

ORIGINAL ARTICLE

Removal and mineralization of toluene under VUV/UV lamp irradiation in humid air: Effect of light wavelength, O_2 and H_2O



Xue Sun^a, Wenhui Wang^{a,*}, Chaolin Li^{a,b,*}

^a School of Civil and Environmental Engineering, Harbin Institute of Technology, Shenzhen 518055, China ^b State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa

Received 13 April 2022; accepted 4 July 2022 Available online 8 July 2022

KEYWORDS

VUV/UV lamp; In humid air; VOCs; Degradation pathways; VUV/UV photodegradation Abstract VUV/UV photodegradation is a promising method that utilizes energetic photons and reactive oxygen species (ROS) generated via the photo-dissociation of H_2O and O_2 to degrade VOCs. In the paper, we investigated the efficiency of removal and mineralization in humid air and the effects of key factors. Toluene of 4–20 ppm can be almost completely removed in 60 s and mineralization efficiency is above 55% at 25 min. 185 nm ultraviolet light plays a key role in the rapid removal and mineralization of toluene. Appropriate amount of O_2 and H_2O promote the removal of toluene due to the generation of ROS. Based on the intermediates and degradation pathway analysis, it is found that in the presence of O_2 , degradation pathways of toluene are more abundant and fewer linear-chain aldehydes are produced, thus resulting in higher mineralization efficiency. This work highlights the importance of practical application of VUV/UV photodegradation in humid air.

© 2022 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Volatile organic compounds (VOCs) are one of the most common air pollutants (Zhu et al., 2013; Wu et al., 2019; Zhang et al., 2021). They contribute to the formation of photochemical smog and tropospheric

Peer review under responsibility of King Saud University.



 O_3 (Hui et al., 2019), which have adverse effects on the global environment (Finlayson-Pitts and Pitts, 1997; Ji et al., 2017) and cause persistent harm to human health (Heymes et al., 2006; Huff, 2007; Wu et al., 2019). With the increasing emission of VOCs, various technologies have been used to decompose VOCs. Thereinto, VUV/UV photodegradation is proved to be a promising method due to its high removal efficiency of VOCs and mild operation condition (Wang and Ray, 2000; Chen et al., 2010; Huang et al., 2014; Huang et al., 2016a; Kang et al., 2018).

The low-pressure mercury lamp emitting 254 nm and a small proportion of 185 nm ultraviolet light is commonly used as the light source (Sayed et al., 2016). There are generally three ways to degrade gaseous VOCs in the VUV/UV photodegradation process, including the direct photolysis by energetic photons, the oxidation of reactive oxygen species (ROS) generated from O_2 photo-dissociation, and the oxidation of

https://doi.org/10.1016/j.arabjc.2022.104108

1878-5352 © 2022 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

^{*} Corresponding author.

E-mail addresses: wangwenhui@hit.edu.cn (W. Wang), lichaolin@ hit.edu.cn (C. Li).

·OH generated from H₂O photo-dissociation or the reaction between O (¹D) and H₂O (Chen et al., 2002; Jeong et al., 2004; Ye et al., 2013; Huang et al., 2016b). Thus, high-energy photons, O₂ and H₂O are the key factors in the VUV/UV photodegradation. Cheng et al. (2011) observed that the removal rate of α -pinene increased with the increasing relative humidity (RH) in N2. In the presence of O2, the removal rate or efficiency of VOCs increased first and then stayed stable or decreased with the increasing RH (Cheng et al., 2011; Huang et al., 2014). Ye et al. (2013) found that H₂O₂ content increased obviously first and then increased slightly with the H₂O content ranging from 2% to 12% in the presence of O₂, indirectly indicating the effect of H₂O on ·OH production. Besides, the introduction of O₂ can improve the removal of VOCs (Koh et al., 2004; Mohseni et al., 2005; Yu et al., 2012). For example, Wang and Ray (2000) presented that the removal rate of toluene in pure O2 was faster than that in the air. Although there were many studies, the in-depth mechanism of the effect of energetic photons, H₂O and O₂ on the removal and mineralization of VOCs is still unclear.

In this study, the removal and mineralization of toluene in the humid air were explored in a closed-loop reactor. Toluene, as one of the common and representative VOCs, was selected as the target substance (Huang et al., 2011). Toluene has been attempted to remedy via VUV/UV photodegradation coupled with photocatalytic oxidation process or wet scrubbing process (Wu et al., 2019; Liang et al., 2020; Wu et al., 2021; Zhang et al., 2021; Xie et al., 2022). The effects of light wavelength, H₂O, and O₂ on the removal and mineralization of toluene were comprehensively discussed. Moreover, the degradation pathways of toluene with and without O₂ and H₂O (i.e., N₂ with 80% RH, air with less than 3% RH, and air with 80% RH) were investigated to reveal the in-depth understanding on the effect of O₂ and H₂O in the VUV/UV photodegradation.

2. Materials and methods

2.1. Materials

Toluene (chromatographic grade) was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). The purified air, N_2 , and O_2 (99.9%) were supplied from Xiangyuan Gas Company (Dongguan, China).

2.2. Equipment setup

The experiments of VUV/UV photodegradation were conducted in a closed-loop reactor with an effective volume of 0.68 L. A 10 W low-pressure lamp (ZW10D15Y-212, Cnlight, Guangzhou, China) with 90% output at 254 nm and 10% at 185 nm was placed inside a quartz cylinder reactor (185 mm in length and 70 mm in diameter). For comparison, a UV lamp with about 100% output at 254 nm (10 W, ZW10D15W-212, Cnlight, Guangzhou, China) was used to evaluate the effect of wavelength on the removal and mineralization of toluene. Fig. 1 is the schematic diagram of experimental device.

