromatics mixture elimination as well as for their risks reduction in PSB. Based on the available physico-chemical data of VOCs and quantum chemical calculations, this study also will try to verify the hypothesis that whether and why ST, PC and their integrated techniques preferred to reduce the OVOCs as well as their acute and chronic risks than monoaromatics. The obtained data would provide very useful guidance for pertinently VOCs pollution and risk control in motorvehicle repair business.

2. Experimental

2.1. Study site and set-up

The experiments were conducted in a PSB of an auto 4S shop in Guangdong, China, which was mainly engaged in repainting damaged car shells. During the working period, high-pressure airbrush was used to spray the designed paint mixture onto the

car shell surfaces, and gaseous VOCs were discharged into atmospheric environment.

An integrated ST-PC reactor (Fig. S1) was fabricated to purify the emitted waste gas. The gas was firstly fed into the ST reactor (Height \times Diameter, approximately 4500 mm \times 2000 mm) and then to PC unit (1900 mm \times 1900 mm \times 1500 mm) by a centrifugal pump mounted at the outlet of PC reactor to obtain a stable flow-rate of $16,000 \text{ m}^3 \text{ h}^{-1}$. Detail information of set-up is provided in Supporting Information (SI).

2.2. Sample collection and analysis

VOCs samples were collected from inlet, outlet of ST and outlet of PC, respectively, using 2.7-L stainless Summa canisters (ENTECH Instruments Inc, Silonite™) during the paint spray processes for three different times (denoted as 1st, 2nd and 3rd). Then the samples were qualitatively and quantitatively analyzed on a Entech 7100 pre-concentrator (Entech Instruments Inc., CA, USA) followed by gas chromatography-mass spectrometry (7890-5975 GC-MS, Agilent technologies, USA) according to the US Environmental Protection Agency (USEPA) TO-15 method (USEPA, 1999). A control point was selected at about 10-m outside of the PSB. Detail sampling and analysis information as well as quality assurance and quality control were provided in the SI and in our previous work (He et al., 2015).

2.3. The calculation of adsorption configuration and adsorption energy

The adsorption configuration and energy of different VOCs molecules onto TiO₂ were also calculated using the Gaussian 09 software package and the detail description of the computation method is provided in the SI.

2.4. Risk assessment

The acute and occupational exposure risks of VOCs emitted during the paint spray processes were evaluated to understand their potential acute and chronic effects on the workers after short- and long-time inhalation, and the corresponding risk evaluation methods were provided in the SI.

3. Results and discussion

3.1. VOC pollution profile and risk evaluation

The components and concentrations of VOCs emitted during the paint spray processes in the PSB were firstly investigated. As Table 1 shows, a total of 23 VOCs were detected and categorized into two groups of monoaromatics and OVOCs for convenience. Fig. 1a and b displays the concentration and percentage of these VOCs, respectively. As can be seen, the sum of VOC concentrations was in the range of 5.8×10^5 to $1.2 \times 10^6 \mu\text{g m}^{-3}$, which was at least six times higher than Guangdong provincial emission pipe emission standard of VOCs for surface coating of automobile manufacturing industry ($9.0 \times 10^4 \mu\text{g m}^{-3}$, DB44/816-2010). This indicated that the atmosphere environment in the PSB was highly contaminated by VOCs, and must be purified before emission. Meanwhile, higher percentage of OVOCs was found (64.8% in average) than that of monoaromatics (35.2% in average) among these VOCs. Similar results were also obtained in other PSBs (Martinez-Soria et al., 2009; Qi et al., 2005). Notably, approximately $5.9 \times 10^3 \mu\text{g m}^{-3}$ of VOCs were detected at the control point, which was almost three times higher than Guangdong fugitive emission standard of VOCs for surface coating of automobile manufacturing industry

($2.0 \times 10^3 \mu\text{g m}^{-3}$, DB44/816-2010). Further, the profile of VOCs at control site was very similar to that inside PSB, suggesting the serious leakage or diffusion of VOCs from the PSB during paint spray processes. Thus, to protect the health of surrounding residents, the tightness of the PSB must be further improved and the VOCs generated must be efficiently treated before discharge.

Further data analysis of individual VOCs is displayed in Figs. S2–S3. Among the sixteen monoaromatics, the highest percentage of o-xylene (51.7% in average) was obtained, followed by ethylbenzene (14.9% in average), toluene (10.3% in average), m/p-xylene (9.8% in average), and styrene (6.9% in average). These indicated that xylene isomers especially o-xylene were the dominant polluted monoaromatics in PSB, possibly due to their widely utilizations in paint industry around the world. These results were good agreement with those of (Nassiri et al. 1999) and Yuan et al. (2010), who reported the predominant emission of xylenes among monoaromatics from paint industries in Tehran of Iran and Beijing of China. In the case of OVOCs, absolutely dominant butyl acetate ($\geq 96.2\%$), but minor portions of ethyl acetate (1.4% in average), n-butanol (1.0% in average), amyl acetate (0.3% in average), methyl methacrylate (0.3% in average), methyl isobutyl ketone (0.1% in average) and isobutanol (0.1% in average) were found in this study. The highly concentrated butyl acetate within the emitted OVOCs might be due to its wide application as an organic solvent in paint industry because of the advantages of high solvent power and convenient range of evaporation for a wide range of resin-based formulation molecules (Lopez-Anreus et al., 1998).

