A coupled technique to eliminate overall nonpolar and polar volatile organic compounds from paint production industry

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Abstract

Volatile organic compounds (VOCs) emitted from their manufacturing have a high recycling value but contribute negatively to the environment. Paints as a significant source of VOCs could largely contribute to their emissions. This study employed a pilot scale system for recovery and elimination of highly concentrated VOCs (up to $1.1 \times 10^6$ mg/m$^3$) from a paint packaging workshop, which uses the integrated adsorption-cryogenic condensation with photocatalytic oxidation (PCO). Over a 60-day continuous treatment period, average recovery efficiencies of 96.1%, 100%, 97.1% and 98.6% were achieved for aromatic hydrocarbons (AHs), aliphatic hydrocarbons (AlHs), halogenated hydrocarbons (HHs) and oxygenated VOCs (OVOCs), respectively. Data analysis and theoretical calculations confirmed that nonpolar VOCs were preferentially adsorbed, enriched and recycled by activated carbon adsorption (AHs, AlHs and OVOCs > HHs), while residual polar VOCs were subject to subsequent PCO decomposed with average removal efficiency of –10.2% to 79.4%. PCO displayed a higher degradation activity toward polar VOCs (OVOCs > AHs > AlHs). Furthermore, high non-cancer, cancer risks and occupational exposure cancer risks were found as exposed to the emitted VOCs, and a dramatic reduction of the risks were achieved after treatment. This coupled recovery-decontamination techniques illustrated an excellent recoverability to nonpolar VOCs and efficient decomposition activity to polar VOCs, to eliminate almost emitted VOCs, with promising potential application in atmospheric purification and improvement of occupational environments.

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1. Introduction

In 2014, more than 43 million tons of paints had been produced globally with an annual rate of increase of ca. 5%. Paints as a major source of VOC emissions contributed negatively to the environment during manufacturing processes. And it has been reported that over 0.02 kg of VOCs are released into the atmosphere per kg of paint through studies on automotive paint production procedures (Papasavva et al., 2001; Dinh et al., 2016). Besides, long-term exposure to emitted VOCs is associated with serious effects on both occupational and public health (Lerner et al., 2012; Ramirez et al., 2012). Another reason about the discharged VOCs from industries such as paint manufacturing needing to be avoided is that they are relatively pure. This means that they have a high potential recycling value, if the particulates were removed. Therefore, the strategic coupling of both recovery and decontamination techniques are greatly needed, not only to accomplish high value organic solvent recovery, but also to effectively eliminate VOCs emission from paint production facilities world-wide.

Recently, various techniques have been applied to VOC removal, but still with limitations. For example, the cryogenic condensation, which allows the direct recovery of VOCs in liquid form, is only cost-effective for very high concentration VOCs ($>10$ 000 ppm) (Gupta and Verma, 2002), which is over ten-fold higher than the concentrations generally emitted from paint factory industries ($<1000$ ppm) (He et al., 2012). Alternatively, carbon adsorption has been established as an effective technique for VOC capture and recovery in lower concentration ranges (parts per million (ppm)) as required for paint manufacture processes (Ghoshal and Manjare, 2002; Dwivedi et al., 2004; Li et al., 2008). It is worthy of note...
that significant limitations still exist as the cost of direct VOC recovery after adsorption is very high due to the complex processes involved (Khan and Ghoshal, 2000) and the inefficient desorption-recovery process may also produce secondary hazardous waste enriched with VOCs (Wang et al., 2001). From these studies, it can be seen that the integration of both methods has been established as being effective in overcoming the limitations of individual condensation and adsorption technologies, displaying a much higher efficiency in the removal and capture of VOCs, than either method alone (Gupta and Verma, 2002). In addition, these integrated adsorption-condensation techniques may be highly suitable for relatively low concentration but high value VOCs recovery, such as in paint factory settings. The adsorption technology allow initial enrichment, increasing the VOC concentration to a level at which it is more practically and economically feasible to recover VOCs using cryogenic condensation, followed by gravity separation and decanting.