The RH of 20%, 40%, 60%, and 80% corresponds to the moisture concentration of 4.6 g/m³, 9.2 g/m³, 13.8 g/m³, 18.4 g/m³ at 25 °C, respectively. The corresponding volume of ultrapure water was injected into a Teflon gas sampling bag filled with 46 L dry N₂/air/O₂. Hot wind was used to accelerate the vaporization of water in the gas sampling bag. When vapor was evenly distributed in the air sampling bag, the required gas with a certain RH was prepared. A certain volume of toluene liquid was injected into the Teflon gas sampling bag. When the toluene liquid was completely volatilized and evenly distributed in the gas sampling bag, the desired gas



Fig. 1 Schematic diagram of experimental device.

was prepared. The gas was pumped into the reactor by a micro-diaphragm pump at a flow rate of 0.6 L min⁻¹. After 40 min, when the humidity and toluene concentration in the reaction were stable, the intake process was stopped and then the reactor was switched to closed-loop control. The initial concentrations of toluene, CO and CO₂ were measured while the gas in the reactor was circulated by the micro-diaphragm pump at a flow rate of 0.6 L min⁻¹. The sampling time for degradation reaction and GC detection was controlled by switching the light on and off. The gas was sampled over time to detect the concentrations of toluene, CO, and CO₂. All experiments were repeated two or three times to confirm their accuracy.

2.3. Analysis methods

2.3.1. Toluene analysis

The concentration of toluene was analyzed by a gas chromatograph (GC) (9790I, Fuli, Zhejiang, China) equipped with a flame-ionization detector (FID) and a capillary column (KB-5, 30 m × 0.32 mm × 0.5 µm). The temperature of vaporizer and detector were both 200 °C and the column temperature was 80 °C. Toluene concentration was determined via the standard curve ($\mathbb{R}^2 = 0.9989$).

2.3.2. Mineralization efficiency

The mineralization of toluene ends with the formation of CO_2 and H_2O in the gas phase (Govindan et al., 2012; Pham et al., 2016). The concentrations of CO_2 and CO were detected by a GC (SP-6890, Lunan Rui Hong, Shandong, China) equipped with an FID and a methanizer. A packed column (GDX-502, 4 m × 3 mm) was used. The temperatures of vaporizer, column, detector 1 and detector 2 were 120 °C, 80 °C, 140 °C and 360 °C, respectively. The concentrations of CO_2 and CO were measured by a standard curve calibrated with standard gas ($R^2 = 0.99991$ and 0.99988).

The mineralization efficiency was calculated from the following equation:

Mineralization efficiency(%) =
$$\frac{C_{\text{tCO}_2} - C_{0\text{CO}_2}}{n \times C_0} \times 100\%$$

where, *n* is the number of carbon atoms in toluene, C_0 and C_{0CO_2} are the concentrations of toluene and CO_2 at the reaction start time ($t_0 = 0$), respectively. C_{tCO_2} is the concentrations of produced CO_2 at reaction time ($t_i = t$).

2.3.3. Intermediates identification

The gas sample was injected into the gas chromatographymass spectrometer (GC–MS, 7890B GC-5977B MS, Agilent Technologies, USA) to identify intermediates. An HP-5 column (60 m × 0.32 mm × 0.25 μ m, Agilent Technologies, USA) was used with GC column temperature program: 40 °C for 3 min, increased to 220 °C at a rate of 5 °C min⁻¹ and held for 2 min. The carrier gas was ultrahigh pure helium at a constant flow rate of 1 ml min⁻¹ with a splitless inlet. The injector temperature was held at 260 °C and the temperature of the transfer line and the ion source were both held at 230 °C. The MS was equipped with an Electron Impact Ionization Detector (EID), which was operated in full scan mode with ionization energy set to 70 eV and a scan range of 50–560 amu.

3. Results and discussion

3.1. Efficient removal and mineralization of toluene via VUV/ UV photodegradation

The removal and mineralization of toluene with concentration ranging from 4 to 20 ppm were carried out in humid air with 80% RH via VUV/UV photodegradation. Fig. 2(a) presents that the ultrafast removal of toluene can be achieved via VUV/UV photodegradation in air with 80% RH. Specifically, despite of the initial concentration in 4–20 ppm, more than 95% and 99% of the toluene is removed in 15 s and 60 s, respectively. The removal rate of toluene at a lower concentration is faster. This is because the number of photons and ROS is constant, thus each toluene molecule can collide with more photons and ROS when toluene concentration is lower. Fig. 2(b) shows that the removal amount of toluene increases with the increasing toluene concentration. The reason is that photons and ROS in the system have higher utilization at higher concentration toluene as the photons and ROS have more chance to collide with the surrounding toluene molecules at higher toluene concentration.

Fig. 3 presents the mineralization efficiency of toluene and generated CO_2 concentration. Mineralization efficiency of toluene of 4 ppm is 57.3% at 25 min. Although the toluene concentration is increased from 4 ppm to 20 ppm, its mineralization efficiency still maintained at 55.3%. The formation of refractory intermediates is a possible reason that toluene is not completely mineralized. Moreover, it is found that CO_2 concentration increases with the increase of toluene concentration. The reason is same with that of the variation in removal amount, namely higher utilization of photons and ROS in the case of higher concentration of toluene.

Therefore, VUV/UV photodegradation can completely remove toluene in a relatively short time in humid air and achieve a favorable mineralization efficiency. The roles of light wavelength, O_2 , and H_2O in the process are discussed below.

