



Mechanistic study and mutagenicity assessment of intermediates in photocatalytic degradation of gaseous toluene

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ABSTRACT

Photocatalytic oxidation is a promising technique for the degradation of volatile organic compounds. However, it is necessary to clarify the genotoxicity mutagenic potential of intermediates formed during photocatalytic degradation. A gas–solid TiO₂ thin film reactor was fabricated to degrade toluene under UV irradiation. The results showed that the degradation efficiencies of toluene at a concentration of about 1500 µg L⁻¹ reached almost 100% within 120 min of illumination. The intermediates produced during the photocatalytic degradation were identified by using gas chromatography–mass spectroscopy. Benzene was the only by-product identified in the gas phase, while small amounts of benzaldehyde and benzoic acid were detected at the TiO₂ surface. Species such as benzene and CO₂ should derive from the photodecarboxylation of benzoic acid, produced by further oxidation of benzaldehyde. Neither the original toluene nor the gaseous intermediates produced at different times presented mutagenic activity to strains TA98 and TA100 in the presence or absence of the S9 mixture at the tested doses by using Ames assay. All of the results indicated that the effluent gas of toluene treated by photocatalysis will not cause mutagenic toxicity to humans or other organisms.

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1. Introduction

Volatile organic compounds (VOCs) are a group of air pollutants widely present in both indoor and outdoor environments. The main emission sources of VOCs are motor vehicle exhausts and solvent utilization (Zou et al., 2006). Due to environmental concerns including their adverse effects on human health, VOCs are receiving an increasing amount of attention (Cerna et al., 2000; Topinka et al., 2000; Wang et al., 2008). Many VOCs are toxic, mutagenic and carcinogenic to human beings, and long-term exposure to VOCs is detrimental to human health for example by causing sick building syndrome (SBS) (Jeong et al., 2004). Their carcinogenic effects are becoming increasingly clear through genotoxicity studies using bacteria (Chang and Chen, 2008; Ben Mansour et al., 2009), mammalian cells (Choi et al., 2008), animals (Dybing et al., 2008) and epidemiological investigations of large groups of people (Claxton and Woodall, 2007). Of these assay methods, the salmonella/microsome (Ames) assay is the most widely used convenient and effective method to evaluate mutagenicity of airborne particles and source emissions (Delgado-Rodriguez et al., 1999; Claxton et al., 2004; Krahl et al., 2009). However, most research on VOCs

has focused mainly on the toxicity of VOCs sources or the degradation conditions rather than the by-products generated during the treatment procedures (Wang et al., 2008).

Recently, photocatalytic oxidation (PCO) has become an attractive technology for VOCs abatement compared with adsorption, biofiltration or thermal treatment (Maira et al., 2001; Sleiman et al., 2009; Vincent et al., 2009). It is noteworthy that, although many works have accomplished the degradation of VOCs by PCO, only a few investigations have focused on evaluating the detoxification of organic pollutants in the environment. Osugi et al. (2006) found that neither remazol turquoise blue dye nor its oxidized intermediates presented mutagenic activity to *Salmonella typhimurium* TA98 and TA100 in the presence or absence of S9 mixtures. Cantavenera et al. (2007) evaluated the genotoxicity of paraquat and its intermediates using in vitro tests, and confirmed the formation of some genotoxic intermediates followed by decontamination. In our previous research, we found that photoelectrocatalytic technology is an effective method to reduce the toxicity of organic pollutants in oilfield produced water (Li et al., 2007). However, these works all focus on the genotoxic assessment of organic pollutants during the wastewater treatment. Mutagenicity assessments of VOCs and their gaseous mixed degradation products during PCO treatment have not yet been reported in the literature frequently. Thus, information regarding the mutagenic toxicity of

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the intermediates from VOCs breakdown is essential to evaluate the feasibility and utilization of photocatalytic degradation technology.

The environmental protection agency (EPA) of the USA has reported that toluene is ubiquitous in the environment because of its large usage in consumer products (Ardizzzone et al., 2008). Thus, in this work, photocatalytic technology was selected to detoxify a model species of VOCs, toluene, and both the chemical identification of the intermediates by gas chromatography–mass spectrometry (GC–MS) and the testing of the genotoxicity of the gaseous degradation by-products by using the Ames assay were carried out. Additionally, a possible degradation pathway based on the GC–MS results was proposed to explain why PCO is an effective method for detoxification of gaseous toluene.