Since the highly concentrated VOCs were discharged during the paint spray process, their adverse effects to the workers after short- and long-term exposure through inhalation should be considered. First, the acute effects of them to the workers were investigated in detail. Based on the available LC50 values for inhalation, twelve quantified VOCs were chosen to assess their acute risks (Table S1). As Fig. 2a–d shows, RQs of all VOCs were below 5.0×10^{-2} , suggesting that individual VOC at current levels posed little acute risk to the workers in the PSB. Notably, OVOCs showed high RQ (in the range of 1.6×10^{-2} to 3.8×10^{-2}), very close to 5.0×10^{-2} across three sampling events, implying the probably acute risk threat by OVOCs, especially by butyl acetate (2.7×10^{-2} for average RQ). Further analysis found that less than half of RQ was from for monoaromatics (1.0×10^{-2} in average and o-xylene accounting for

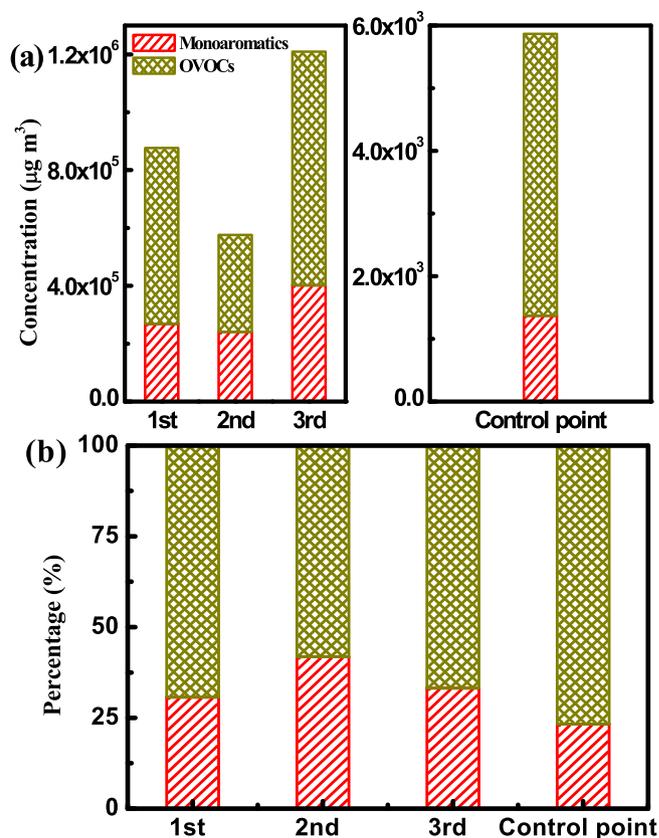


Fig. 1. Concentrations (a) and percentages (b) of monoaromatics and oxygenated VOCs emitted during paint spray process.

approximately 60% (0.6×10^{-2})), suggesting much lower acute risk threat of monoaromatics than OVOCs in this PSB. Interestingly in previous lab researches, when at relatively low inhalation dose, OVOCs such as alcohols ($5.0 \times 10^3 \mu\text{g m}^{-3}$) (Belsito et al., 2010) and ketones ($2.2 \times 10^4 \mu\text{g m}^{-3}$) (Zaleski et al., 2007), possessed low or even no acute toxicity to mammals, while highly acute adverse effects were observed for monoaromatics at the comparable level (eg., $5.0 \times 10^3 \mu\text{g m}^{-3}$ of toluene (Kodavanti et al., 2015)). Obviously,

Table 1

Category, Henry's law constant for water as solvent, dielectric constant and adsorption energy on TiO_2 of VOCs detected during paint spray process.