3.2. Effect of light wavelength

The low-pressure mercury lamp used in the VUV/UV photodegradation process emits ultraviolet light with wavelengths of 254 nm and 185 nm. To distinguish the contributing wavelength for toluene degradation, an experiment using a UV lamp emitting a single wavelength light of 254 nm was carried out.

Fig. 4(a) exhibits the removal of 20 ppm toluene under VUV/UV lamp irradiation and under UV lamp irradiation in air with 80% RH. Under VUV/UV irradiation, it is at 15 s that more than 95% toluene is removed. However, under UV lamp irradiation, it takes 120 min to reach the removal efficiency of about 91%. The removal of toluene is found to follow the first-order kinetic model, as shown in the insert of Fig. 4(a). The removal rate constant of toluene under VUV/UV irradiation is 0.1772 s^{-1} , which is 443 times higher than the removal rate constant of 0.0004 s^{-1} under UV irradiation. For mineralization, 55.3% of toluene is converted to CO₂ and H₂O under VUV/UV lamp irradiation and no CO₂ is produced under UV lamp irradiation (Fig. 4(b)). The rapid degradation



Fig. 2 (a) Removal efficiency and (b) removal amount of toluene at initial concentrations ranging from 4 to 20 ppm in the air with 80% RH.



Fig. 3 Mineralization efficiency and generated CO_2 concentration at initial concentrations of toluene ranging from 4 to 20 ppm in the air with 80% RH. The reaction time is 25 min.

of VUV/UV system can be ascribed to (1) high energy of 185 nm ultraviolet light (6.7 eV) that is higher than the energy of photons at the wavelength of 254 nm (4.88 eV) (Kaneko et al., 2018; Singh et al., 2020) and can break the chemical bonds of toluene (Table 1); (2) 185 nm ultraviolet light can generate ROS through interacting with O_2 and H_2O in the system. The reactions of the generation of ROS are shown in Fig. 5 (Atkinson et al., 2004; Ye et al., 2013; Zhan et al., 2018).

To elucidate the contribution of direct photolysis, degradation experiments of 20 ppm toluene were carried out in dry N₂ with less than 3% RH. As shown in Fig. 6, about 96% of toluene is removed at 90 s via the direct photolysis of photons at 185 nm and 254 nm and about 94% of toluene is removed at 120 min via the direct photolysis of photons at 254 nm. The removal rate constant under VUV/UV lamp irradiation, which obtained via first-order kinetic model, is about 73 times higher than that under UV lamp irradiation (0.0293 s⁻¹ vs. 0.0004 s⁻¹). It indicates that direct photolysis of energetic photons at 185 nm obviously promotes the removal of toluene. In addition, under VUV/UV lamp irradiation, removal rate constant of toluene in humid air is larger than that in dry N₂ (0.1772 s⁻¹ vs. 0.0293 s⁻¹). Thus, the oxidation of ROS gener-

 Table 1
 Bond energy of chemical bonds of toluene (Kohno et al., 1998; Yang et al., 2020).

Chemical bond	bond energy (eV)
C ₆ H ₅ -CH ₃	4.14
C ₆ H ₅ CH ₂ -H	3.7
C-C ₅ H ₅ CH ₃	5.0-5.5
H-C ₆ H ₄ CH ₃	4.19



Fig. 5 Reactions of the generation of reactive oxygen species (ROS).

ated from the photo-dissociation of H_2O and O_2 also contributes to the fast removal of toluene. The roles of H_2O and O_2 on toluene degradation will be further discussed below.

3.3. Effect of O_2

Experiments were carried out in the N₂, air, and O₂ with 80% RH to investigate the effect of O₂ on the removal and mineralization of toluene. The removal efficiency of toluene in the three atmospheres can reach above 99.0% at 60 s, as shown in Fig. 7. It can be clearly observed that the presence of O₂ improves the removal rate of toluene. This is because the photo-dissociation of O₂ can generate O(¹D), O(³p) and O₃, where O(¹D) would further react with H₂O to generate OH



Fig. 4 Effect of light wavelength on toluene (a) removal and (b) mineralization in the air with 80% RH.



Fig. 6 Effect of light wavelength on (a) toluene removal and (b) removal rate constant in dry N_2 with less than 3% RH.



Fig. 7 Effect of O_2 on the removal of 20 ppm toluene in humid atmospheres.

according to Fig. 5. Thus, more O_2 promotes the generation of more ROS, which in turn improves the removal rate of toluene. However, the removal rate of toluene in O_2 atmosphere hardly increases when compared with that in air atmosphere, which indicates that the excess O_2 contributes little to the removal of toluene. Therefore, it is more practical to remove toluene in humid air in term of the application of VUV/UV photodegradation.

It can be seen in Fig. 8 that the mineralization efficiency of toluene in humid air is the highest at 55.3%, followed by in humid O_2 at 45.2%, and the mineralization efficiency of toluene in humid N_2 is the lowest at 41.9%. On one hand, the mineralization efficiency in the presence of O_2 is higher than that in humid N_2 due to the generation of more ROS. On the other hand, excessive O_2 decreases the mineralization efficiency of toluene. This may be due to the fact that excess O_2 hinders the absorption of photons by toluene and H_2O , which inhibits direct photolysis and photo-dissociation of H_2O to generate $\cdot OH$. Moreover, $O(^1D)$ will be consumed by excess O_2 , reducing the opportunity to react with H_2O and decreasing the generation of $\cdot OH$. As a result of compromise of these two effects, toluene has a higher mineralization efficiency of the set.