2. Materials and methods

2.1. Reagents

Dimethyl sulfoxide (DMSO, purity >99.9%), glucose-6-phosphate (purity: 98–100%) and Dexon (purity: 99%) were purchased from Sigma Chemical Corporation (Saint Louis, MO, USA). 2-Aminofluorene (purity >97.0%) was purchased from Fluka Chemical Corporation (Ronkonkoma, NY, USA). NADP, D-biotin, L-histidine, agar, nutrient broth and other chemicals of analytical grade were all purchased from Huankai (Guangzhou, China). The rat liver enzymes (S9) as well as *S. typhimurium* strains TA98 and TA100 were obtained from the Guangzhou Sanitation Prevention Station, China. All reagents were used as received without further purification. The indium-tin oxide (ITO) conducting glasses (80–100 Ω per square) were bought from Shenzhen in China.

2.2. Photocatalysis procedures

The nano-crystalline TiO₂ thin films were prepared according to our previous paper (Sun et al., 2009). All photocatalytic experiments of gaseous toluene at the gas–solid interface were performed in a sealed Pyrex glass reactor with 5 L total volume as shown in Fig. 1. A 125 W high-pressure mercury lamp with a maximum emission radiation of 365 nm (GGZ125, Shanghai Yaming

Lighting CO., Ltd.) was used as the UV light source (light intensity: 5.3 mW cm⁻²). Film photocatalysts were installed facing the light source which was placed in the centre of a double-walled quartz cylinder. In all experiments, the reaction temperature was maintained at about 40 °C by continuous circulation of cooling water in the quartz glass jacket. At the bottom of the reactor, a minitype fan stirrer was used as the air blender for the reaction gas during the operation, which ensures effective diffusion of the gaseous molecules in the reactor. In a typical experimental procedure, four identical prepared TiO₂/ITO films (12 × 5.7 cm² pieces) were installed and the reactor was filled with dry air. The liquid toluene and a small fraction of distilled water were injected into the batch reactor, and then allowed to vaporize, mix, and reach the gas–solid adsorption equilibrium after the reactor was flushed and filled with air. The initial concentration of total toluene was about 1500 $\mu\text{g L}^{-1}$ and the relative humidity was chosen to be about 45%. The lamp was turned on and the PCO of toluene was started (PCO 0 min). Subsequently, at PCO intervals of 15, 30, 60, 90 and 120 min, portions of gaseous sample were collected and resealed in 1 L volumetric Teflon bags which filled with 250 mL dry air for mechanism studies. At the same time, another Teflon bags filled with 250 mL dry air was detected without addition of sample as a blank contrast to deduct the interference with background in each analysis. And the other gaseous sample portions were trapped and absorbed into DMSO solution with a gentle stream of high-purity nitrogen blowing from the reactor for genotoxicity assessment.

2.3. Chemical analysis

A gas chromatograph (HP 5890, Series II, equipped with a split/splitless injector, a flame ionization detector and a DB-1 capillary column (60 m × 0.32 mm × 1.0 μm , Agilent Technologies, USA)) was used to study the photocatalytic degradation kinetics of gaseous toluene. The temperatures of the injector and the detector were set as 230 °C and 270 °C, respectively. 300 μL gaseous samples taken at given intervals by using a 500 μL gas-tight locking syringe (Agilent, Australia) were injected into the GC for toluene determination. The column was kept at 40 °C for 2 min, the temperature was then increased to 220 °C at a rate of 6 °C min⁻¹, increased to 250 °C at a rate of 20 °C min⁻¹, and then held at 250 °C for 5 min. The concentrations of toluene were quantified by external standard calibration. The degraded gaseous mixtures formed during PCO of gaseous toluene were also analyzed by an Entech 7100 Preconcentrator (Entech Instruments Inc., CA, USA) coupled to an HP6890 gas chromatography-5973 N mass selective detector (GC-MSD, Agilent Technologies, USA) operated with an electronic multiplier voltage of 2200 V. Ultrahigh purity helium at a constant flow rate of 4.0 mL min⁻¹ was used as the carrier gas. A 100 mL air sample (1 atm, 0 °C) was drawn in the splitless mode. The column and programmed procedure were the same as for the GC quantification. The MSD was operated in full scan mode with the ratio of mass to proton of 35–300 amu. The gaseous target species were identified by their mass spectra by using the Wiley database (Wiley Mass Spectral Library).