Although more than 90% of VOCs can be potentially recovered by adsorption-condensation processes, residual VOCs still pose a significant problem, resulting in high concentrations of some VOCs after adsorption processes due to different properties (Shi and Huang, 2014). These residual VOCs have been established to be dominated with polar varieties, as carbon based adsorbents without any modification have a significantly higher affinity to nonpolar VOCs (Anfruns et al., 2013). The application of TiO₂ based photocatalytic oxidation (PCO) technology may mitigate this issue, because it has been shown to display highly efficient preferential ability to remove polar VOCs (e.g., ethyl acetate > toluene (Chen et al., 2011) and butyl acetate > m-xylene (Palau et al., 2011)). Furthermore, our previous study proved that the PCO technique preferentially removed polar or hydrophilic oxygenated VOCs, over nonpolar or hydrophobic aromatic hydrocarbons in paint spray booth environments (Chen et al., 2017).

Therefore, in the present work, in order to comprehensively verify the preferential activity and removal mechanisms in both adsorption and PCO technologies, their abilities to eliminate four types of VOCs emitted from an industrial paint factory were assessed comparably. Specifically, for the former one technology of adsorption-condensation, was designed to preferentially adsorb and recovery nonpolar VOCs than polar one; while the subsequent photocatalytic technology, mainly designed to the decomposition of residual polar VOCs after the formal recovery process. That is, the two preferential purification technologies were skillfully selected to couple together as a coupled technique of adsorption-condensation with PCO to targeted solve different kind VOCs for the first time. To further evaluate the removal performance and preferential removal ability of adsorption and PCO technology, recovery and degradation efficiencies were considered individually and compared for different polar or nonpolar VOCs, with supporting data established from quantum chemical calculations. Furthermore, health risks to the workers, who exposed to emitted VOCs from the paint packaging workshop (PPW) were also evaluated pre- and post-treatment with the coupled technique applied continuously throughout a 60-day operational period.

2. Experimental section
2.1. Integrated experimental setup

The experiment was conducted in a PPW (detail description of the PPW could be found in our previous paper (He et al., 2012)) between January and March 2016. All experiments were performed in a custom-made integrated recovery-decontamination stainless steel system (Fig. S1), with an exhaust fan mounted at the end of the system to directly introduce PPW waste gas into the reactor (recovery unit followed by the PCO unit) at a rate of 1000 m³ h⁻¹.

The recovery unit (2590 mm × 1125 mm × 2000 mm) contained three major components: 1) two honeycomb activated carbon beds (1000 mm × 1000 mm × 200 mm for each); 2) a thermal desorption system; and 3) a cryogenic condensation system. When the adsorption process was complete (duration for ca. 30 min), clean heated air generated by the thermal desorption system was applied to the activated carbon bed by exhaust pump, allowing desorption of enriched VOCs, which were then carried out by air-flow through the condenser with a lowest temperature of ~18 °C to recover organic solvents (duration for ca. 60 min).

The PCO unit (1020 mm × 1255 mm × 1350 mm) containing an integrated reactor of electrostatic precipitation and PCO with ozonation unit, which was previously successfully applied to long-term VOC purification in electronic waste recycling industry environments (Chen et al., 2016) and was directly employed in the present study without any modification. The detail description of experimental conditions were listed in Table S1.

2.2. Sample collection and analysis

Gaseous samples were collected at the morning and afternoon of Jan. 22nd and 26th, Feb. 24th as well as Mar. 3rd with total eight times during the continuous operation of the system which were defined as: 1st, 2nd, 3rd, 4th, 5th, 6th, 7th and 8th, to accurately reflect the pollutant level and to assess the stability of the coupled technique in continual VOC purification. The 2.7-L stainless steel canisters (Entech Instruments Inc, SiloniteTM) were used to collect gaseous samples at the inlet and outlet of the recovery unit and the PCO unit outlet. Samples collected were then qualitatively and quantitatively analyzed using an Entech 7100 pre-concentrator (Entech Instruments Inc., CA, USA) and gas chromatography-mass spectrometer (7890A GC-5975CS, MS, Agilent technologies, USA) with the standard United States Environmental Protection Agency (USEPA) TO-15 method, and detailed description of the analytical procedure and conditions can be found in our early published study (Liu et al., 2017).

2.3. Quality assurance and quality control

For each sampling event, triplicate gaseous samples were collected and analyzed within 24 h after collection. Calibration of experimental instrument was conducted prior to all measurements and blank sample analyses revealed no contaminating target compounds within the system. In addition, quality assurance and quality control measurements were performed based on the standard USEPA Compendium Method TO-15, including establishing detection limits, using comparative field blanks and assessing retention time consistency, accuracy, precision and with standard reference sample comparison (USEPA, 1999).