Fig. 8 Effect of O_2 on the mineralization of 20 ppm toluene in humid atmospheres.

ciency in humid air. It is more efficient and cost-effective for the application of VUV/UV photodegradation in the air with 80% RH.

3.4. Effect of H_2O

The effect of H_2O content on the removal of 20 ppm toluene was conducted in the air and N_2 with the RH ranging from 0% to 80%. As can be seen from Fig. 9(a), toluene is almost completely removed in 60 s in humid N_2 , and the removal rate increases with the increase of RH. This phenomenon can be easily understood as more H_2O would generate more $\cdot OH$ via H_2O photo-dissociation. In the experiments with humid air, the removal rate of toluene improves as the RH increases from 0% to 60%, while the removal rate of toluene hardly improves when the RH is further increased to 80%, as shown in Fig. 9(b). The different trend in humid air and humid N_2 should be caused by the interaction between H_2O and O_2 .

In the presence of H_2O and O_2 , OH is produced through the photo-dissociation of H_2O and the reaction between O_2 derived $O(^1D)$ and H_2O . Because the absorption cross section



Fig. 9 Effect of RH on the removal of 20 ppm toluene (a) in the N_2 and (b) in the air.

of H₂O at 185 nm is higher than that of O₂ (7.2 \times 10⁻²⁰ cm²molecule⁻¹ vs. 1.2×10^{-20} cm² molecule⁻¹) (Creasey et al., 2000), photo-dissociation of H₂O is easier than the photodissociation of O_2 to derive $O(^1D)$. Therefore, more H_2O will hinder the generation of $O(^{1}D)$, which reduces the generation of OH based on the chain reaction related with O2. Moreover, the reaction between $O(^1D)$ and H_2O occurs more easily than the reaction of O_3 generation between O and O_2 , because the former rate constant is greater than that of the latter (i.e., 2.2 \times 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ vs. 6.0 \times 10⁻³⁴ cm³molecule⁻¹ s⁻¹) (Atkinson et al., 2004). In addition, more H_2O generates more $\cdot H$ and $\cdot HO_2$ to consume O_3 derived from O_2 via Eqs. (1)-(2). As a result, the interaction between H_2O and O₂ may hinder production of ROS (·OH and O₃) in the system via complex chain reactions. This effect is competing with the fact that more OH will be generated from H₂O photo-dissociation, leading to an optimal ratio of H_2O to O_2 in the system and thus an optimal RH in the air.

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{1}$$

$$H + O_3 \rightarrow OH + O_2 \tag{2}$$

The mineralization efficiency is about 55–60% in the air with RH ranging from 0% to 80%, as shown in Fig. 10. In the first 2 min, toluene is rapidly mineralized into CO_2 , and after 2 min, CO_2 is slowly produced. In the air with a RH of 20%, the mineralization rate of toluene is slightly faster. Overall, the effect of H₂O on the mineralization of toluene in air is not significant.

In conclusion, the removal efficiency and mineralization efficiency of toluene can reach above 99% and 55–60% in the air with the RH of 0%-80%, respectively. Although the presence of H_2O has little effect on toluene mineralization, it can improve the removal rate of toluene. Therefore, the degradation of toluene in humid air is practical and cost-effective.

3.5. Intermediates and degradation pathways of toluene

To clarify the effect of O_2 and H_2O derived ROS on the degradation pathway of toluene, the intermediate evolution during the degradation of toluene in the air with 80% RH, in the air with less than 3% RH and in the N₂ with 80% RH were



Fig. 10 Effect of RH on the mineralization of 20 ppm toluene in the air.

tracked by GC–MS over time. The results are shown in Table 2. According to the detected intermediates and previous studies, the degradation pathways of toluene are proposed and presented in Fig. 11.

(1) Degradation pathways in the air with 80% RH.

There are three reaction pathways for toluene degradation in the air with 80% RH, including (1) hydrogen abstraction, (2) •OH addition, and (3) demethylation, as shown in Fig. 11 (a).

The energy of C-H bond on the methyl group is the smallest among the chemical bonds in toluene (3.7 eV) (Ogata et al., 2002; Yang et al., 2020). The primary pathway of toluene degradation is to abstract the hydrogen of methyl group by energetic photons, ·OH and ·O, resulting in the generation of benzyl radical (Huang and Li, 2011; Einaga et al., 2013; Shayegan et al., 2018; Zhan et al., 2018; Shu et al., 2019). Benzyl radical is oxidized to form benzaldehyde by ·OH/·O (Xia et al., 2018; Jafari et al., 2019). Besides, H-abstraction of methyl group by ·OH can also generate benzyl alcohol

Table 2	Intermediates	detected	in 1	three	atmospheres
---------	---------------	----------	------	-------	-------------

Compound	Peak time (min)	Structural formula	Detected in		
			N ₂ with 80% RH	Air with less than 3% RH	Air with 80% RH
Hexanal	5.295		•		
Heptanal	8.37		•		•
<i>p</i> -Benzoquinone	8.888				•
4-Methyl-2-heptanone	9.758		•		
Benzaldehyde	10.227		•	•	•
6-Methyl-2-heptanone	10.27	<u>он</u>	•		
Phenol	11.025				•
6-Methyl-5-hepten-2-one	11.152		•		•
4,6-Dimethyl-2-heptanone	11.372		•		
Octanal	11.645		•		
Methyl-p-benzoquinone	11.951		•		•
1-Methyl-4-(1-methylethenyl)-cyclohexene	12.473		•		
Benzyl alcohol	12.683				•
3,3,5-Trimethylcyclohexanol	13.179				•
2,6-Heptanedione	13.273	CH ₃	•		
p-Cresol	13.328	HO	•	•	•
Acetophenone	13.636				•
1-Octen-5,7-dione	14.11		•		
Nonanal	14.848	OH OH	•	•	•
2,4-Dimethylcyclohexanol	16.727	$\mathbf{\hat{\mathbf{Y}}}$	•		
2-Nonen-1-ol	16.815	ОН			•
Decanal	17.867		•	•	•