In order to identify the intermediates adsorbed on the surfaces of TiO₂ thin films, the intermediates deposited on the thin films were analyzed by chemical analysis of a methanol ultrasonic extract. The collected filtrate was dried with a gentle stream of high-purity nitrogen and the solvent was changed to hexane. The solution was analyzed by GC (Agilent 7890A)-MSD (Agilent 5975C with Triple-Axis Detector). The carrier gas was ultrahigh purity helium at a constant flow rate of 1.5 mL min⁻¹. The injector and detector temperatures were set at 230 °C and 270 °C, respectively. The GC column was DB-5 (30 m × 0.32 mm × 0.25 μm , Agilent technology). The temperature of the GC oven was initially set

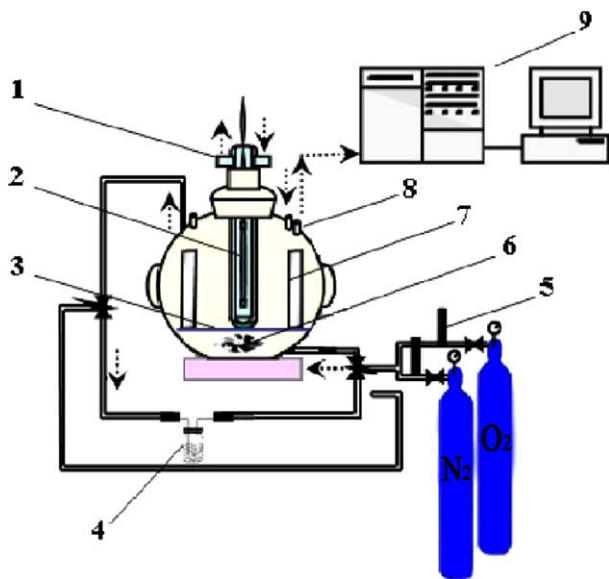


Fig. 1. Schematic diagram of experimental set-up: 1. Quartz cylinder; 2. UV light; 3. Pedestal; 4. DMSO; 5. Gas flowmeter; 6. Minitype fan; 7. TiO₂ thin film; 8. Gas inlet & outlet and 9. Detection system.

at 70 °C for 2 min, then raised at 6 °C min⁻¹ to 180 °C and increased to a final 220 °C at a rate of 20 °C min⁻¹, then it was held at this temperature for 5 min. 1.0 μL of sample was injected in the splitless mode. The target compounds were identified according to the spectra library as described previously.

2.4. Mutagenicity assessment

Ames assays were performed according to the standard plate incorporation method with *S. typhimurium* classical strains TA98 and TA100, which are capable of detecting base frameshift type and base pair substitution-type mutagenicity, respectively (Maron and Ames, 1983). Toluene and its photocatalytic degradation intermediates after 15, 30, 60, 90 and 120 min were absorbed and dissolved completely in DMSO. Four different dose groups (2500, 1250, 625 and 312.5 μg plate⁻¹) for each sample were assayed in triplicate. Tests were operated under the same conditions with or without S9 metabolic activation. Two known mutagens, Dexon (without S9) and 2-aminofluorene (with S9) were used as the positive controls. The strains without any addition of foreign compounds as a negative control and solvent controls were also employed in each assay. The revertant colonies on each plate were counted and scored after 48 h of incubation at 37 °C, and the number of *his*⁺ revertants in each sample was recorded as the mean value from three plates. A sample was considered to be mutagenic when the number of revertants was at least double that of the negative control and if it had a reproducible dose–response curve (Valent et al., 1993).

3. Results and discussion

3.1. Photocatalytic degradation kinetics

The photocatalytic degradation kinetics of toluene was investigated and the results are shown in Fig. 2. It was known that water vapor plays an important role in the photocatalytic degradation of gaseous VOCs, and many researchers have investigated the effect of water vapor on the photocatalytic degradation of gaseous reactants (Demeestere et al., 2007). In the absence of water vapor, PCO of some chemical compounds is seriously retarded or total mineralization to CO₂ does not occur. However, excessive water vapor on the catalyst surface will lead to a decrease of the reaction rate because water molecules can occupy the active sites of the reactants on the surface (Zhao and Yang, 2003; An et al., 2005). Considering that the air humidity in the region of Guangzhou (China) varies significantly in different seasons, and based on our group's earlier report on the effects of relative humidity in PCO of toluene in the gas