Monoaromatics	Henry's law constant ($\text{mol m}^{-3} \text{Pa}^{-1}$)	Dielectric constant	Adsorption energy (kcal mol^{-1})	Oxygenated VOCs	Henry's law constant ($\text{mol m}^{-3} \text{Pa}^{-1}$)	Dielectric constant	Adsorption energy (kcal mol^{-1})
Benzene	1.8×10^{-3}	2.28	-27.42	Isobutanol	1.0	17.26	-37.32
Toluene	1.5×10^{-3}	2.38	-31.30	n-Butanol	1.2	17.84	-37.69
Ethylbenzene	1.3×10^{-3}	2.45	-31.65	Methyl isobutyl ketone	7.0×10^{-2}	13.11	-39.87
Styrene	3.8×10^{-3}	2.43	-28.14	Methyl methacrylate	3.1×10^{-2}	6.32	-42.94
m,p-Xylene	1.4×10^{-3}	2.32	-34.15 ^a , -34.41 ^b	Ethyl acetate	1.1×10^{-1}	6.08	-39.34
o-Xylene	2.0×10^{-3}	2.56	-33.79	Butyl acetate	3.5×10^{-2}	5.07	-41.24
Propylbenzene	1.1×10^{-3}	2.37	-31.69	Amyl acetate	2.8×10^{-2}	4.79	-43.64
Isopropylbenzene	6.8×10^{-4}	2.38	-31.08				
o-Ethyltoluene	1.9×10^{-3}	2.60	-34.03				
m-Ethyltoluene	1.3×10^{-3}	2.37	-35.45				
p-Ethyltoluene	2.0×10^{-3}	2.27	-34.84				
m-Isopropyltoluene	1.4×10^{-3}	2.23	-34.94				
p-Isopropyltoluene	1.2×10^{-3}	2.23	-34.75				
2,5-Dimethylethylbenzene	N/A	2.28	-37.59				
1,2,3-Trimethylbenzene	3.1×10^{-3}	2.66	-34.84				
1,2,4-Trimethylbenzene	1.7×10^{-3}	2.38	-36.45				

N/A: Not available.

^a Value for m-xylene.

^b Value for p-xylene.

much higher acute risk of OVOCs than monoaromatics observed in this study might be contributed to their extraordinarily high concentrations ($5.8 \times 10^5 \mu\text{g m}^{-3}$ in average), suggesting the acute toxicity of OVOCs in the PSB would be significantly enhanced with increasing their exposure concentrations. Therefore, to protect the workers from the acute effect of VOCs in the PSB, OVOCs elimination is highly needed.

Furthermore, since the employees would intermittently work for months and even years in the PSB, the chronic exposure cancer risks of generated VOCs were also evaluated according to the OSHA method. Table S2 showed the time-weighted average exposure values of these available VOCs. As Fig. 3a shows, the E_i values of all studied VOCs from the control point were by far below 0.1, indicating the negligible adverse effects of these VOCs at 10 m outside of the PSB. However, much higher risks were obtained inside the PSB (Fig. 3b–d). For instance, both E_i values of OVOCs (1.13) and monoaromatics (1.10) at the 3rd sampling event were higher than 1, suggesting their cancer risks to the workers at the current pollution levels after long-term exposure. Besides, possible adverse effects were found at the 1st (0.83 for OVOCs and 0.76 for monoaromatics) and 2nd sampling event (0.47 for OVOCs and 0.65 for monoaromatics). Meanwhile, the average E_i OVOCs (0.81) was very close to that of monoaromatics (0.84), revealing both high occupational cancer risks of them to the workers in the PSB from a point view of the chronic exposure.

In case of individual VOCs, only the E_i of butyl acetate (1.11) at the 3rd sampling event was over 1, indicating its long-term cancer risk to the workers. Moreover, its E_i values at the 1st (0.82) and 2nd (0.46) sampling event were between 0.1 and 1, suggesting the potential chronic cancer risks due to the long-term exposure of these emitted VOCs. In addition, potential chronic cancer risks might be

caused by o-xylene (from 0.26 to 0.51 at all sampling events), toluene (0.13 at the 1st sampling event), 1,2,3-trimethylbenzene (0.12 at the 1st sampling event), ethylbenzene (0.15 at the 3rd sampling event) and styrene (0.13 at the 3rd sampling event) at the current levels.

In summary, serious VOC pollution was found during paint spray process in PSB, which was mainly contributed to very high concentrated OVOCs. This subsequently resulted in both high acute and chronic risks to the workers, especially from butyl acetate. Meanwhile, high chronic risks were also observed from monoaromatics, although their concentrations were much lower than OVOCs. This further indicates that the long-term exposure of this group VOCs should be also seriously concerned in the PSB. Clearly, to protect the environment and human health, all risk evaluation results strongly suggested the elimination of these VOCs before discharge.

3.2. Purification of VOCs by the integrated technique

To efficiently eliminate these high level and dangerous VOCs, an integrated technique of ST with PC was consciously designed and applied in practically. ST was able to efficiently trap particles to protect the subsequent catalysts from continuous staining, while water-soluble gaseous organics (eg., most of OVOCs) could also be easily absorbed in water of ST, which has been solidly confirmed in previous studies (Koo et al., 2010). Then, the combination effect of porous foam nickel TiO_2 film and vacuum ultraviolet lamp can effectively and stably decompose the particle-free VOCs in PC system mainly with oxidant species $\cdot\text{OH}$. At the same time, the ozone-producing lamps used in this study also simultaneously generated other strong oxidant species, O_3 , in this system. Then, the

