

Photo-catalytic degradation of gaseous pollutants in paper mills of southern China

XIN TONG, JIAO LI, JUN MA, XIAOQUAN CHEN, AND WENHAO SHEN

ABSTRACT: Studies were undertaken to evaluate gaseous pollutants in workplace air within pulp and paper mills and to consider the effectiveness of photo-catalytic treatment of this air. Ambient air at 30 sampling sites in five pulp and paper mills of southern China were sampled and analyzed. The results revealed that formaldehyde and various benzene-based molecules were the main gaseous pollutants at these five mills. A photo-catalytic reactor system with titanium dioxide (TiO_2) was developed and evaluated for degradation of formaldehyde, benzene and their mixtures. The experimental results demonstrated that both formaldehyde and benzene in their pure forms could be completely photo-catalytic degraded, though the degradation of benzene was much more difficult than that for formaldehyde. Study of the photo-catalytic degradation kinetics revealed that the degradation rate of formaldehyde increased with initial concentration fitting a first-order kinetics reaction. In contrast, the degradation rate of benzene had no relationship with initial concentration and degradation did not conform to first-order kinetics. The photo-catalytic degradation of formaldehyde-benzene mixtures indicated that formaldehyde behaved differently than when treated in its pure form. The degradation time was two times longer and the kinetics did not reflect a first-order reaction. The degradation of benzene was similar in both pure form and when mixed with formaldehyde.

Application: The developed photo-catalytic system had an excellent degradation performance on the gaseous pollutants in the paper mills. The findings from this work will be useful in the further development of workplace air conditioning devices.

Pulp and paper mills can be significant sources of liquid pollutants [1-4] and gaseous pollutants, such as volatile organic compounds (VOCs), nitrous oxide (NO_x), sulfur dioxide (SO_2), and formaldehyde (HCHO) [5,6], some of which may be associated with health risks [7,8]. While some work reporting gaseous constituents in paper mill workplace environments is available [9,10], the qualitative and quantitative analysis of gas compositions in these environments are scarce.

Treatment strategies for gaseous pollutants include condensation [11], solvent absorption [12], porous material adsorption [13], incineration [14], membrane separation [15], low temperature plasma [16], biological treatment [17], and photo-catalytic oxidation [18]. Among these techniques, photo-catalytic oxidation has attracted considerable attention for degrading organics, given its reaction conditions at room temperature and pressure and non-selective oxidation [18,19]. Numerous VOCs with small and large molecular weights can be successfully photo-catalytic degraded under various conditions [20-22]. However, application of this treatment technique to ambient air in paper mills is limited to only a few studies with methanol [23,24].

In this article, the ambient air at 30 sampling sites in five pulp and paper mills located in southern China was sampled and analyzed. Subsequently, photo-catalysis oxidation using nanometer-titanium dioxide (TiO_2) was evaluated to treat molecules identified in these ambient air samples. A photo-catalytic reactor was developed, optimized, and applied to de-

grade formaldehyde and benzene. The findings from this work will be useful in the further development of workplace air conditioning devices.