2.4. Theoretical verification

Gaussian 09 software package was used to calculate the adsorption configuration and adsorption energy for specific VOC molecules onto activated carbon or TiO₂, and a detailed description of computation methods provided in Supporting Information (SI).

2.5. Risk assessment

Non-cancer risk, cancer risk and occupational cancer risk from VOCs exposure, were evaluated using standard USEPA methods to assess risks of occupational inhalation of VOCs in a PPW environment, pre- and post-treatment, with detailed calculation process provided in SI.
3. Results and discussion

3.1. VOC level and composition pre- and post-recovery treatment

During paint packing processes in the PPW, a total of 25 VOCs were detected with five dominated species observed to be ethylbenzene (average concentration of $4.1 \times 10^4 \text{mg/m}^3$; 23.1% of total VOCs (TVOCs) concentration); n-heptane (average concentration of $4.0 \times 10^4 \text{mg/m}^3$; 22.3% of TVOCs concentration); xylene (average concentration: $3.1 \times 10^4 \text{mg/m}^3$; 17.7% of TVOCs concentration); bromodichloromethane (average concentration: $3.0 \times 10^4 \text{mg/m}^3$; 17.0% of TVOCs concentration); and styrene (average concentration: $2.3 \times 10^4 \text{mg/m}^3$; 12.9% of TVOCs concentration) (Fig. S2). The aromatic hydrocarbons ethylbenzene, xylene and styrene were clearly the most dominant VOC groups in the PPW environment, which is consistent with the findings of our previous study (He et al., 2012). The detected VOCs were categorized into four groups as listed in Table S2: aromatic hydrocarbons (AHs); aliphatic hydrocarbons (AlHs); halogenated hydrocarbons (HHs); and oxygenated VOCs (OVOCs), with their compositions and concentrations presented in Fig. 1. It was observed that at all eight sampling events, the concentrations of AHs were the highest (ranging from $4.6 \times 10^2$ to $6.3 \times 10^5 \text{mg/m}^3$ with an average of $1.0 \times 10^5 \text{mg/m}^3$), followed by AlHs (ranging from 41 to $2.7 \times 10^5 \text{mg/m}^3$ with an average of $4.0 \times 10^4 \text{mg/m}^3$ with an average of $3.2 \times 10^4 \text{mg/m}^3$), with OVOCs having the lowest detectable concentrations (ranging from 36 to $2.1 \times 10^5 \text{mg/m}^3$ with an average of $4.7 \times 10^3 \text{mg/m}^3$). It is note that the significantly higher concentrations of AHs were observed, which might due to the widespread application of monoaromatic solvents in the paint production industry (Lyu et al., 2016).

To efficiently recycle these high levels of VOCs and subsequently eliminate VOC residues, an coupled technique of adsorption-condensation with PCO was applied, where the nonpolar VOCs (eg, AlHs, AHs) can be efficiently captured and enriched firstly by non-polar activated carbon substrates, which are then condensed to recycle organic solvent. After that, the residual more polar VOCs (eg, HHs, OVOCs) could be decomposed by the subsequent polar TiO2 catalysts based PCO unit, which allowed the combination of recovery with PCO decontamination techniques to completely and effectively purify a wide range of VOCs at pilot scale.