phase (Zeng et al., 2009), the relative humidity was selected to be 45% in this work. From kinetics profiles, it can be observed that gaseous toluene can reach its evaporation and adsorption–desorption equilibria within 60 min under dark conditions with an adsorption efficiency of 18.0%. Only 12.5% of the toluene vapor was photolyzed within 120 min of UV light irradiation in the absence of catalyst. However, in the presence of TiO₂ films, the concentration of toluene decreased to 20 μg L⁻¹ and approximately 99% of toluene was degraded within 120 min. Linear plots of $\ln\left(\frac{C_0}{C_t}\right)$ versus time are shown in the inset of Fig. 2. The degradation kinetics of toluene followed a first-order degradation consistent with the Langmuir–Hinshelwood (L–H) model (Hoffmann et al., 1995). Hence the photocatalytic degradation rate constant and the half-life were obtained using the algorithm $\ln\left(\frac{C_0}{C_t}\right) = Kt$, where C_0 is the initial concentration of toluene, C_t is the concentration of toluene in gas at time t , and K and t are the degradation rate constant (min⁻¹) and degradation time in minutes, respectively. The rate constant, the slope of the linear fit of $\ln\left(\frac{C_0}{C_t}\right)$ versus time was calculated as 0.041 min⁻¹, and the half-life was also calculated as 16.90 min in our system. The high rate constant and short half-life suggest that toluene can undergo fast photocatalytic degradation in the gaseous phase at the TiO₂ film photocatalyst.

3.2. Identification of photocatalytic degradation intermediates

The gaseous mixtures obtained after gas–solid phase photocatalytic degradation were subjected to GC–MS analysis for identification of intermediates. The total ion chromatograms (TICs) of gaseous compounds detected at different reaction times are shown in Fig. 3. Mass spectrum analysis showed that benzene (1), hexamethylene (2), heptane (3) and toluene (4) were detected in the gas phase. The trace amount of toluene in the blank contrast (Fig. 3g) is the residua or background in the Teflon bags itself detected by the preconcentrator GC–MS, and the little interference can be ignored completely. In Fig. 3a–f, the peaks (2) and (3) can be observed in the blank contrast (Fig. 3g). Due to the trace amounts and small changes in the abundances of peaks (2) and (3), hexamethylene and heptane were considered to be background peaks. However, the abundance of peak (4) decreased obviously, and the abundance of peak (1) first increased and then decreased with an increasing reaction time. The TIC diagram analysis showed that peak (4) (toluene) was degraded and almost completely disappeared within 120 min, while the by-product peak (1) (benzene) was produced as an intermediate and then degraded during the later course of PCO (Fig. 3f). The amount of benzene increased gradually with reaction time from 0 to 30 min, and reached its maximum concen-

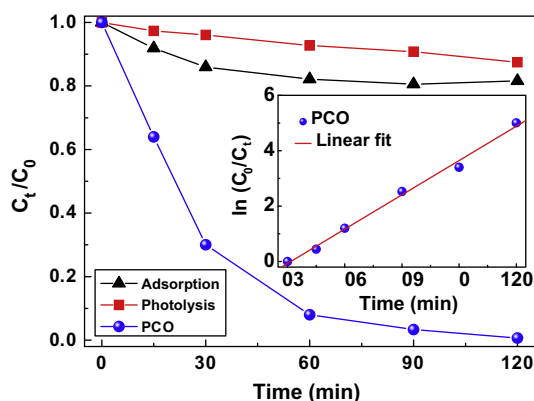


Fig. 2. Photocatalytic degradation kinetics of toluene. Inset: linear plots of $\ln\left(\frac{C_0}{C_t}\right)$ versus time.

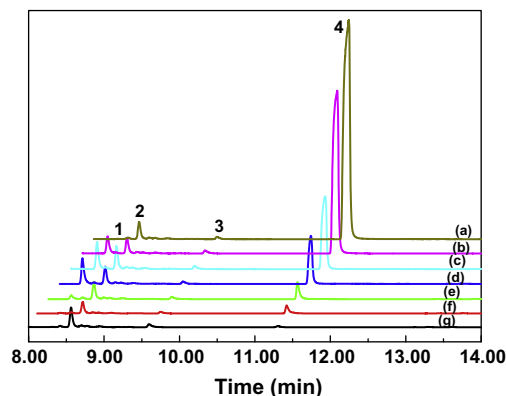


Fig. 3. TIC diagram for gaseous compounds formed during PCO of toluene: (a) 0 min; (b) 15 min; (c) 30 min; (d) 60 min; (e) 90 min; (f) 120 min and (g) blank contrast.