(continued on next page)

 Table 2
 (continued)

Compound	Peak time (min)	Structural formula	Detected in		
			N ₂ with 80% RH	Air with less than 3% RH	Air with 80% RH
2,4-Dimethylbenzaldehyde/ 3,4-Dimethylbenzaldehyde	18.137		•	•	•
4-Methoxybenzaldehyde	19.255			•	•
1,2-Epoxydodecane	20.704	\sim	•	•	
Phthalic anhydride	20.902			•	•
3,3,5-Trimethylcyclohexyl acetate	21.69				•
3,3,5-Trimethylcyclohexyl methacrylate	21.883	- Lo	•		•
1-Isopropyl-1,4,5-trimethylcyclohexane	22.61			•	•
Dodecanal	23.387		•	•	
2,6-Bis(1,1-dimethylethyl)-2,5- cyclohexadiene-1,4-dione	24.902		•	•	•
3,3,5-Trimethylcyclohexyl isobutyrate	25.48	Ϋ́́			•
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	28.014	La that			•
Pentadecanal	28.3		•	•	
3,5-Di- <i>tert</i> -butyl-4-hydroxybenzaldehyde	31.716	XXX	•	•	
<i>n</i> -hexadecanal	32.729		•		

(Sleiman et al., 2009) that can be further oxidized to benzaldehyde by ·OH/·O. Further oxidation of benzyl alcohol and benzaldehyde will lead to the opening of aromatic ring (Van Durme et al., 2007; Sleiman et al., 2009; Huang and Li, 2011; Xia et al., 2018; Shu et al., 2019).

The addition of \cdot OH to aromatic ring of toluene leads to the formation of *p*-cresol (Sleiman et al., 2009; Zhan et al., 2018). The oxidation products of *p*-Cresol are methyl*p*-benzoquinone (Chen et al., 2020) and *p*-hydroxybenzaldehyde.

Third reaction pathway is the demethylation of toluene to generate phenol. The bond of C_6H_5 -CH₃ can be broken by energetic photons to form phenyl radical and methyl radical.

Phenol is the oxidation product of phenyl radical and can be further oxidized and undergo double bond rearrangement to form *p*-benzoquinone (Zhang et al., 2006; Huang et al., 2016b; Yang et al., 2020).

While above intermediates are decomposed by ROS and energetic photons, they also react with methyl or alkyl radicals to generate substances with more complex structures. 2,4-Di methylbenzaldehyde/3,4-dimethylbenzaldehyde, 2-methylbenzaldehyde, and acetophenone are the products of the reaction of benzaldehyde and methyl radical. 2-Methylbenzaldehyde is oxidized to phthalic anhydride. 4-methoxybenzaldehyde is generated through the reaction of *p*-hydroxybenzaldehyde



Fig. 11 Degradation pathways of toluene (a) in the air with 80% RH, (b) in the air with less than 3% RH, and (c) in the N_2 with 80% RH. The substances framed are speculated.

and methyl radical. *p*-Benzoquinone and methyl-*p*-benzoquinone react with alkyl radicals to generate 2,6-bis(1,1 -dimethylethyl)-2,5-cyclohexadiene-1,4-dione.

(2) Degradation pathways in the air with less than 3% RH

It is inferred that there are also three reaction pathways for toluene degradation in the air with less than 3% RH according to the detected intermediates (Fig. 11(b)). But the pathways are slightly different from that in the air with 80% RH. Benzaldehyde is detected, but benzyl alcohol and acetophenone are not detected in the air with less than 3%. This indicates that there isn't the reaction of H-abstraction of methyl group to generate benzyl alcohol in the pathway of hydrogen abstraction. And the reactions of benzaldehyde and methyl radical are fewer than that in the air with 80% RH. During the pathway of ·OH addition, p-cresol is oxidized to p-hydroxybenzaldehyde, and the reaction of the oxidation of p-cresol to methyl-pbenzoquinone doesn't occur. In addition to 4-methoxybenzaldehyde, 3,5-di-tert-butyl-4-hydroxybenzaldehyde detected in the air with less than 3% RH is another product of the reaction between *p*-hydroxybenzaldehyde and methyl/alkyl radicals.

(3) Degradation pathways in the N_2 with 80% RH.

Reaction pathways for toluene degradation in the N_2 with 80% RH are significantly fewer than that in the air with 80% RH and in the air less than 3% RH, as shown in Fig. 11(c). During the pathway of hydrogen abstraction, there isn't the reaction to generate benzyl alcohol. The products between benzaldehyde and methyl radical are fewer than that in the air, only 2,4-dimethylbenzaldehyde/3,4-dimethylbenzal dehyde is detected. Moreover, *p*-Hydroxybenzaldehyde reacts with alkyl radicals to form 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, but not 4-methoxybenzaldehyde. In addition, no evidence shows that toluene can be degraded via demethylation pathway in the N₂ with 80% RH. 2,6-Bis(1,1-dimethyle thyl)-2,5-cyclohexadiene-1,4-dione is more likely generated by the reaction of methyl-*p*-benzoquinone and methyl/alkyl radicals in the \cdot OH addition pathway.