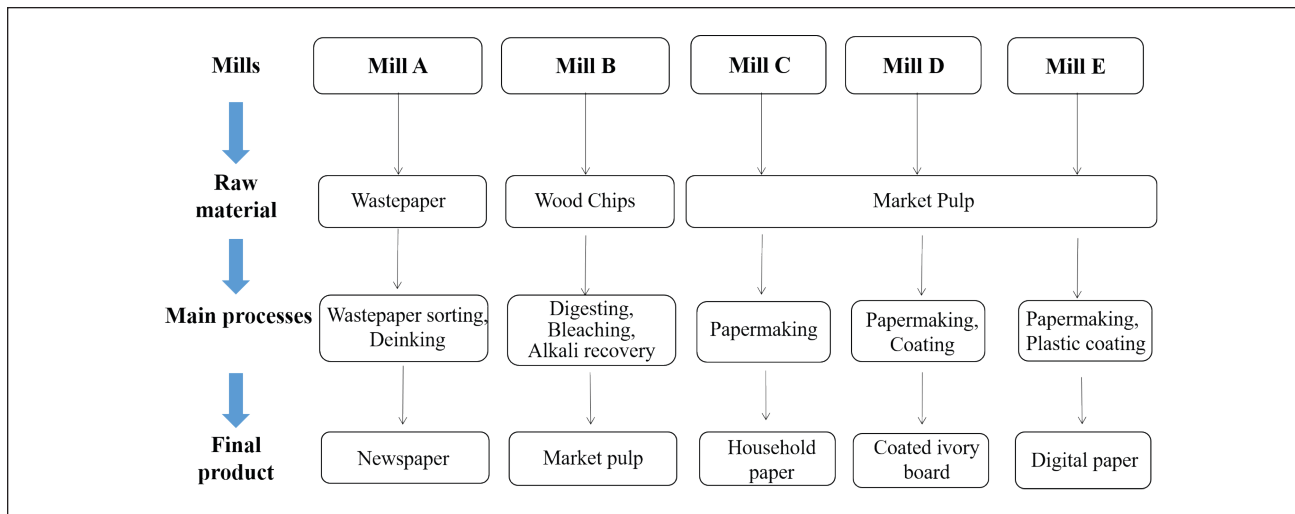
EXPERIMENTS AND METHODS

Sampling and analysis of ambient air samples

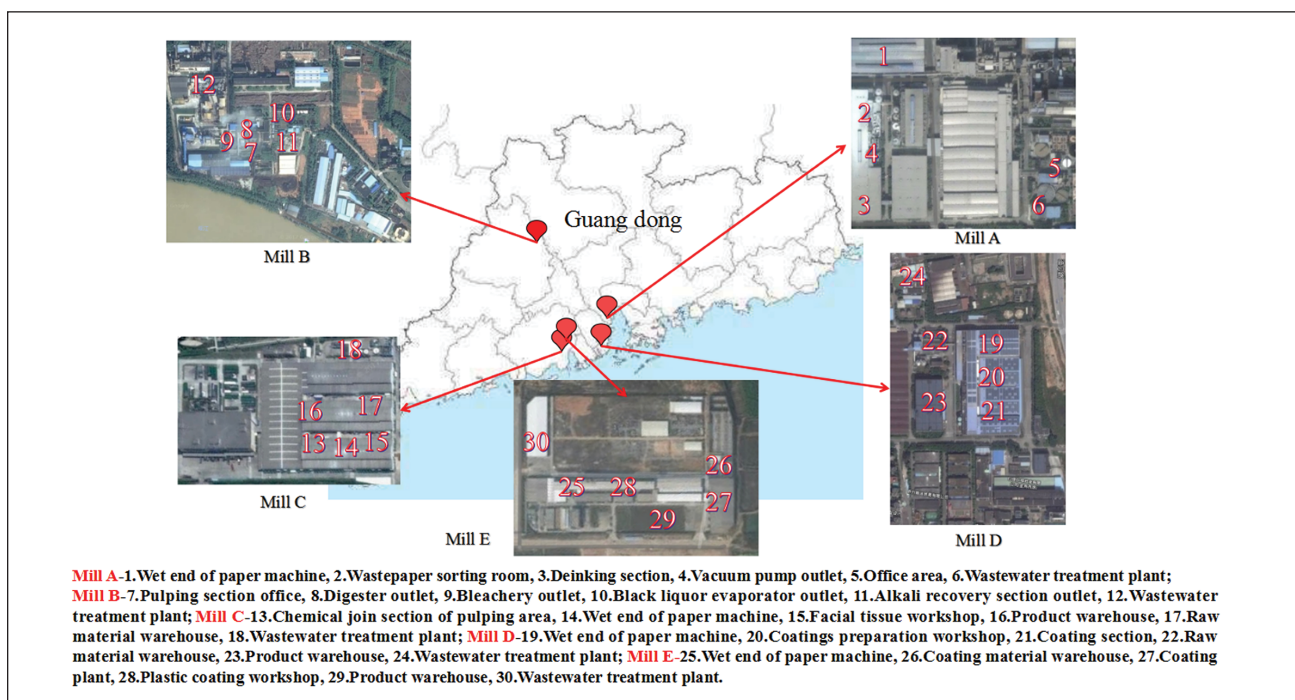
Five pulp and paper mills (Mills A-E) in southern China were selected to investigate their gaseous pollutants. Details regarding these facilities are presented in **Fig. 1**. Six ambient air samples from different sites in each mill were collected and analyzed (30 sites in total). The location of the five mills and the distribution of sampling sites at each mill are shown in **Fig. 2**.

Air samples were analyzed for total VOC (TVOC) and formaldehyde. The TVOC concentration was continuously measured in-situ by a portable gas detector for 15 min at a height of 1.5 m, with a resolution of 1 ppb, and at a flow rate of 220 mL/min (FirstCheck+ 5000, Ion Science Ltd.; Royston, UK). The composition of formaldehyde in the air sample was collected with an active air sampler (TWA-300Z, Tianyue Instrument Co.; Yancheng, China) at a height of 1.5 m from the ground and at a flow rate of 500 mL/min for 20 min. The formaldehyde content in the ambient air sample was analyzed by acetylacetone spectrophotometry. Further study on the composition of VOCs in paper mills was conducted with the gas chromatography-mass spectrometry (GC-MS) analysis method described fully in our previous work [7].

The calculation of the standard-exceeding multiple (SeM) of gaseous pollutants over the standards was given in Eq. 1.



1. Process schematics of five pulp and paper mills.



2. Overview of five mills in southern China and the sampling locations in each mill.

$$SeM = \frac{\text{detected value} - \text{standard value}}{\text{standard value}}$$

Degradation of gaseous pollutants by photo-catalytic oxidation

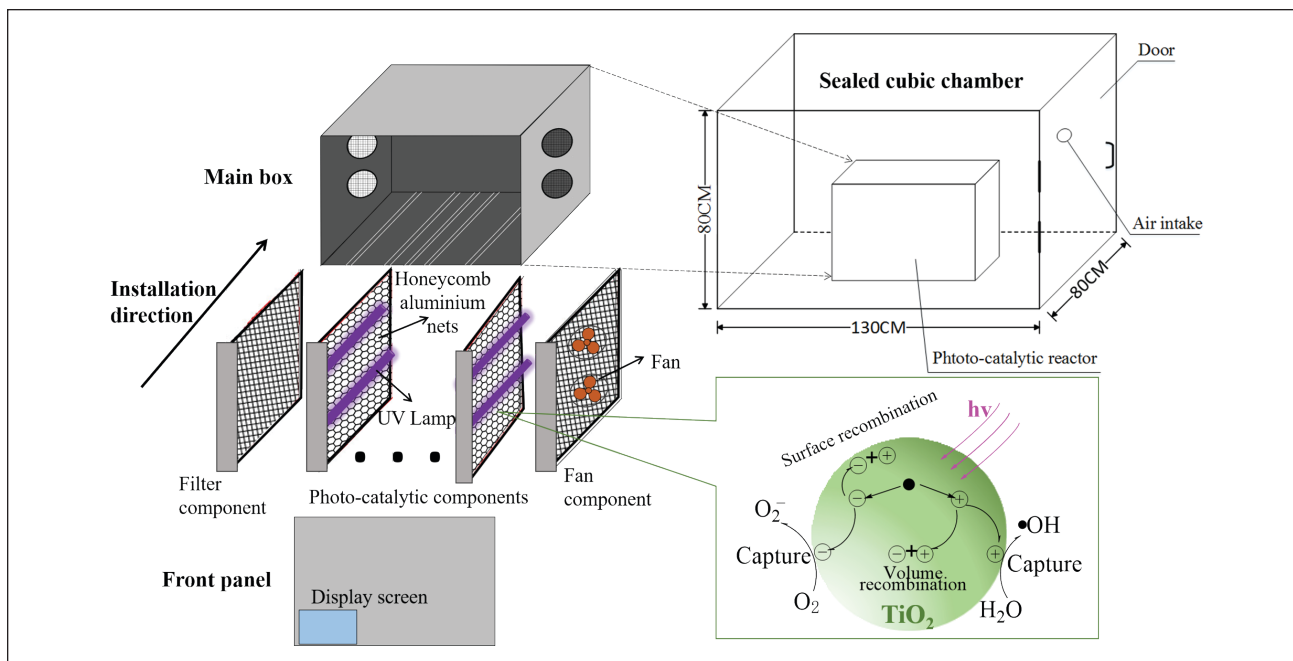
Photo-catalytic reactor system

A photo-catalytic reactor system was designed and studied for treatment of formaldehyde and benzene, as the latter was a parent molecule for a number of the VOCs detected in ambient air. The overall framework of the system is shown in **Fig. 3** and includes a front panel, multiple components, and a main box.