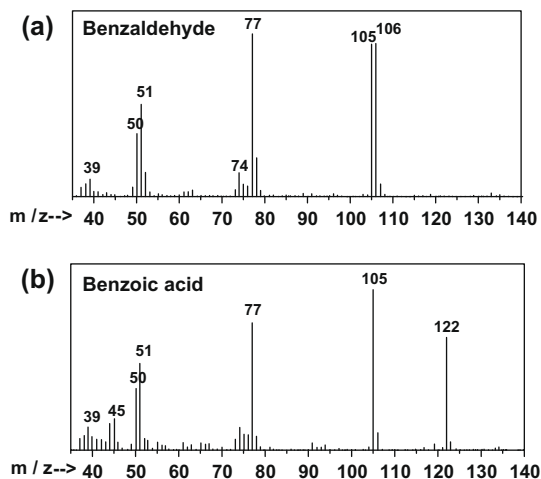


Fig. 4. Mass spectra of adsorbed intermediates: (a) benzaldehyde and (b) benzoic acid.

tration of $89 \mu\text{g L}^{-1}$. Its concentration decreased again after 30 min. Both toluene and the sole gaseous phase intermediate benzene were mineralized completely to CO_2 and H_2O within 120 min.

In order to obtain further insight into the other intermediates, those deposited on the TiO_2 films, the mixed intermediates were analyzed by GC–MS. We found that the color of TiO_2 thin films gradually changed from white to pale yellow to yellow brown after photocatalytic degradation with increasing reaction time, suggesting that some intermediates might be produced on the TiO_2 surfaces. Mass spectral analysis of the extract solution indicated that the adsorbed intermediates were mainly composed of benzalde-

hyde and benzoic acid rather than toluene. Their mass spectra are shown in Fig. 4a and b, respectively. The identifications of these two intermediates were also confirmed with authentic standards of benzaldehyde and benzoic acid. It was noticeable that the concentrations of the two main intermediates, benzaldehyde and benzoic acid, were also very low.

On the basis of the three identified intermediates from both the gas phase and the adsorbed phase in our experimental system, possible PCO pathways of toluene are proposed in Fig. 5. The primary pathway is recognized as hydrogen abstraction from the methyl group leading to a benzyl radical followed by formation of benzaldehyde. Benzaldehyde was easily oxidized to benzoic acid, and benzene was then derived from the photo-decarboxylation of benzoic acid. According to the kinetic results, these two identified deposited intermediates and the final gaseous intermediate benzene can be completely mineralized into CO_2 and H_2O within 120 min. This pathway is confirmed in other work by Augugliaro et al. (1999). Thus, from the viewpoint of chemical analysis, the intermediates of photocatalytic degradation of toluene are all present at a very low concentration and can then be mineralized completely.

3.3. Mutagenicity assay of gaseous intermediates formed during PCO of toluene

In order to evaluate the detoxification ability of PCO, the Ames assay was employed to assess the safety of reaction intermediates in the gaseous phase. Ames test results of gaseous intermediates of toluene formed during photocatalytic degradation with reaction times of 0, 15, 30, 60, 90 and 120 min are shown in Table 1. The results showed that the range of spontaneous reversions (negative control) for TA98 strain without S9 mixture metabolic activation (–S9) was at 29–37 revertants plate⁻¹, while TA100 strain reverts spontaneously (–S9) was at 127–148 revertants plate⁻¹ in our laboratory. The spontaneous reversions were slightly increased with S9 mixture metabolic activation (+S9) for TA98 strain at 32–47 revertants plate⁻¹ and TA100 strain at 143–169 revertants plate⁻¹. For toluene, at the highest tested dose of 2500 $\mu\text{g plate}^{-1}$, the number of revertants plate⁻¹ obtained were only 31 ± 2.1 (–S9) and 37 ± 2.5 (+S9) for TA98 strain. The number of revertants plate⁻¹ obtained were 138 ± 7.1 (–S9) and 146 ± 5.6 (+S9) for TA100 strain. Thus no obvious increase in the number of revertants was found for toluene compared with the negative control. These results indicated that toluene did not present mutagenic activity to *S. typhimurium* TA98 and TA100 strains, either in the presence or absence of S9 metabolic activation.