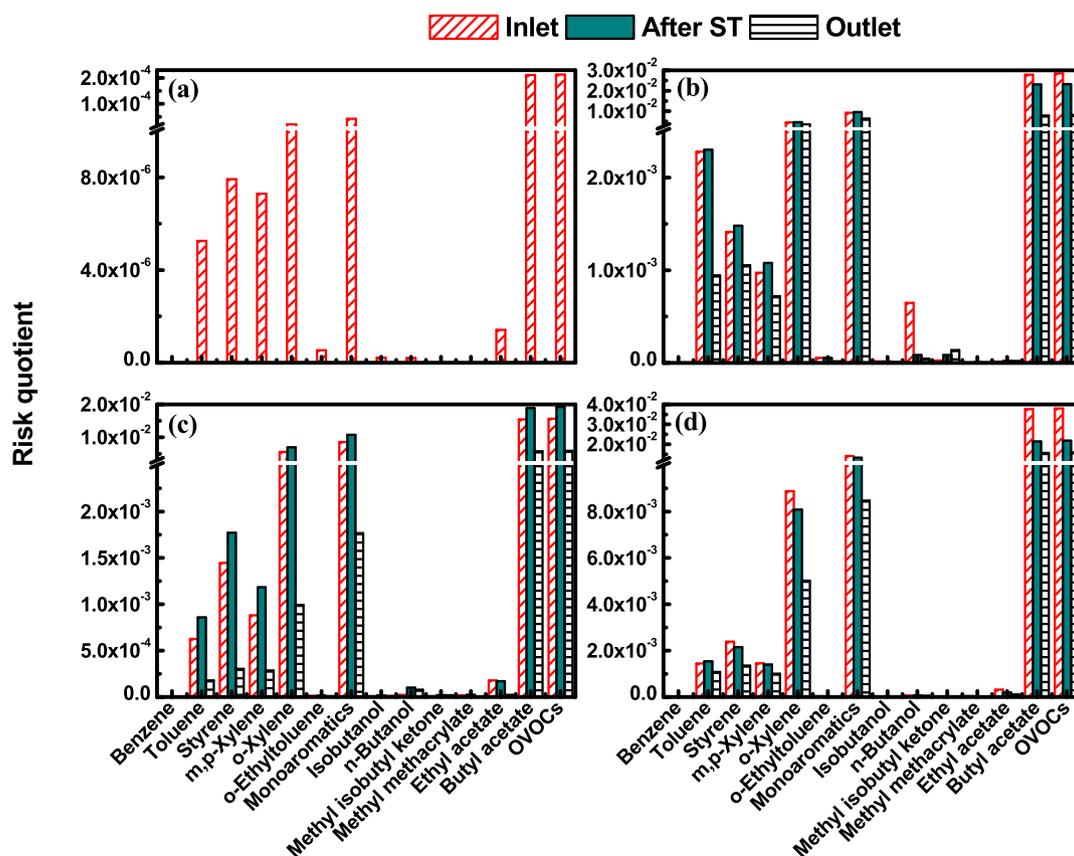


Fig. 2. Acute risk quotients of monoaromatics and oxygenated VOCs before and after the treatment. ((a) Control point, (b) to (d) at the 1st to 3rd sampling event).