- (1) Combined with a microcontroller unit (MCU), the front panel with a liquid crystal display screen was used for real-time indications of gaseous pollutants concentrations, temperature/humidity, and gas flow rate during the photo-catalytic degradation. The gas flow rate could be adjusted from 0–324 m³/h using the MCU.

Three types of components were included in the reactor: a filter component for the removal of the solid particles in gas, several sets of photo-catalytic components for the degradation of gaseous pollutants, and a fan for adjusting the gas flow rate in the reactor.

Formaldehyde and benzene were the two target gases treated. A formaldehyde sensor (EC803-CH₂O, Bluemoon



3. Schematic diagram of the photo-catalytic system.

Technology Co. Ltd.; Shenzhen, China), a portable benzene sensor (FirstCheck+ 5000, Ion Science Ltd.), and a digital temperature/humidity sensor (DHT11, Aosong Electronics Co. Ltd.; Guangzhou, China) were mounted on the filter component. The photo-catalytic components included three sets of honeycomb aluminium nets coated with nanometer-TiO₂ (30 wt%), which were subjected to the illumination using UVC lamps (254 nm, 15W). The morphology and surface element distribution of the honeycomb aluminum nets were studied by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS), respectively.

Two sets of small circular holes on two sides of the main box were designed for importing and exporting of gas.

As constructed, the system had two operational modes, manual and automatic, which could be controlled using the MCU to determine the optimal photo-catalytic conditions.

Photo-catalytic oxidation degradation experiments

The degradation experiments with the photo-catalytic reactor

were conducted in the following sequence: blank experiments (BE) (**Table I**), optimization experiments (OE), and degradation experiments (DE). Formaldehyde was applied as the target pollutant in the BE and OE. Temperature and relative humidity were approximately 30°C and 48% in the study.

All the experiments were carried out in a sealed cubic chamber (top right corner of Fig. 3) made of polyvinyl chloride and polymethyl methacrylate, to simulate the gaseous environment of a paper mill. The reactor system was placed into the chamber, which had a working volume of 832 L. After the reactor system had operated for 5–10 min, all the sensor data became stable and the target gaseous pollutants were injected into the chamber using a 50 mL injector at the air intake on the chamber. The UV lamps were turned on to start the photo-catalytic DEs. During the degradation process, experimental data were recorded every 5 min. After finishing one DE, the chamber was opened by taking away the door (top right corner of Fig. 3) to discharge the residual gas and prepare for the next experiment.

Experiment No.	Experimental Conditions			Objective
	UV Lamp	Honeycomb Aluminum Nets	HCHO	
BE 1	√	√	×	Testing the zero pollution of the system.
BE 2	√	×	×	Testing if the illumination of UV lamps causes pollution.
BE 3	×	√	×	Testing if the honeycomb aluminum nets cause pollution.
BE 4	×	×	×	Testing if the cubic chamber causes pollution.
BE 5	√	×	√	Testing the effects of UV lamps on the degradation of formaldehyde.

I. Experimental conditions of blank experiments (BE): √ = yes, × = no.

Composition	Mills with Pulping Process		Mills without Pulping Process		
			Mill without Post-processing	Mills with Post-Processing	
	Mill A	Mill B	Mill C	Mill D	Mill E
TVOC	60.83	589.50	6.35	6.59	73.46
HCHO	0.28	1.75	1.30	0.00	0.03

II. Average standard-exceeding multiples (SeMs) of total volatile organic compounds (TVOC) and formaldehyde (HCHO) in the ambient air of five mills.

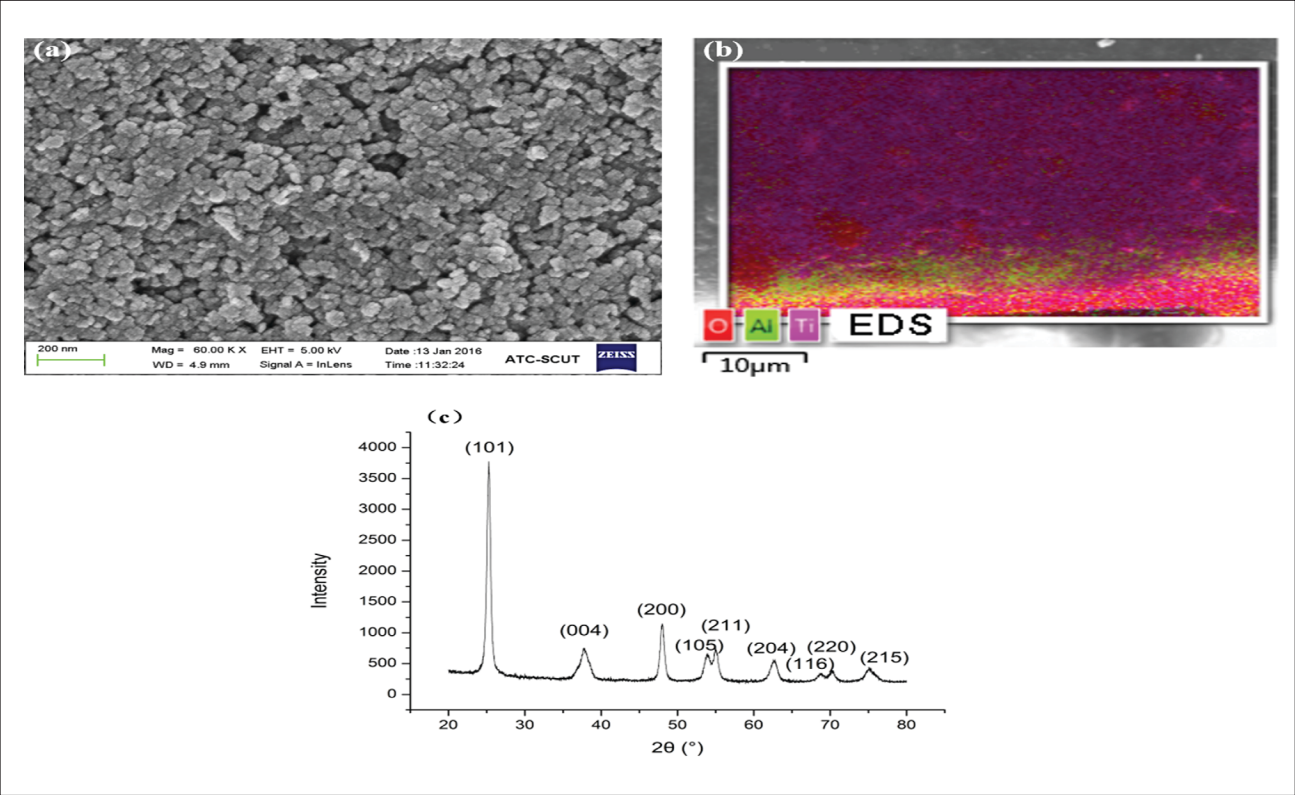
In the photo-catalytic OEs, three parameters thought to influence photo-catalytic degradation were studied: gas flow rates (32.4, 97.2, 162, 259, and 324 m³/h), number of photo-catalytic components (1, 2, and 3 sets), and the geometric size (2 and 3 mm) of the honeycomb aluminium mesh. Formaldehyde solution (36%–38%) and pure liquid benzene (analytical reagent, 99.5%) were used as the sources of the gaseous pollutants in the photo-catalytic experiments.