Moreover, for 15, 30, 60 and 120 min for TA 98 strain, the numbers of revertants plate⁻¹ obtained were 33 ± 4.5 , 29 ± 1.5 , 37 ± 6.1 , 35 ± 3.8 and 33 ± 5.5 , respectively, without S9 and 34 ± 5.6 , 36 ± 3.1 , 48 ± 3.0 , 45 ± 6.1 and 35 ± 2.5 , respectively, with S9 at the highest tested dose of 2500 $\mu\text{g plate}^{-1}$. In addition, no increase in the number of revertants per plate was detected compared with the negative control in the doses of 1250, 625 and 312.5 $\mu\text{g plate}^{-1}$ for TA98 strain both with and without S9. The ratios of the numbers of revertants of all these samples to those of the negative control were all less than 2. Thus, the results were all negative to TA98 strain in all the dose groups, which indicated that the intermediates in the gaseous phase will not cause base frameshift type mutagenicity in organisms. Similar results were obtained for TA100 strain. No increase in the number of revertants per plate was detected compared with the negative control in any of the doses with or without S9. These results indicated that the intermediates in the gaseous phase will not cause base pair substitution-type mutagenicity in organisms.

Therefore, neither toluene nor the gaseous degradation intermediates showed any mutagenicity in the Ames assay. This is

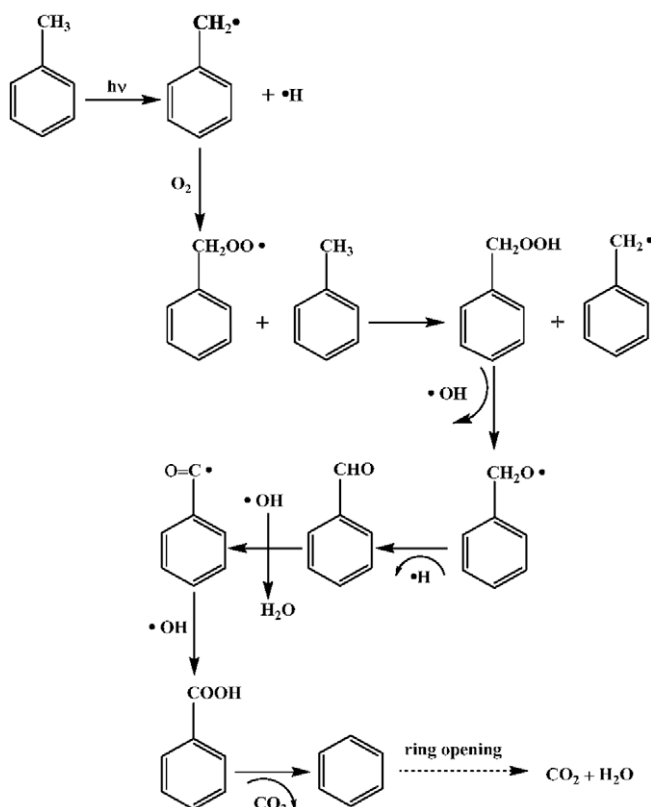


Fig. 5. Reaction mechanism for the production of benzene in the gaseous phase during PCO of toluene.

Table 1
Results of the Ames assay during photocatalytic degradation of toluene.