Further decomposition of these aromatic intermediates by ROS and energetic photons leads to the opening of aromatic rings. Some intermediates are further oxidized into CO₂ and H₂O, others are not completely degraded. As shown in Table 2 and Fig. 11, linear-chain aldehydes are generated after the cleavage of aromatic ring in all three atmospheres, which may be responsible for the incomplete mineralization of toluene. More linear-chain aldehydes are produced in humid N₂ due to the effect of ROS. Correspondingly, the mineralization efficiencies of toluene in dry air and in humid air are 56.7% and 55.3%, respectively, higher than 41.9% in humid N₂. It demonstrates that the presence of O₂ contributes to higher mineralization efficiency by increasing the reaction pathways of toluene and reducing the generation of linearchain aldehydes.

4. Conclusion

In the paper, the removal and mineralization of toluene in humid air were systematically discussed. Toluene of 4–20 ppm can be almost completely removed at 60 s in air with 80% RH. The mineralization

efficiencies are about 55%-58% at 25 min. 185 nm ultraviolet light plays a significant role in the rapid removal and mineralization of toluene. The presence of appropriate amounts of O_2 and H_2O facilitate the removal of toluene. O_2 rather than H_2O can promote the mineralization of toluene. According to the detected intermediates, the reaction pathways of toluene are deduced in three atmospheres (air with 80% RH, air with less than 3% RH, and N_2 with 80% RH). It is found that there are more reaction pathways and fewer linear-chain aldehydes formed in the presence of O_2 , which may account for the higher mineralization efficiency in humid/dry air than in humid N_2 . The study suggests that the application of VUV/UV photodegradation in humid air is more practical and cost-efficient and presents a deep insight into the effect of light wavelength, O_2 and H_2O on toluene degradation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R. F., Hynes, R.G., et al, 2004. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species. Atmos. Chem. Phys. 4, 1461– 1738. https://doi.org/10.5194/acp-4-1461-2004.
- Chen, J.M., Cheng, Z.W., Jiang, Y.F., Zhang, L.L., 2010. Direct VUV photodegradation of gaseous α-pinene in a spiral quartz reactor: Intermediates, mechanism, and toxicity/biodegradability assessment. Chemosphere 81, 1053–1060. https://doi.org/10.1016/j. chemosphere.2010.09.060.
- Chen, F.Y., Pehkonen, S.O., Ray, M.B., 2002. Kinetics and mechanisms of UV-photodegradation of chlorinated organics in the gas phase. Water Res. 36, 4203–4214. https://doi.org/10.1016/S0043-1354(02)00140-9.
- Chen, Z., Peng, Y., Chen, J.J., Wang, C.Z., Yin, H.B., Wang, H.M., et al, 2020. Performance and mechanism of photocatalytic toluene degradation and catalyst regeneration by thermal/UV treatment. Environ. Sci. Technol. 54, 14465–14473. https://doi.org/10.1021/ acs.est.0c06048.
- Cheng, Z.W., Jiang, Y.F., Zhang, L.L., Chen, J.M., Wei, Y.Y., 2011. Conversion characteristics and kinetic analysis of gaseous α-pinene degraded by a VUV light in various reaction media. Sep. Purif. Technol. 77, 26–32. https://doi.org/10.1016/j.seppur.2010.11.014.
- Creasey, D.J., Heard, D.E., Lee, J.D., 2000. Absorption cross-section measurements of water vapour and oxygen at 185 nm. Implications for the calibration of field instruments to measure OH, HO₂ and RO₂ radicals. Geophys. Res. Lett. 27, 1651–1654. https://doi.org/ 10.1029/1999GL011014.
- Einaga, H., Mochiduki, K., Teraoka, Y., 2013. Photocatalytic oxidation processes for toluene oxidation over TiO₂ catalysts. Catalysts 3, 219–231. https://doi.org/10.3390/catal3010219.
- Finlayson-Pitts, B.J., Pitts, J.N., 1997. Tropospheric air pollution: Ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles. Science 276, 1045–1052. https://doi.org/ 10.1126/science.276.5315.1045.
- Govindan, M., Chung, S.J., Moon, I.S., 2012. Mineralization of gaseous acetaldehyde by electrochemically generated Co(III) in H₂SO₄ with wet scrubber combinatorial system. ACS Comb. Sci. 14, 359–365. https://doi.org/10.1021/co300012a.
- Heymes, F., Manno-Demoustier, P., Charbit, F., Fanlo, J.L., Moulin, P., 2006. A new efficient absorption liquid to treat exhaust air loaded with toluene. Chem. Eng. J. 115, 225–231. https://doi.org/ 10.1016/j.cej.2005.10.011.