Fig. 1 presents the concentrations of all four groups of VOCs following recovery treatment, where after consecutive treatments of approximately 30 min adsorption and 60 min condensation, the average concentrations of residual AHs, AlHs, HHs and OVOCs, significantly decreased to $3.9 \times 10^3$, 0.21, 9.2 x $10^2$ and 87 mg/m$^3$, with average recovery efficiencies of 96.1%, 100%, 97.1% and 98.6% (Fig. S3), respectively. These findings suggest that the applied combination recovery technique results in excellent removal capability to all four groups of VOCs assessed. Further analysis revealed that the average relative contributions of AHs, AlHs and OVOCs decreased from 79.4%, 8.1% and 2.3% to 51.6%, 0% and 0.6%; while the average relative abundance of HHs significantly increased from 10.2% to 47.8% (Fig. S4), suggesting preferential capture of AHs, AlHs and OVOCs by this recovery system. This effect may be due to the nonpolar properties of these groups VOCs, as opposed to that of HHs (E.g., with the dielectric constants of dichloromethane (9.1) > ethyl acetate (6.1) > ethylbenzene (3.0) and n-heptane (1.9)), reducing the desorption from activated carbon substrate and hence recovered by cryogenic condensation. Cardoso et al., (2008) also observed a phenomenon of higher adsorption capacities to less polar substances such as methyl ethyl ketone, n-hexane and cyclohexane, than more polar substances such as 1,1,1-trichloroethane, on hydrophobic activated carbon (Cardoso et al., 2008). Besides, it has been established that the polarization of VOCs generally show well positive linear relationships with condensation with PCO was applied, where the nonpolar VOCs (eg, AlHs, AHs) can be efficiently captured and enriched firstly by non-polar activated carbon substrates, which are then condensed to recycle organic solvent. After that, the residual more polar VOCs (eg, HHs, OVOCs) could be decomposed by the subsequent polar TiO2 catalysts based PCO unit, which allowed the combination of recovery with PCO decontamination techniques to completely and effectively purify a wide range of VOCs at pilot scale.

Fig. 1. Concentrations of VOCs before and after the treatment by the coupled technique. (a): AHs; (b): AlHs; (c): HHs; (d) OVOCs.
hydrophobic properties of adsorbent (Chen et al., 2011), therefore, the VOCs with higher dielectric constants and therefore more polarity, have a lower adsorption affinity to hydrophobic activated carbon, as found in the present study.

To verify this hypothesis, different VOC adsorption configurations and adsorption energies adsorbed onto activated carbon were investigated in detail with the method of quantum chemistry calculations, using ethylbenzene, n-heptane, dichloromethane and ethyl acetate as examples of AHs, AlHs, HHs and OVOCs, respectively. As shown in Fig. 2, ethylbenzene, n-heptane, dichloromethane and ethyl acetate adsorb onto activated carbon via C, H, Cl and O atoms respectively, forming ethylbenzene-activated carbon, n-heptane-activated carbon, ethyl acetate-activated carbon and dichloromethane-activated carbon complexes, respectively. The corresponding bond distances for adjacent C–C (3.30 and 3.36 Å), C–H (2.69 and 2.76 Å), C–Cl (3.28 and 3.37 Å) and C–O (2.71 Å) bonds were obtained, indicating that four VOC groups are likely to be strongly adsorbed onto activated carbon via covalent bonds. Observations revealed that the longest bond was C–Cl (3.37 Å); with the bond energy of C–Cl (327 kJ mol$^{-1}$) was found to be significantly smaller than that of C–C (346 kJ mol$^{-1}$), C–H (411 kJ mol$^{-1}$) and C–O (358 kJ mol$^{-1}$). These results suggest that weaker bonding exists in the C–Cl bond of dichloromethane-activated carbon complex than for the C–C, C–H and C–O bonds in other activated carbon complexes, respectively, resulting in the C–Cl bond being more easily broken during desorption-condensation processes. Additionally, the calculated adsorption energies of n-heptane-activated carbon, ethylbenzene-activated carbon and ethyl acetate-activated carbon complexes were obtained as −6.05, −8.69 and −33.08 kcal mol$^{-1}$, respectively, all being at least 0.93 kcal mol$^{-1}$ less than the absorption energy of the dichloromethane-activated complex (−5.12 kcal mol$^{-1}$). As expected, all obtained adsorption energies were negative, indicating that these VOCs are adsorbed onto activated carbon surfaces.

![Fig. 2. Adsorption configuration and energy of ethylbenzene (a), n-heptane (b), dichloromethane (c) and ethyl acetate (d) onto active carbon material.](image-url)
via spontaneous chemisorption processes. Therefore, based on both experimental and theoretical findings, it could be concluded that activated carbon preferentially adsors and enriches nonpolar AHs, AlHs and OVOCs, resulting in the release of more polar HHs residue.