Sample	Dose ($\mu\text{g plate}^{-1}$)	Number of revertants plate ⁻¹ in <i>Salmonella typhimurium</i> ^a			
		TA98		TA100	
		–S9	+S9	–S9	+S9
Toluene	2500	31 ± 2.1	37 ± 2.5	138 ± 7.1	146 ± 5.6
	1250	30 ± 7.6	40 ± 4.7	131 ± 3.6	139 ± 9.1
	625	29 ± 2.3	38 ± 2.1	142 ± 8.6	146 ± 10.7
	312.5	36 ± 4.7	41 ± 5.0	134 ± 8.1	133 ± 4.0
	0 ^b	34 ± 4.5	40 ± 3.8	137 ± 4.6	151 ± 8.0
PCO 15 min	2500	33 ± 4.5	34 ± 5.6	138 ± 7.0	151 ± 9.0
	1250	30 ± 6.0	33 ± 2.3	132 ± 4.6	142 ± 13.2
	625	31 ± 3.1	36 ± 3.1	138 ± 7.1	148 ± 12.1
	312.5	32 ± 2.6	33 ± 1.2	139 ± 13.7	143 ± 8.5
	0	33 ± 2.1	32 ± 2.6	135 ± 5.6	143 ± 9.5
PCO 30 min	2500	29 ± 1.5	36 ± 3.1	141 ± 18.0	153 ± 12.1
	1250	32 ± 2.5	34 ± 1.7	127 ± 10.6	143 ± 13.5
	625	33 ± 3.6	34 ± 3.6	148 ± 7.1	148 ± 14.4
	312.5	31 ± 4.0	33 ± 1.0	141 ± 17.1	145 ± 9.3
	0	32 ± 3.5	36 ± 4.6	135 ± 6.0	153 ± 4.6
PCO 60 min	2500	37 ± 6.1	48 ± 3.0	139 ± 13.0	157 ± 7.8
	1250	30 ± 1.5	46 ± 3.2	133 ± 12.3	154 ± 4.0
	625	33 ± 6.8	42 ± 2.6	129 ± 6.7	155 ± 15.8
	312.5	33 ± 5.0	43 ± 2.6	133 ± 10.8	161 ± 10.1
	0	36 ± 3.5	43 ± 2.1	137 ± 2.0	169 ± 4.6
PCO 90 min	2500	35 ± 3.8	45 ± 6.1	130 ± 4.7	151 ± 3.1
	1250	36 ± 4.9	46 ± 3.6	132 ± 2.6	150 ± 5.5
	625	36 ± 2.5	41 ± 2.6	136 ± 5.5	158 ± 10.5
	312.5	34 ± 1.5	44 ± 4.4	136 ± 6.7	153 ± 11.0
	0	36 ± 3.0	47 ± 2.6	145 ± 7.1	149 ± 8.1
PCO 120 min	2500	33 ± 5.5	35 ± 2.5	131 ± 3.8	142 ± 5.0
	1250	30 ± 2.0	34 ± 2.0	128 ± 5.1	136 ± 7.5
	625	30 ± 3.6	37 ± 4.0	141 ± 13.6	145 ± 7.4
	312.5	29 ± 4.2	36 ± 5.5	134 ± 8.0	134 ± 5.0
	0	32 ± 2.5	38 ± 4.4	134 ± 4.6	152 ± 7.9
Solvent control ^c	100 $\mu\text{L plate}^{-1}$	37 ± 4.0	34 ± 3.1	145 ± 7.0	148 ± 4.5
Positive control ^d	50	1248 ± 52.5		569 ± 36.3	
	20		2974 ± 126.9		1192 ± 68.2

^a Mean ± standard deviation.

^b Negative control.

^c DMSO only.

^d 50 $\mu\text{g plate}^{-1}$ Dexon without S9 and 20 $\mu\text{g plate}^{-1}$ 2-aminofluorene with S9.

because, according to the chemical analysis of gaseous photocatalytic degradation intermediates, only a mixture of toluene and benzene was obtained in the gas phase during PCO. At the same time, only a small amount of benzaldehyde and benzoic acid were found on the TiO₂ thin film. Moreover, benzaldehyde and benzoic acid also yield negative results in the Ames assay according to previous reports (Zeiger et al., 1988; Kubo et al., 2002). Thus, we can conclude that the effluent mixture of toluene treated by photocatalytic degradation does not pose a risk to human beings or other organisms, based on the chemical analysis and toxicity assessment.

4. Conclusions

Gaseous toluene was successfully detoxified by PCO technology using nano-crystalline TiO₂ thin films within a 120 min photocatalytic reaction, and the degradation kinetics of toluene followed a first-order degradation. The high rate constant (0.041 min⁻¹) and short half-life (16.90 min) indicate that toluene can quickly be photocatalytically degraded in the gaseous phase at the TiO₂ film photocatalyst. The main by-product in the gas phase was identified as benzene, and then the original toluene and benzene were finally mineralized into CO₂ and H₂O within 120 min. Furthermore, Ames assay results showed that neither toluene nor the gaseous degradation intermediate posed any genotoxicity during the course of

degradation. Thus, by combining chemical analysis with the Ames assessment of intermediates, we can conclude that photocatalytic technology is an effective detoxification method for toluene in the gaseous phase.

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