- Huang, H.B., Li, W.B., 2011. Destruction of toluene by ozoneenhanced photocatalysis: Performance and mechanism. Appl. Catal. B-Environ. 102, 449–453. https://doi.org/10.1016/j. apcatb.2010.12.025.
- Huang, H.B., Leung, D.Y.C., Li, G.S., Leung, M.K.H., Fu, X.L., 2011. Photocatalytic destruction of air pollutants with vacuum ultraviolet (VUV) irradiation. Catal. Today 175, 310–315. https:// doi.org/10.1016/j.cattod.2011.04.015.
- Huang, H.B., Huang, H.L., Zhang, L., Hu, P., Xu, Y., Ye, X.G., et al, 2014. Photooxidation of gaseous benzene by 185 nm VUV irradiation. Environ. Eng. Sci. 31, 481–486. https://doi.org/ 10.1089/ces.2014.0100.
- Huang, H.L., Huang, H.B., Zhan, Y.J., Liu, G.Y., Wang, X.M., Lu, H.X., et al, 2016b. Efficient degradation of gaseous benzene by VUV photolysis combined with ozone-assisted catalytic oxidation: Performance and mechanism. Appl. Catal. B-Environ. 186, 62–68. https://doi.org/10.1016/j.apcatb.2015.12.055.
- Huang, H.B., Lu, H.X., Huang, H.L., Wang, L., Zhang, J.N., Leung, D.Y.C., 2016a. Recent development of VUV-based processes for air pollutant degradation. Front. Environ. Sci. 4, 17. https://doi. org/10.3389/fenvs.2016.00017.
- Huff, J., 2007. Benzene-induced cancers: Abridged history and occupational health impact. Int. J. Occup. Environ. Health 13, 213–221. https://doi.org/10.1179/och.2007.13.2.213.
- Hui, L.R., Liu, X.G., Tan, Q.W., Feng, M., An, J.L., Qu, Y., et al, 2019. VOC characteristics, sources and contributions to SOA formation during haze events in Wuhan. Central China. Sci. Total Environ. 650, 2624–2639. https://doi.org/10.1016/j. scitotenv.2018.10.029.
- Jafari, A.J., Arfaeinia, H., Ramavandi, B., Kalantary, R.R., Esrafily, A., 2019. Ozone-assisted photocatalytic degradation of gaseous toluene from waste air stream using silica-functionalized graphene oxide/ZnO coated on fiberglass: Performance, intermediates, and mechanistic pathways. Air Qual. Atmos. Health 12, 1181–1188. https://doi.org/10.1007/s11869-019-00732-6.
- Jeong, J., Sekiguchi, K., Sakamoto, K., 2004. Photochemical and photocatalytic degradation of gaseous toluene using short-wavelength UV irradiation with TiO₂ catalyst: comparison of three UV sources. Chemosphere 57, 663–671. https://doi.org/10.1016/j. chemosphere.2004.05.037.
- Ji, Y.M., Zhao, J., Terazono, H., Misawa, K., Levitt, N.P., Li, Y.X., et al, 2017. Reassessing the atmospheric oxidation mechanism of toluene. Proc. Natl. Acad. Sci. U. S. A. 114, 8169–8174. https://doi. org/10.1073/pnas.1705463114.
- Kaneko, K., Tsumura, K., Ishii, K., Onuma, T., Honda, T., Fujita, S., 2018. Deep-Ultraviolet Luminescence of Rocksalt-Structured Mg_x-Zn_{1-x}O (x > 0.5) Films on MgO Substrates. J. Electron. Mater. 47, 4356–4360. https://doi.org/10.1007/s11664-018-6303-9.
- Kang, I.S., Xi, J.Y., Hu, H.Y., 2018. Photolysis and photooxidation of typical gaseous VOCs by UV irradiation: Removal performance and mechanisms. Front. Env. Sci. Eng. 12, 8. https://doi.org/ 10.1007/s11783-018-1032-0.
- Koh, L.H., Kuhn, D.C.S., Mohseni, M., Allen, D.G., 2004. Utilizing ultraviolet photooxidation as a pre-treatment of volatile organic compounds upstream of a biological gas cleaning operation. J. Chem. Technol. Biotechnol. 79, 619–625. https://doi.org/10.1002/ jctb.1030.
- Kohno, H., Berezin, A.A., Chang, J.S., Tamura, M., Yamamoto, T., Shibuya, A., Honda, S., 1998. Destruction of volatile organic compounds used in a semiconductor industry by a capillary tube discharge reactor. IEEE Trans. Ind. Appl. 34, 953–966. https://doi. org/10.1109/28.720435.
- Liang, S.M., Shu, Y.J., Li, K., Jian, J., Huang, H.B., Deng, J.G., et al, 2020. Mechanistic insights into toluene degradation under VUV irradiation coupled with photocatalytic oxidation. J. Hazard. Mater. 399,. https://doi.org/10.1016/j.jhazmat.2020.122967 122967.
- Mohseni, M., Koh, L.H., Kuhn, D.C.S., Allen, D.G., 2005. Ultraviolet photooxidation for the biodegradability enhancement of airborne

o-xylene. J. Environ. Eng. Sci. 4, 279–286. https://doi.org/10.1139/S04-060.