RESULTS AND DISCUSSION

Determination of ambient air in five pulp and paper mills

The TVOC and HCHO compositions of ambient air were collected and analyzed from 30 sites in five pulp and paper mills

(Fig. 2). Published Chinese standards for TVOC and formaldehyde are 0.60 mg/m³ and 0.10 mg/m³, respectively [25,26]. Average SeMs for TVOC and formaldehyde at the six sites at each mill, calculated using Eq. 1, are listed in **Table II**. Most of the the SeM values were above zero, meaning that almost all the detected levels of TVOC and formaldehyde in the ambient air at the five pulp and paper mills exceeded the standards. In particular, the SeMs of TVOC were generally much higher than those of formaldehyde. As disclosed in our published work, the VOCs composition in the air samples of Mill A (a secondary fiber paper mill), desorbed with the non-polar and polar reagents, included benzene, alkane, phenols, esters, and other substances, in which the benzene homologues were the main hazardous substances [7].



4. Scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), and X-ray diffraction (XRD) images of the surface of honeycomb aluminum mesh in the photo-catalytic reactor: (a) SEM image in the direction perpendicular to the gas flow; (b) EDS elemental mapping in the direction parallel to the gas flow: oxygen (red), aluminum (green), titanium (purple); and (c) XRD peaks of the titanium dioxide (TiO₂).

These ambient air results revealed that formaldehyde and benzene series were the main gaseous pollutants at the five pulp and paper mills studied. Due to its toxicity and resistance to degradation [27,28], benzene has often been used for evaluating the performance of photo-catalysts and photo-catalyst reactor systems. Therefore, in this study, formaldehyde, benzene, and mixtures of the two were selected to assess the performance of the photo-catalytic reactor system.

Degradation of gaseous pollutants by photo-catalytic oxidation

SEM and EDS analysis of honeycomb aluminum nets

The morphology and the surface element distribution of the honeycomb aluminum nets play an important role in photo-catalytic oxidation and these were characterized by SEM, EDS, and X-ray diffraction (XRD) analysis methods. Results are given in **Fig. 4**. The net surface was covered with the spherical particles whose average size was 15 nm (Fig. 4a) and the elements on the net surface contained oxygen, aluminum, and titanium (Fig. 4b). Moreover, as shown in Fig. 4c, the diffraction peaks at $2\theta = 25.2^\circ, 37.7^\circ, 48.0^\circ, 53.8^\circ, 54.9^\circ, 62.8^\circ, 68.6^\circ, 70.2^\circ$, and 75.1° were identified to be the (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal faces of TiO_2 with anatase phase (JCPDF No. 21-1272), respectively. In other words, the characterizations in Fig. 4 show that the honeycomb aluminum nets were covered with the spherical nanometer- TiO_2 wherein the large specific surface area and anatase phase were beneficial to the photo-catalytic degradation of gaseous pollutants.

To ensure the accuracy and reliability of the experimental results, prior to the degradation performance study of the photo-catalytic reactor system, the BEs and OEs were conducted as described in the previous “Photo-catalytic oxidation degradation experiments” section.