As shown in Fig. 55, for the four dominant individual VOCs from all groups, the recovery efficiencies of ethylbenzene (AHs), n-heptane (AlHs), bromodichloromethane (HHs) and ethyl acetate (OVOCs) were all over 95.7%, confirming high recovery activity in this system. In terms of VOC group compositions, taking AHs as an example, as shown in Fig. 56, ethylbenzene and xylene were found to be the two most dominant compounds before (45.5% and 40.5%) and after recovery treatment (36.4% and 35.3%), while a significant increase in the abundance of toluene and benzene was observed, from 2.1% and 1.0% to 19.5% and 5.0% post-recovery, respectively. This phenomenon might be explained higher vapor pressures of benzene (12.7 kPa) and toluene (2.8 kPa) as compared with ethylbenzene (1.33 kPa) and xylene (1.20 kPa), resulting in more rapid volatilization under the same cryogenic condensation conditions, despite having similar dielectric constants (from 2.28 of benzene to 2.45 of ethylbenzene). It is also noted that a similar pattern of findings was established for the other three assessed VOC groups (Figs. S7–S9).

In summary, the above results indicate that the adsorption-condensation recovery technique shows highly efficiently recycling ability to nonpolar VOCs with lower dielectric constants.

3.2. Residual VOC decomposition using PCO

Although almost all emitted VOCs in PPW were successfully recovered by the former adsorption-condensation integrated technique applied, some VOCs emission was still detectable, especially at the 7th sampling event with high concentration (2.7 x 10^6 μg m^-3) (Fig. 1), nearly close to the Guangdong provincial pipe VOC emission standard for surface coating industries (9.0 x 10^4 μg m^-3, DB44/816-2010). This suggests that the concentrations of VOCs after the recovery process still require further purification prior to release into atmospheric environments. In fact, the in-house designed PCO reactor displayed excellent removal activity to AHs, AlHs, HHs and OVOCs, although with a very low total loading concentration of ca. 1.6 x 10^4 μg m^-3 (Chen et al., 2016). Thus, it may be expected that the later PCO reactor would also efficiently eliminate the residual VOCs in the present study. It is noted that the PCO reactor was used subsequently in the present study to assess the ability to abate residual VOCs.

As shown in Fig. S10, for eight times sampling, total VOCs removal efficiencies ranging from −10.2% to 79.4% was achieved using PCO treatment during the whole experiment process, with an average VOC concentrations decreasing from 5.1 x 10^3 to 3.3 x 10^2 μg m^-3 (Fig. 1). It can be found that the removal efficiencies decreased gradually with the increase of treatment time during 60-day period, indicating that some compounds absorbed on to the catalyst and the catalyst need to be regenerated properly. In addition, it worth noting that, a negative removal efficiency (−10.2%) was observed at the 4th sampling event. That is, the total VOC concentration at the outlet after PCO treatment was slightly higher than at the inlet. This is probably due to that the absorbed VOCs released from the catalyst, which resulted in an increase of the VOC concentration at the outlet. Additionally, data shows that the PCO reactor displayed a notable preference in removal among different groups of VOCs (Fig. 3), with average elimination efficiencies of only 29.2% of AHs; 49.6% of OVOCs and 57.8% of HHs. Notably, a negative removal efficiency (−1192.4%) was observed for AHs, which may be due to the generation of n-hexane as a VOC degradation intermediate during PCO processes (Fig. S11).

These findings establish that the PCO degradation efficiency of the four investigated groups of VOCs, follows the order of: AHs < AlHs < OVOCs < HHs. It has been established in the literature that, PCO degradation of organic substances is mainly dependent upon their efficient adsorption onto the catalyst surface (Zhang et al., 2006; An et al., 2011; Kim et al., 2013), with high adsorption affinities to catalysts subsequently accelerating photocatalytic degradation processes (An et al., 2005; Tasbihi et al., 2012). In the present study, during the preparation of the TiO2-based catalyst in a water environment, the hydroxyl groups on the catalyst surface are rapidly enriched, becoming more hydrophilic and inducing higher adsorption affinities of TiO2-based catalyst to polar VOCs with a higher dielectric constant (E.g., dichloromethane (9.1) > ethyl acetate (6.1) > ethylbenzene (3.0) > n-heptane (1.9)). This optimization allows HHs, the dominant residual VOC group emitted after the recovery processes, to be preferentially and efficiently decomposed by PCO, as compared to AHs, AlHs and OVOCs, allowing potentially complete elimination of all emitted VOCs from painting production industry in this study.