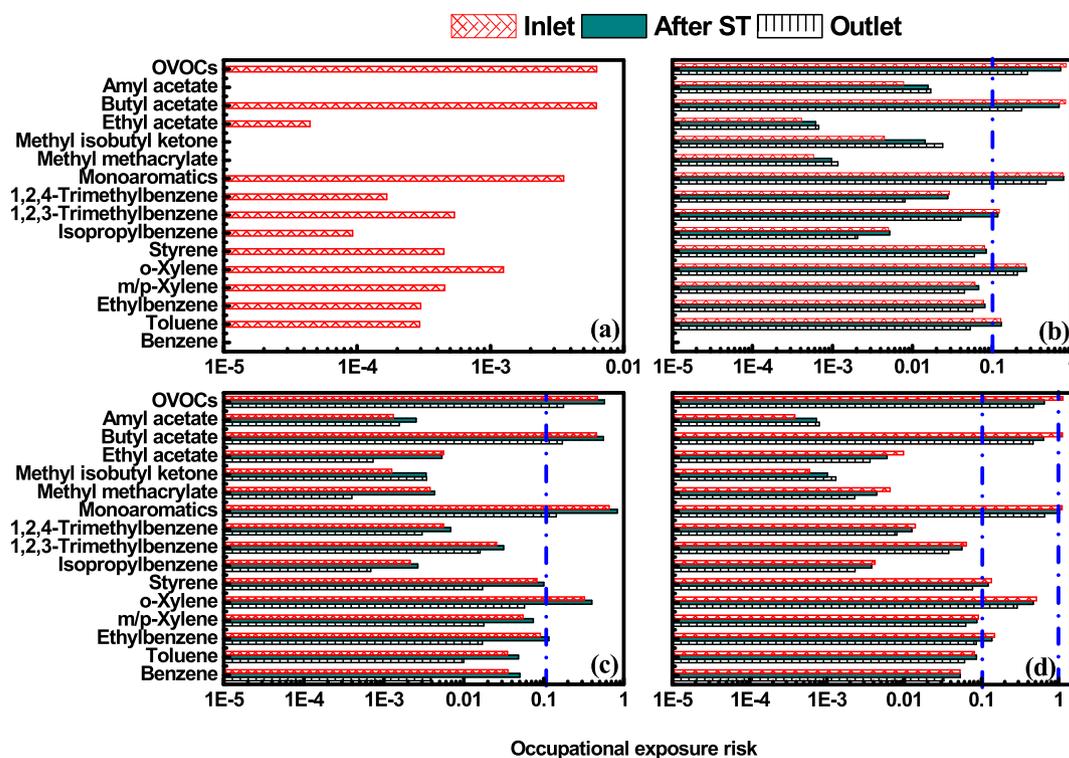


Fig. 3. Chronic occupational exposure cancer risks of monoaromatics and oxygenated VOCs before and after treatment. ((a) Control point, (b) to (d) at the 1st to 3rd sampling event).

synergetic effect of PC and ozonation could further increase the VOC removal. More importantly, the high photocatalytic activity of the catalyst could be preserved, due to its excellent regeneration ability after using vacuum ultraviolet lamps. Typically, similar PC system has been successfully applied in the purification of complex VOCs from electronic waste recycling industry (Chen et al., 2016) and paint factory (He et al., 2012), confirming the practicability of this technique in real organic waste gas abatement.

Fig. S4 shows the total ion chromatograms of three sampling events before and after treatment by the integrated technique. Clearly, the peak areas of most VOCs remained after ST treatment (except for butyl acetate at the 3rd sampling event) with even the increased peak areas for some individual VOCs (eg., toluene from all sampling events). These indicated the inefficient removal of monoaromatics than OVOCs by ST. Comparatively, all peak areas decreased significantly with the further treatment using PC technique (eg., all VOCs at the 1st sampling event), verifying the efficient removal of various VOCs. Notably, no reaction byproducts were detected or under detection limit in the outlet gas stream in this work, suggesting the possible formation of unstable intermediates in the surface of the catalyst rather than in the air.

Furthermore, the elimination performance of the integrated technique toward these mixture VOCs were evaluated using elimination capacity (EC, the amount of VOCs degraded per unit of the reactor volume and time), which can be calculated by Eq. (1):

$$EC = \frac{Q(C_I - C_O)}{10^6 V} \quad (1)$$

where C_I and C_O were the inlet and outlet VOC concentrations ($\mu\text{g m}^{-3}$) of each unit, respectively. Q was the gas flow ($\text{m}^3 \text{h}^{-1}$) and V was the effective volume (m^3).

As Fig. 4 shows, the EC of the integrated ST-PC reactor to monoaromatics was in the range of 77.4–159.1 $\text{g m}^{-3} \text{h}^{-1}$, which was less than half of that to OVOCs (ranging from 176.3 to 395.3 g m^{-3}

h^{-1}). Obviously, the elimination of VOCs by the designed combined technologies prefers OVOCs to monoaromatics, which might be the synergetic effect of ST with PC units. To clarify this hypothesis, the removal of these two groups of VOCs by each unit was further investigated.

As Fig. 4a shows, in case of ST, poor EC even with negative ECs some time (-10.8 and $-71.4 \text{ g m}^{-3} \text{h}^{-1}$ at the 1st and 2nd sampling event) toward monoaromatics (with the highest value of $33.4 \text{ g m}^{-3} \text{h}^{-1}$) was achieved, consistent with the total ion chromatogram results. This was probably due to their much weak water solubility (see discussion below) that the captured monoaromatics species into the water would be easily released again as the exhaust gas passed with high flow rate, leading to the possible higher concentration at outlet than inlet. Comparatively, much higher EC ($144.0 \text{ g m}^{-3} \text{h}^{-1}$ in average) was achieved for OVOCs by the same technology (Fig. 4b), and peaked at $393.5 \text{ g m}^{-3} \text{h}^{-1}$ for the 3rd sample event. The great difference in removal abilities across these two VOC groups on ST should be significantly associated with their different water solubility property. Table 1 summarizes the corresponding Henry's law constants for water as solvent of these VOCs; and the higher the constant, the easier be absorbed by water (Sander, 2015). From the table, the Henry's law constants of detected monoaromatics were in the range of 6.8×10^{-4} to $3.8 \times 10^{-3} \text{ mol m}^{-3} \text{Pa}^{-1}$ ($1.7 \times 10^{-3} \text{ mol m}^{-3} \text{Pa}^{-1}$ in average), which was two orders of magnitude lower than that of OVOCs (from 2.8×10^{-2} to $1.2 \text{ mol m}^{-3} \text{Pa}^{-1}$ with $3.5 \times 10^{-1} \text{ mol m}^{-3} \text{Pa}^{-1}$ in average). Thus, much higher solubility of OVOCs (eg., $3.5 \times 10^{-2} \text{ mol m}^{-3} \text{Pa}^{-1}$ for butyl acetate) than monoaromatics (eg., $2.0 \times 10^{-3} \text{ mol m}^{-3} \text{Pa}^{-1}$ for o-xylene) in water, leading to the followed average EC orders of butyl acetate ($139.8 \text{ g m}^{-3} \text{h}^{-1}$) \gg o-xylene ($-6.0 \text{ g m}^{-3} \text{h}^{-1}$) (Fig. S5) and then OVOCs \gg monoaromatics by ST technology. All these results suggested that ST applied in this work was solubility decisive, which could more efficiently remove hydrophilic VOCs with even much higher inlet concentration than hydrophobic ones from paint