Blank experiments (BE) of photo-catalytic system

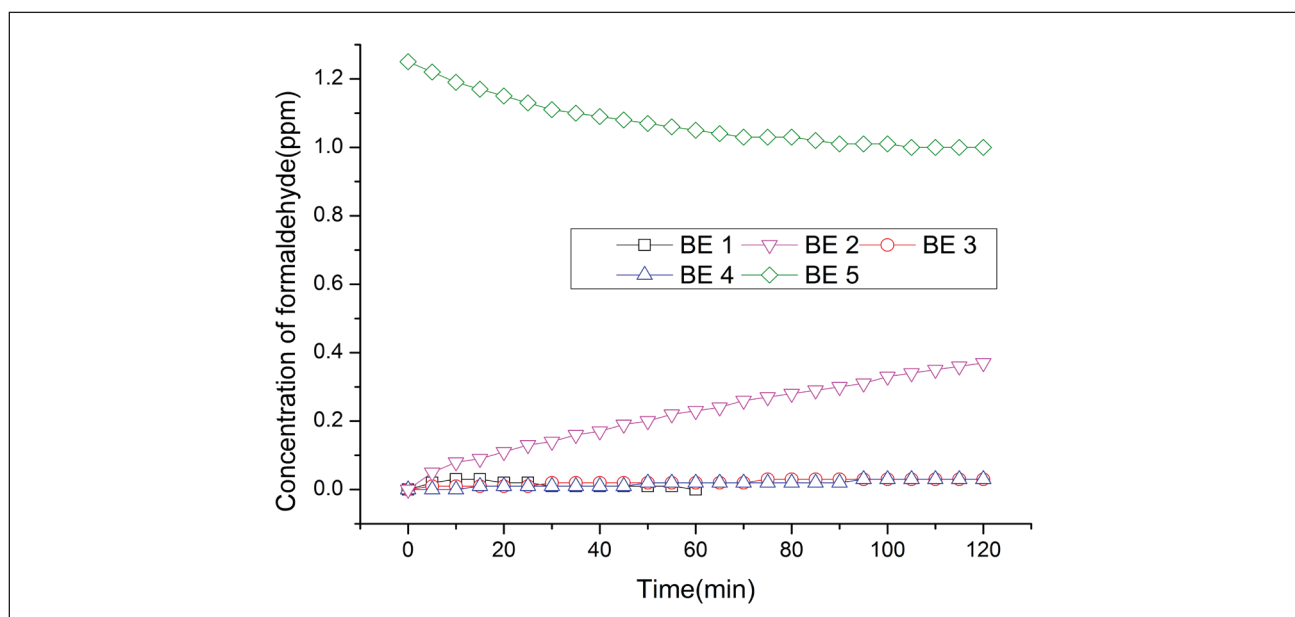
To achieve the objectives listed in Table I, five BEs were conducted. Results are given in **Fig. 5**. These BE results can be explained as follows:

1. BEs 1 and 2 revealed that the ozone produced by the UV lamps (wavelength of 253.7 nm) [29] influenced the formaldehyde sensor data, but formaldehyde could be degraded by the photo-catalytic components [30].
2. BEs 3 and 4 demonstrated that no formaldehyde was detected, which meant that the honeycomb aluminum nets and the cubic chamber did not introduce formaldehyde in the experiments.
3. BE 5 suggested that the UV lamps themselves could degrade formaldehyde about 20% in 120 min.

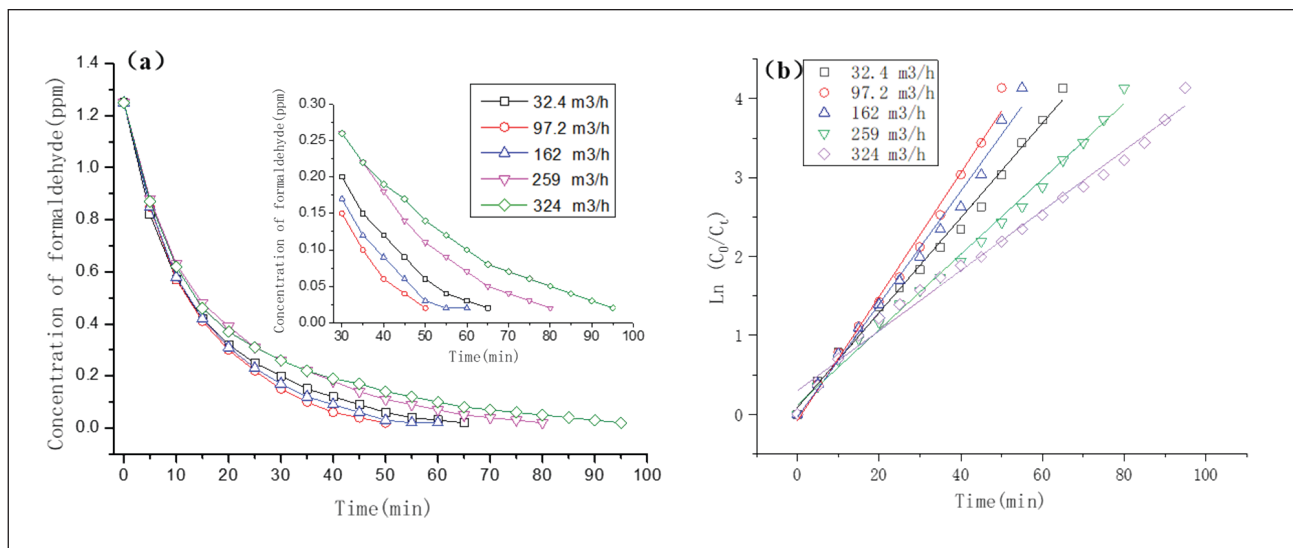
Optimization experiments (OE) of photo-catalytic system

A series of OEs were conducted to investigate the optimal conditions of the photo-catalytic reactor system.

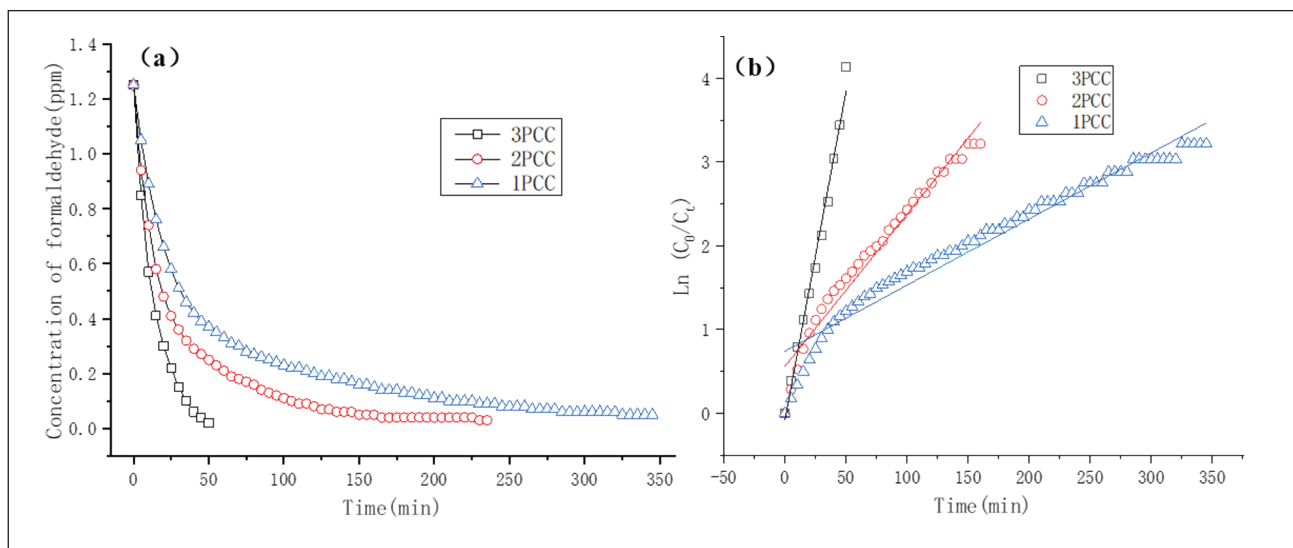
Gas flow rate. Since the gas flow rate indirectly implies the residence time of gas on the photo-catalyst in the range of 32.4 to 324 m^3/h (corresponding to the residence time range [92 to 9 s]), the influence of gas flow rate on the photo-catalytic degradation was studied. Results are shown in **Fig. 6** plots with the flow rates of 32.4, 97.2, 162, 259, and 324 m^3/h . Times for complete degradation were 65, 50, 60, 80, and 95 min (Fig. 6a), and the first order rate constants were 0.060, 0.078, 0.072, 0.048, and 0.038/min (Fig. 6b), respectively. The photo-catalytic degradation processes were slower at high flow rates (324 and 259 m^3/h) relative to low flow rates (162, 97.2, and 32.4 m^3/h). The photo-catalytic reaction rate could be expressed by the time needed to degrade the same amount of formaldehyde (Fig. 6a) or the first order rate constant cal-