To verify this hypothesis and better understand the relationship between degradation activity and adsorption performance as well as physiochemical properties of VOCs and catalysts, the quantum chemical calculations were employed to clarify adsorption configurations and adsorption energies of individual VOC and the TiO2. As shown in Fig. 4, the phenyl C atoms of ethylbenzene; the H atom of n-heptane; Cl atoms of dichloromethane; and O atom of ethyl acetate all interact with Ti atom of TiO2 to form adsorption complexes. Moreover, similar with our previous findings (Chen et al., 2017), these covalent interactions were found to be tight with varying bond distances (E.g., 2.69 and 2.72 Å for ethylbenzene; 2.11 and 2.13 Å for n-heptane; 2.40, 2.75 Å for dichloromethane; and 2.08 Å for ethyl acetate). It was also found that the absolute adsorption energies of ethylbenzene, n-heptane and ethyl acetate onto TiO2 follow the order of: ethyl acetate (−39.34 kcal mol^-1) > ethylbenzene (−31.65 kcal mol^-1) > n-heptane (−18.95 kcal mol^-1), which is consistent with their order of the dielectric constants as well as the degradation efficiencies, indicating that the degradation efficiencies of AHs, AlHs and OVOCs onto TiO2 exhibit a linear correlation with their dielectric constants which was determined parameter to the adsorption performances.

Conversely, an inverse order was established for the adsorption energy of the dichloromethane-TiO2 complex (−17.86 kcal mol^-1) being 1.09 kcal mol^-1 more positive than representatives of the other three VOC groups, despite the highest dielectric constant and degradation efficiency. Alberici and Jardim (1997) observed a similar phenomenon (Alberici and Jardim, 1997), suggesting that dielectric constant is not the only influencing parameter on adsorption performance or degradation efficiency of organics in
PCO systems. It is possible that in the present study, for HHs, other parameters maybe VOC bond energies have a significant influence besides dielectric constant and adsorption ability. For instance, the bond energy of C\(_2\)Cl (327 kJ mol\(^{-1}\)) in dichloromethane was significantly lower than that of C\(_2\)C (346 kJ mol\(^{-1}\)), C\(_2\)H (411 kJ mol\(^{-1}\)), C\(_2\)O (358 kJ mol\(^{-1}\)) and C=O (799 kJ mol\(^{-1}\)) in n-heptane, ethylbenzene and ethyl acetate, respectively. This suggests that the C\(_2\)Cl bond would be easily broken when attacked by strong reactive oxidant species (e.g., \(^{1}\)OH and O\(_3\)), resulting in higher degradation efficiency observed for HHs in the PCO systems.

In summary, the applied adsorption-condensation integrated recovery system has been shown to be effective in recycling of nonpolar VOCs, and the PCO unit mainly contributing to the additional degradation of residual polar VOCs after the former recovery processes. Therefore, the use of combined techniques as presented here with can effectively recycle and eliminate mixed VOCs, demonstrating the high potential of this coupled technique in applications in atmospheric emissions purification at PPW sites.

### 3.3. Risks assessment

To evaluate the ability of the coupled technique to reduce potential risk to non-cancer and cancer risks caused by long-term VOC exposure, risks were firstly evaluated according to standard USEPA risk assessment methods (An et al., 2014). Herein, 20 kinds of VOCs were selected to assess non-cancer risks and 9 kinds of VOCs are selected to assess cancer risks, and the details are listed in Table S3. As shown in Fig. 5, the average HRs less than 0.1 were found for cyclohexane (0.09); chloroethane (0.01); dichloromethane (0.08); and methyl methacrylate (0.08); suggesting that they are below the defined level of concern according to standard methods (Ramirez et al., 2012). Average HRs that exceeded the defined level of potential concern (from 0.1 to 1) were obtained for toluene (0.48); styrene (0.34); n-hexane (0.53); and 1,2-dichloropropane (0.12); while some were found to present a higher level of concern (>1), such as 1,2-dichloroethane (1.32); chlorobenzene (7.86); and methyl butyl ketone (7.78). Notably, some HRs were found to be well above the defined level of concern as compared with reference data (McCarthy et al., 2009), as found for benzene (11.70); ethylbenzene (41.01); xylene (538.75); trimethylbenzene (30.07); n-heptane (98.93); bromodichloromethane (1507.35); 1,1,2,2-tetrachloroethane (324.21); benzyl chloride (148.76); and ethyl acetate (63.28).