- Ogata, A., Ito, D., Mizuno, K., Kushiyama, S., Gai, A., Yamamoto, T., 2002. Effect of coexisting components on aromatic decomposition in a packed-bed plasma reactor. Appl. Catal. A-Gen. 236, 9– 15. https://doi.org/10.1016/S0926-860X(02)00280-6.
- Pham, T.D., Lee, B.K., Lee, C.H., 2016. The advanced removal of benzene from aerosols by photocatalytic oxidation and adsorption of Cu-TiO₂/PU under visible light irradiation. Appl. Catal. B: Environ. 182, 172–183. https://doi.org/10.1016/j. apcatb.2015.09.023.
- Sayed, M., Fu, P.F., Shah, L.A., Khan, H.M., Nisar, J., Ismail, M., Zhang, P.Y., 2016. VUV-photocatalytic degradation of bezafibrate by hydrothermally synthesized enhanced {001} facets TiO₂/Ti Film. J. Phys. Chem. A 120, 118–127. https://doi.org/10.1021/acs. jpca.5b10502.
- Shayegan, Z., Lee, C.S., Haghighat, F., 2018. TiO₂ photocatalyst for removal of volatile organic compounds in gas phase - A review. Chem. Eng. J. 334, 2408–2439. https://doi.org/10.1016/j. cej.2017.09.153.
- Shu, Y.J., He, M., Ji, J., Huang, H.B., Liu, S.W., Leung, D.Y.C., 2019. Synergetic degradation of VOCs by vacuum ultraviolet photolysis and catalytic ozonation over Mn-xCe/ZSM-5. J. Hazard. Mater. 364, 770–779. https://doi.org/10.1016/j.jhazmat.2018.10.057.
- Singh, S.K., Vuppuluri, V., Son, S.F., Kaiser, R.I., 2020. Investigating the Photochemical Decomposition of Solid 1,3,5-Trinitro-1,3,5triazinane (RDX). J. Phys. Chem. A 124, 6801–6823. https://doi. org/10.1021/acs.jpca.0c05726.
- Sleiman, M., Conchon, P., Ferronato, C., Chovelon, J.M., 2009. Photocatalytic oxidation of toluene at indoor air levels (ppbv): Towards a better assessment of conversion, reaction intermediates and mineralization. Appl. Catal. B-Environ. 86, 159–165. https:// doi.org/10.1016/j.apcatb.2008.08.003.
- Van Durme, J., Dewulf, J., Sysmans, W., Leys, C., Van Langenhove, H., 2007. Abatement and degradation pathways of toluene in indoor air by positive corona discharge. Chemosphere 68, 1821– 1829. https://doi.org/10.1016/j.chemosphere.2007.03.053.
- Wang, J.H., Ray, M.B., 2000. Application of ultraviolet photooxidation to remove organic pollutants in the gas phase. Sep. Purif. Technol. 19, 11–20. https://doi.org/10.1016/S1383-5866(99)00078-7.
- Wu, M.Y., Zhang, Y.G., Szeto, W., Pan, W.D., Huang, H.B., Leung, D.Y.C., 2019. Vacuum ultraviolet (VUV)-based photocatalytic oxidation for toluene degradation over pure CeO₂. Chem. Eng. Sci. 200, 203–213. https://doi.org/10.1016/j.ces.2019.01.056.
- Wu, M.Y., Kwok, Y.H., Zhang, Y.G., Szeto, W., Huang, H.B., Leung, D.Y.C., 2021. Synergetic effect of vacuum ultraviolet photolysis and ozone catalytic oxidation for toluene degradation over MnO₂-rGO composite catalyst. Chem. Eng. Sci. 231. https:// doi.org/10.1016/j.ces.2020.116288.
- Xia, D.H., Xu, W.J., Hu, L.L., He, C., Leung, D.Y.C., Wang, W.J., Wong, P.K., 2018. Synergistically catalytic oxidation of toluene over Mn modified g-C₃N₄/ZSM-4 under vacuum UV irradiation. J. Hazard. Mater. 349, 91–100. https://doi.org/10.1016/j. jhazmat.2018.01.048.
- Xie, R.J., Lei, D.X., Xie, X.W., Suo, Z.Y., Leung, D.Y.C., Cao, J.P., et al, 2022. Accelerated oxidation of VOCs via vacuum ultraviolet photolysis coupled with wet scrubbing process. J. Environ. Sci. https://doi.org/10.1016/j.jes.2022.05.002.
- Yang, R.J., Han, P.P., Fan, Y.Y., Guo, Z.J., Zhao, Q.T., Wang, Y., et al, 2020. The performance and reaction pathway of δ-MnO₂/ USY for catalytic oxidation of toluene in the presence of ozone at room temperature. Chemosphere 247, https://doi.org/10.1016/j. chemosphere.2020.125864 125864.
- Ye, J.H., Shang, J., Song, H., Li, Q., Zhu, T., 2013. Generation of reactive oxygen species in simulated flue gas under vacuum ultraviolet radiation. Chem. Eng. J. 232, 26–33. https://doi.org/ 10.1016/j.cej.2013.07.056.

- Yu, J.M., Cai, W.J., Chen, J.M., Feng, L., Jiang, Y.F., Cheng, Z.W., 2012. Conversion characteristics and mechanism analysis of gaseous dichloromethane degraded by a VUV light in different reaction media. J. Environ. Sci. 24, 1777–1784. https://doi.org/ 10.1016/S1001-0742(11)61021-8.
- Zhan, Y.J., Ji, J., Huang, H.B., He, M., Leung, D.Y.C., Liu, S.L., et al, 2018. A facile VUV/H₂O system without auxiliary substances for efficient degradation of gaseous toluene. Chem. Eng. J. 334, 1422–1429. https://doi.org/10.1016/j.cej.2017.11.056.
- Zhang, Y.G., Wu, M.Y., Wang, Y.F., Kwok, Y.H., Pan, W.D., Szeto, W., et al, 2021. Fluorinated TiO₂ coupling with alpha-MnO₂ nanowires supported on different substrates for photocatalytic

VOCs abatement under vacuum ultraviolet irradiation. Appl. Catal. B-Environ. 280,. https://doi.org/10.1016/j.apcatb.2020.119388 119388.

- Zhang, S.C., Zheng, Z.J., Wang, J.H., Chen, J.M., 2006. Heterogeneous photocatalytic decomposition of benzene on lanthanumdoped TiO₂ film at ambient temperature. Chemosphere 65, 2282– 2288. https://doi.org/10.1016/j.chemosphere.2006.05.027.
- Zhu, J.P., Wong, S.L., Cakmak, S., 2013. Nationally representative levels of selected volatile organic compounds in Canadian residential indoor air: Population-Based survey. Environ. Sci. Technol. 47, 13276–13283. https://doi.org/10.1021/es403055e.