5. Results of five blank experiments (BE) in the experimental photo-catalytic system.



6. Influence of gas flow rate on the photo-catalytic degradation process: (a) evolutions of formaldehyde concentration with time, and (b) correlations of $\ln(C_0/C_t)$ with time.



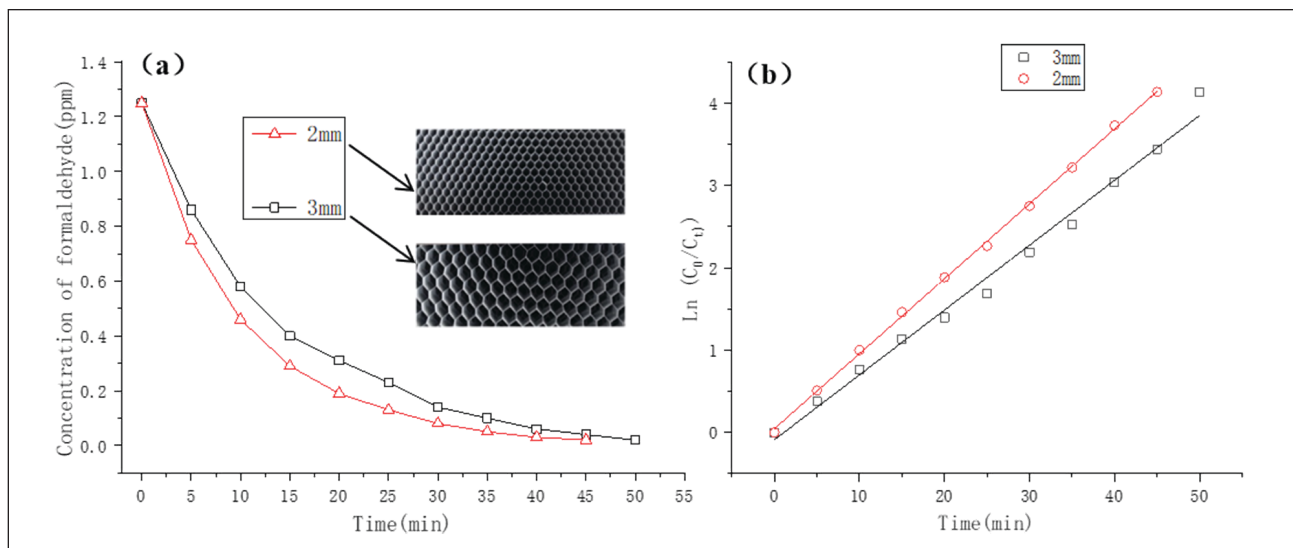
7. Influence of the number of photo-catalytic components (PCC) on the photo-catalytic degradation process: (a) evolutions of formaldehyde concentration with time, and (b) correlations of $\ln(C_0/C_t)$ with time.

culated by fitting curve in Fig. 6b. From these results it was determined that the optimal gas flow rate was 97.2 m³/h (residence time of 31s).

It was evident from the results in Fig. 6 that suboptimal gas flow rates decreased the photo-catalytic degradation rate. This phenomenon is attributed to the effect of flow rate on photo-catalytic reaction, which is double antagonistic [29]. When the flow rates were low (in the range of 32.4 and 97.2 m³/h with residence times of 92 and 31 s, respectively), photo-catalytic oxidation was mainly a mass transfer in which the reaction rate increased with the increase of flow rate. When the flow rate became high (in the range of 162 and 324 m³/h with residence times of 18 and 9 s, respectively), the photo-catalytic reaction dominated the mass transfer reaction. In this

case, lower flow rate with longer residence time on the photo-catalyst increased the reaction rate, which is in agreement with Monteiro et al. [31] and could explain why a medium gas flow rate (97.2 m³/h) performed best in the study.

Number of photo-catalytic components. Under the optimal gas flow rate of 97.2 m³/h, when the number of photo-catalytic components increased from 1 to 3, the necessary time for the complete degradation of formaldehyde was 345, 235, and 50 min (**Fig. 7a**), and the first order rate constant increased from 0.008 to 0.018 to 0.079/min (Fig. 7b), respectively. From the perspective of degradation time and rate constant, the photo-catalytic activity was remarkably enhanced with the use of three photo-catalytic components, allowing



8. Effect of the geometric size of honeycomb aluminum mesh on the photo-catalytic degradation process: (a) evolutions of formaldehyde concentration with time, and (b) correlations of $\ln(C_0/C_t)$ with time.

greater catalyst surface area, more contact area between catalyst and pollutants, and a higher concentration of pollutants adsorbed on the photo-catalyst. More photo-catalytic components also meant higher UV light intensity, which could generate more photons and electron-hole pairs [29,32]. Therefore, the optimal number of photo-catalytic components was determined as three in the study.