Alternatively, the average potential cancer risk posed from bromodichloromethane (11.2 in average); ethylbenzene (1.03 × 10\(^{-1}\) in average); 1,1,2,2-tetrachloroethane (2.07 × 10\(^{-2}\) in average); 1,1,2-trichloroethane (1.04 × 10\(^{-2}\) in average); benzyl chloride (7.29 × 10\(^{-3}\) in average); benzene (2.74 × 10\(^{-3}\) in average); and 1,2-dichloroethane (2.41 × 10\(^{-4}\) in average); were all found to pose a definite risk as shown in Fig. 6, based on established risk level classification methods (Sexton et al., 2007).

As shown, the VOCs emitted during PPW processes, present...
high levels of both non-cancer and cancer exposure risks, resulting in an urgent need to purify prior to discharge into the atmospheric environment. The pattern in reduction of VOC concentrations, corresponds to the reduction in both non-cancer and cancer risks for all investigated VOCs after the recovery unit treatment was also checked (Figs. 5 and 6). For example, the reduction in non-cancer risks were found to be significant for bromodichloromethane (from 1507.35 to 0); benzyl chloride (from 148.76 to 0); n-heptane (from 98.93 to 0); and methyl butyl ketone (from 7.78 to 0); as well as significant reduction in cancer risks for bromodichloromethane (from 1.12 to 0); 1,1,2,2-Tetrachloroethane (from 2.07 × 10^{-2} to 0); and benzyl chloride (from 7.29 × 10^{-1} to 0). However, due to the notably enriched concentrations of some VOCs during the recovery process, the HRs and LCRs of some VOCs were observed to remain high (e.g., 16.27 for xylene; 9.72 for 1,1,2-trichloroethane; 4.37 × 10^{-3} for ethylbenzene; and 5.95 × 10^{-4} for benzene).

Data shows that beneficially, both non-cancer and cancer risks were further reduced to below 0.1 and 10^{-4} after subsequent treatment by PCO, respectively, showing that PCO technology has high VOC risk reduction capability, consistent with our previous findings (He et al., 2012; Chen et al., 2016). It is that the HRs observed for xylene (10.65) and 1,1,2-trichloroethane (4.18), as well as the LCRs for ethylbenzene (3.31 × 10^{-3}) and benzene (3.80 × 10^{-4}), were still high after treated by the integrated technique of recovery with decontamination, suggesting that they pose a high potential risk to the workers in PPW. Therefore, even with the implementation of this system, effective ventilation systems still need to be further developed and optimized to ensure PPW occupational protection.

The methods specified by American Conference of Industrial Hygienists were also applied to assess the occupational exposure cancer risks of 19 VOCs detected in the present system (Table S4). As shown in Fig. 7, the average $E_i$ values of xylene, benzene and ethylbenzene, presented risk levels higher than 0.1 prior to treatment, revealing possible harmful effects associated with occupational PPW exposure. While the $E_i$ values of overall VOCs was reduced to lower than 0.1 after the treatment by integrated technique of recovery with PCO, suggesting that the applied integrated recovery-decontamination technique effectively reduces occupational exposure cancer risks in paint industrial environments.

4. Conclusion

In this study, a pilot-scale integrated technique of recovery with...
Fig. 6. Lifetime cancer risk of VOCs before and after the treatment by the coupled technique.

Fig. 7. Occupational exposure risk of VOCs before and after the treatment by the coupled technique.
decontamination technology was developed for the first time to evaluate complete elimination of mixture VOCs with the coupled technique of recycling with decomposition as well as the reduction in health risk. Results showed that the integrated technique displayed excellent recovery efficiencies, residue elimination and effective attenuation of potential risk for the overall VOC species, due to its complete abatement possibility to both nonpolar and polar VOCs emitted from paint industrial workshop by the newly-developed active carbon recovery-photocatalytic decontamination technique. The successful application of this integrated system in the recycling of valuable VOCs, as well as the degradation of residual VOCs, provides a new approach to atmospheric environment purification. The application will also improve public and occupational health in solvent production industries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jclepro.2018.03.037.

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