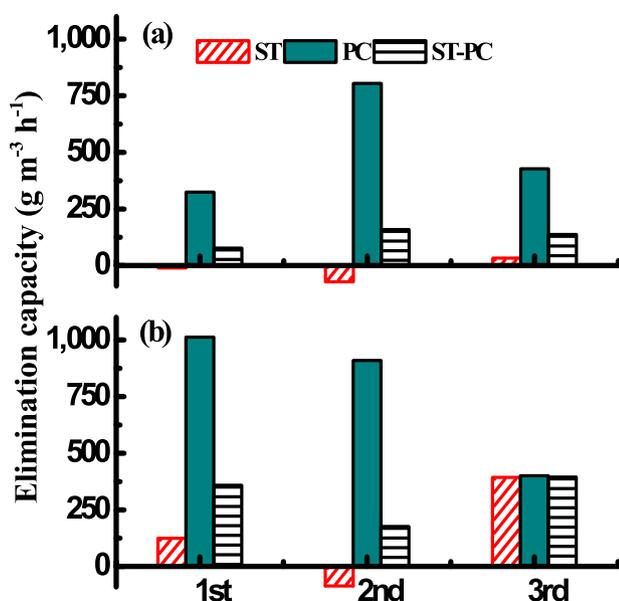


Fig. 4. Elimination capacities of monoaromatics (a) and OVOCs (b) by the integrated technique.

spray industry.

As compared with ST, PC showed much higher removal capability to all VOCs. The EC of $774.5 \text{ g m}^{-3} \text{ h}^{-1}$ in average was obtained for OVOCs, which was approximately 1.5 times higher than that for monoaromatics ($518.5 \text{ g m}^{-3} \text{ h}^{-1}$ in average) (Fig. 4). Similar order was observed for the EC of dominantly individual OVOCs, butyl acetate ($761.6 \text{ g m}^{-3} \text{ h}^{-1}$ in average) and monoaromatics, *o*-xylene ($267.1 \text{ g m}^{-3} \text{ h}^{-1}$ in average) (Fig. S6). Clearly, similar with ST, more efficient elimination of OVOCs than monoaromatics by PC unit was also obtained. As well known, PC degradation activity toward different organics was essentially dependent upon the efficient adsorption of VOCs onto the catalyst surface (An et al., 2011; Kim et al., 2013; Zhang et al., 2006). Higher adsorption affinities to catalyst would lead to higher photocatalytic degradation rate (An et al., 2005; Tasbihi et al., 2012). In the present study, since the immobilized TiO_2 catalyst was prepared in the solution environment, which could easily enrich hydroxyl groups to get more hydrophilic property. As such, the catalyst should more easily adsorb hydrophilic OVOCs than hydrophobic monoaromatics due to their higher dielectric constants ($4.79\text{--}17.84 > 2.23\text{--}2.66$) (Table 1), accelerating the followed degradation process.

To verify above hypothesis, the correspondingly quantum chemical calculations of adsorption configurations and adsorption energies of OVOCs and monoaromatics onto TiO_2 (the main active material in the composite photocatalyst) surface were conducted. As Figs. 5, S7 and Table 1 show, two dominant species of OVOCs and monoaromatics, butyl acetate and *o*-xylene, were selected as examples for the following discussion. In case of *o*-xylene, its phenyl carbon atoms would interact with the Ti atom of TiO_2 to form TiO_2 -*o*-xylene complexes. Seen from Fig. 5 about this complex's structure, Ti atom sites above the ring plane of *o*-xylene, and the adjacent C–Ti bond distances were 2.66 and 2.72 Å. The similar case could be observed in butyl acetate, which is the formation of TiO_2 -butyl acetate complex. The distances between Ti atom of TiO_2 and two O atoms of butyl acetate were 2.23 and 2.31 Å. These adsorption configuration results confirmed the feasibility of these two VOCs tightly adsorbed on TiO_2 through covalent bonds. Further, the adsorption energy of TiO_2 -butyl acetate complexes of $-41.24 \text{ kcal mol}^{-1}$ was found more negative by $7.45 \text{ kcal mol}^{-1}$ than the TiO_2 -*o*-xylene complexes ($-33.79 \text{ kcal mol}^{-1}$), indicating that TiO_2 -