Geometric size of honeycomb aluminum mesh. Functioning as the substrate of the photo-catalyst, geometric size of the honeycomb aluminum mesh can influence the contact area between the catalyst and the gaseous pollutants. With the optimal gas flow rate of 97.2 m³/h and 3 photo-catalytic components, two sizes of the honeycomb aluminum mesh, 2 mm and 3 mm, were applied and compared in the study. As displayed in **Fig. 8a**, the photo-catalytic degradation performance with 2 mm mesh was slightly better than that with 3 mm mesh. It took 45 and 50 min for the same amount of formaldehyde to be completely degraded with 2 mm mesh and 3 mm mesh, respectively. As shown in Fig. 8b, the photo-catalytic degradation with different geometric sizes of honeycomb aluminum mesh also accorded with the first order kinetics, and the rate constants were 0.091 and 0.079/min by 2 mm and 3 mm meshes, respectively. These results demonstrated that the smaller the mesh size performed slightly better due to the larger contact area with the catalyst.

The previously described OEs indicated that the optimal conditions for the photo-catalytic reactor system were as follows: gas flow rate 97.2 m³/h, 3 photo-catalytic components, and a 2 mm geometric size for the honeycomb aluminum mesh.

Degradation performance of the photo-catalytic reactor

After having performed the BEs and OEs of the photo-catalytic reactor system, degradation performance studies were conducted under the optimal conditions.

To study the kinetic behavior of photo-catalytic degradation of formaldehyde and benzene, the degradation rate equation of the simplified model of Langmuir-Hinshelwood (L-H) [33], which is a well-known kinetic model for describing the heterogeneous photo-catalytic oxidation, was applied in the study. The simplified L-H model can be expressed as:

$$\gamma = -\frac{dC}{dt} = kC \quad (2)$$

where γ is the degradation rate, C is concentration of reactant, t is the reaction time, and k is the reaction rate constant. The integral form of Eq. 2 is:

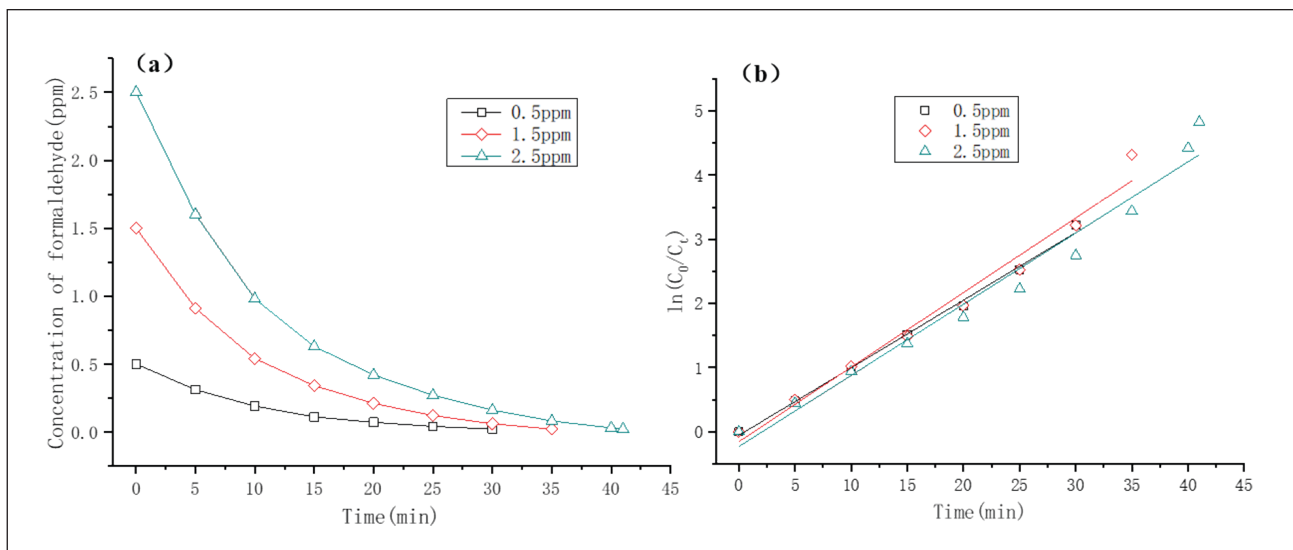
$$\ln \frac{C_0}{C_t} = kt \quad (3)$$

where C_0 and C_t are the concentrations of reactant at the initial time and the reaction time, t .

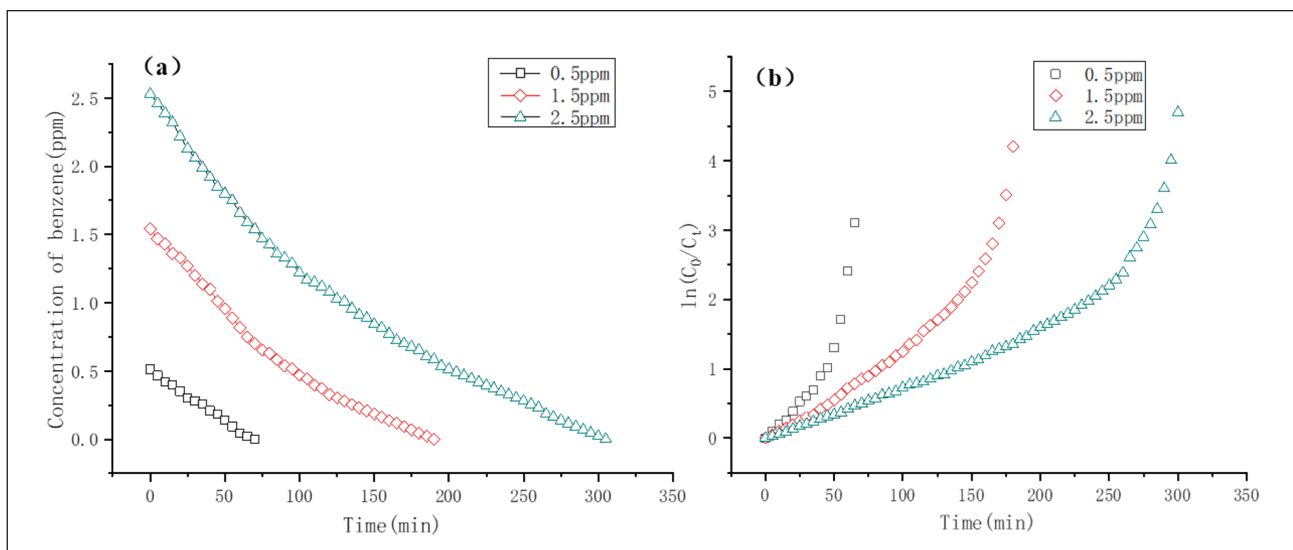
Formaldehyde as the target pollutant. The DEs results of formaldehyde with different initial concentrations are given in **Fig. 9**.