based photocatalyst preferred to adsorb and enrich butyl acetate through Ti–O bond. Similar results were also obtained for other OVOCs (the adsorption energy of $-40.29 \text{ kcal mol}^{-1}$ in average) and monoaromatics (the adsorption energy of $-33.32 \text{ kcal mol}^{-1}$ in average) (Fig. S7). In this work, the adsorption energies of studied VOCs on the TiO_2 were all negative, varying from -27.42 to $-43.64 \text{ kcal mol}^{-1}$. In all, the adsorption performances are belong to chemisorption rather than physical adsorption, due to that the physical adsorption has very low adsorption energies of $-1.20\text{--}9.56 \text{ kcal mol}^{-1}$, while the chemisorption has much higher adsorption energies of -9.56 to $-191.30 \text{ kcal mol}^{-1}$ (Nollet et al., 2003). Therefore, all detected VOCs were adsorbed onto TiO_2 through spontaneous chemisorption processes, revealing that the applied photocatalyst was able to easily adsorb and trap all VOCs onto the catalysts, facilitating subsequent degradation, especially for OVOCs. This result was also consistent with our previous observation that more negative adsorption energy of vinyl group of styrene onto TiO_2 led to faster PC degradation rate (Wang et al., 2015). Further, it should be noted that the PC showed relatively low removal ability toward some OVOCs, such as ethyl acetate (Fig. S8), probably due to that they were also the ring opening by-products of monoaromatics (Zhong et al., 2007a). Of course, further experiments were also needed to figure out the transformation pathway and mechanism from monoaromatics to OVOCs.

In all, due to their synergetic effects of high water solubility and adsorption affinity onto photocatalysts, *ca.* 2.5 times higher EC to OVOCs (average EC: $309.9 \text{ g m}^{-3} \text{ h}^{-1}$) than monoaromatics (average EC: $124.5 \text{ g m}^{-3} \text{ h}^{-1}$) was obtained on the integrated ST-PC technique.

3.3. Risk reduction of VOCs during the elimination by the integrated technique

3.3.1. Acute risk attenuation

Since risk assessments could reveal the potential acute inhalation threat of VOCs to the workers in the PSB, the acute risk after the treatment by the integrated technique was then investigated. As Fig. 2 shows, the RQs of monoaromatics and OVOCs decreased from 1.1×10^{-2} and 2.7×10^{-2} to 5.5×10^{-3} and 1.0×10^{-2} with the reduction efficiency (RE) of 48.3% and 63.6%, respectively, after treatment by the combined ST and PC techniques. This revealed the high risk attenuation of toward all VOCs, especially for OVOCs by the integrated technique.

Specifically, the RQs for almost all monoaromatics increased after ST treatment with some exceptions. These exceptions included *o*-ethyltoluene at the 1st (from 5.4×10^{-5} to 5.3×10^{-5}) and 2nd sampling event (from 2.7×10^{-5} to 2.4×10^{-5}), *o*-xylene (from 8.9×10^{-3} to 8.1×10^{-3}), styrene (from 2.4×10^{-3} to 2.1×10^{-3}) and *m,p*-xylene (from 1.5×10^{-3} to 1.4×10^{-3}) at the 3rd sampling event. However, all these still resulted in the increase of average RQ of monoaromatics from 1.0×10^{-2} to 1.1×10^{-2} with the RE of -4.6% . In contrast, very obvious decrease of average RQs was observed for OVOCs (from 2.7×10^{-2} to 2.1×10^{-2} with the RE of 21.9%). This confirmed the preferential risk reduction of OVOCs by the ST technique, especially for *n*-butanol at the 1st sampling event (from 6.5×10^{-4} to 8.3×10^{-5} with the RE of 87.2%), possibly due to its highest Henry's law constant ($1.2 \text{ mol m}^{-3} \text{ Pa}^{-1}$). These results confirmed a water solubility determined risk attenuation technology of ST in this study.

After PC treatment, significant decreases of RQs for both groups of VOCs were observed. For monoaromatics, the RE of RQs ranged from 45.0% to 64.6%, leading to the average RQ of monoaromatics reduced from 1.1×10^{-2} to 5.5×10^{-3} . As expected, PC showed much higher acute risk attenuation toward OVOCs (RQ reduced from 2.1×10^{-2} to 1.0×10^{-2}), although an obvious increase of RQ

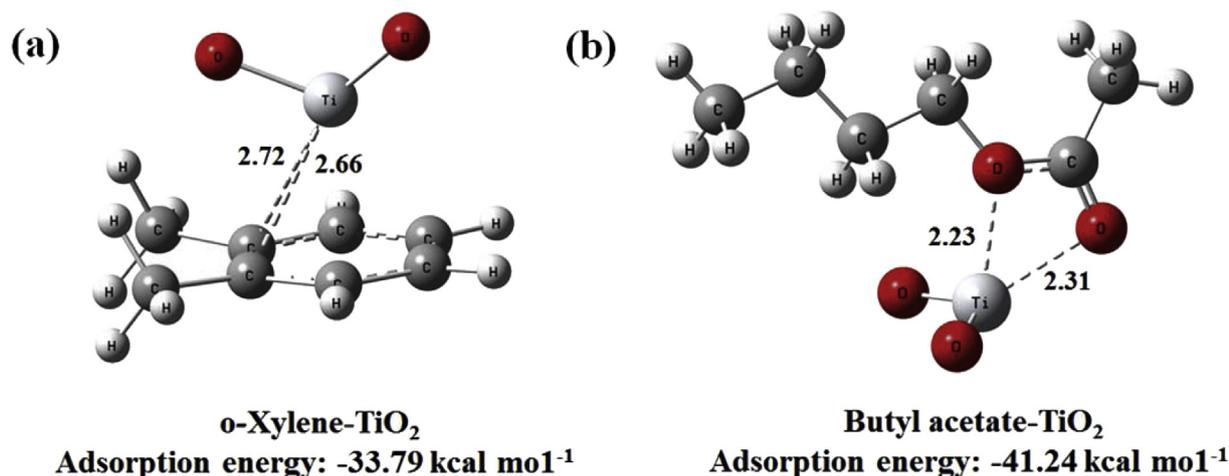


Fig. 5. Adsorption configurations and adsorption energies of o-xylene (a) and butyl acetate (b) onto TiO₂ photocatalyst.

for methyl isobutyl ketone (from 3.7×10^{-5} to 5.6×10^{-5}) was observed after PC treatment, probably due to that it was a PC degradation intermediate of monoaromatics (Shen et al., 2012; Zhong et al., 2007b). Luckily, the increased RQ of methyl isobutyl ketone was still far lower than LOC (5.0×10^{-2}), implying a negligible acute risk threat of this compound at current pollution level. However, after long-term treatment, some of generated intermediates might be partially degraded and even be mineralized, while most of them would accumulate and enrich on the catalyst surface to form a “complex community”. This would result in highly potential acute risk to workers, since the acute risk was highly linear to the concentration. Therefore, to prevent the risks from both groups VOCs and their degradation intermediates, further investigation on the PC degradation intermediates identification and then the mechanism clarification of mixed OVOCs and monoaromatics as well as the mineralization performance of the PC system should be considered.

3.3.2. Chronic exposure risk attenuation

Similar to acute risk, the couple of ST with PC technologies led to more advantageously attenuation to the occupational exposure cancer risk of OVOCs (62.0% of RE) than monoaromatics (49.6% of RE) (Fig. 3), which was also ascribed to the synergetic contribution of ST and PC units. As shown in the figure, ST showed much higher risk reduction activity toward OVOCs than monoaromatics ($20.5\% \gg -4.3\%$ in average of RE), indicating preferential and efficient attenuation of OVOCs with the chronic risk by this technique. Similar result was also observed for individual VOC (eg., 21.6% for butyl acetate $\gg -3.3\%$ for o-xylene (Fig. S9)). Moreover, all these results were highly consistent with the concentration degradation results. Unfortunately, E_i values of most VOCs at the outlet of ST were still high (>0.1). For instance, after ST treatment, the E_i value of monoaromatics (1.02) and OVOCs (0.65) remained higher than 0.1 at the 3rd sampling event, suggesting still existence of chronic cancer threat, which were needed further risk elimination.

As expected, more efficient reduction of cancer risk was observed for all VOCs after further PC treatment. Typically, the average E_i values of monoaromatics and OVOCs reduced from 0.87 and 0.64 to 0.42 and 0.31 with the average REs of 51.7% and 52.1%, respectively. In the case of dominant VOCs, 53.7% and 51.2% of E_i values of butyl acetate and o-xylene were reduced by PC technique (Fig. S9). All these results again confirmed the preferential risk reduction of OVOCs than monoaromatics by the PC technology as

well as the integrated technique.

Despite the obtained significant decrease, the risks still remained to some extent for OVOCs and monoaromatics based on the high inlet concentrations, especially for butyl acetate (0.28 in average) and o-xylene (0.18 in average). Therefore, more effective waste gas collection strategies and safer personal protective devices are needed to further reduce the exposure risk levels.

4. Conclusions

From the emitted waste gas of PSB in an auto 4S shop, OVOCs and monoaromatics were identified as two dominant groups with the highest contributions of butyl acetate ($\geq 96.2\%$) and o-xylene (51.7% in average), respectively. An integrated ST-PC technology was then applied reduce the risks of these VOCs, which displayed preferentially concentration elimination ($309.9 \text{ g m}^{-3} \text{ h}^{-1}$ of OVOCs $\gg 124.5 \text{ g m}^{-3} \text{ h}^{-1}$ of monoaromatics) and potential risk attenuation ability toward OVOCs than monoaromatics, due to their higher water solubility and better adsorption affinities ($-40.29 \text{ kcal mol}^{-1}$ of adsorption energy for OVOCs $< -33.32 \text{ kcal mol}^{-1}$ of that for monoaromatics) to the catalyst. The successful application of the integrated ST-PC system in the degradation of targeted VOCs provided us an efficient approach to pertinently purify atmospheric environment and then well improve human health in car repairing business.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jclepro.2017.02.040>.

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