As indicated in Fig. 9a, regardless of what the initial levels of formaldehyde were, it could all be completely degraded by the photo-catalytic reactor, and the times needed for complete degradation were 41, 35, and 30 min for the 2.5, 1.5, and 0.5 ppm initial concentrations of formaldehyde, respectively. Moreover, according to Eq. (2), the degradation rate, γ , of formaldehyde increased with higher initial concentration, C_0 .

Considering the kinetic behavior of the photo-catalytic degradations of formaldehyde, as shown in Fig. 9b, the coefficients of determination of linear fitting curves for 2.5, 1.5, and 0.5 ppm formaldehyde were 0.968, 0.975, and 0.996,



9. Influence of initial formaldehyde concentration on the photo-catalytic degradation under optimal conditions: (a) evolutions of formaldehyde concentration with time, and (b) correlations of $\ln(C_0/C_t)$ with time.



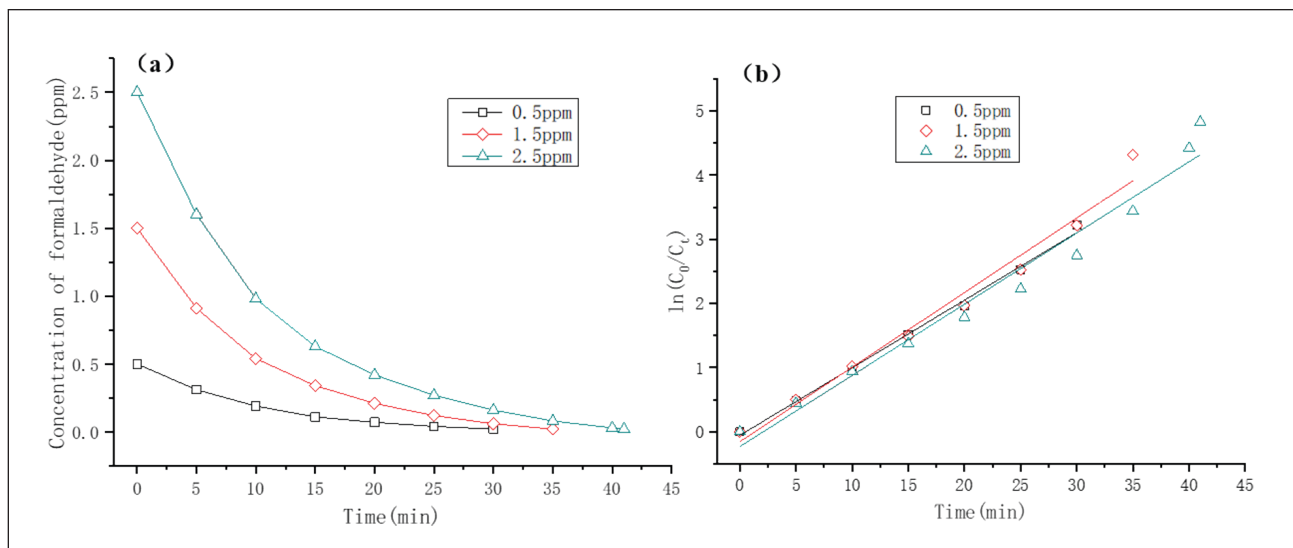
10. Influence of initial benzene concentration on the photo-catalytic degradation under the optimal conditions: (a) evolutions of benzene concentration with time, and (b) correlations of $\ln(C_0/C_t)$ with time.

respectively, which was close to 1. According to Eq. 3, these high linear correlations indicated that the photo-catalytic degradation process of formaldehyde fitted the first-order reaction, and the first-order reaction rate constants, k , for 2.5, 1.5, and 0.5 ppm formaldehyde were 0.111, 0.116, and 0.105 /min, which was similar and independent of the initial concentration.

Benzene as the target pollutant. Under the optimal conditions, the DE results of benzene with different initial concentrations are shown in **Fig. 10**. Compared with the results in Fig. 9, although the photo-catalytic reactor could completely degrade benzene in 310, 180, and 70 min for 2.5, 1.5, and 0.5 ppm initial concentrations of benzene, respectively, the

degradation processes were considerably longer than those for formaldehyde degradation at the same initial concentrations. As shown in Fig. 10a, the degradation behavior was very different from that of formaldehyde (Fig. 9a). When the initial concentration of benzene increased, the time for total degradation increased linearly. Because of these differences, the kinetic behavior of the photo-catalytic degradation of benzene was studied further. As shown in Fig. 10b, no linear correlation between $\ln \frac{C_0}{C_t}$ and the reaction time, t , was observed, indicating that the degradation of benzene did not conform to the first-order kinetics.

To compare the degradation behaviors of formaldehyde and benzene, their degradation curves with the same initial concentrations of 1.25 ppm are plotted in **Fig. 11**. From Fig.



11. Comparison of the photo-catalytic degradation profiles of formaldehyde and benzene in pure forms with the same initial concentration: (a) evolutions of concentration with time, and (b) correlations of $\ln(C_0/C_t)$ with time.

11a, it was evident that the necessary complete degradation time for benzene was almost four times longer than that for formaldehyde.

The possible reasons why the benzene was more difficult to degrade than formaldehyde are as follows:

1. Owing to a lower bond energy than that of benzene [34], formaldehyde can be easily degraded to formic acid and then completely converted into carbon dioxide and water, displaying a short pathway for degradation [35]. However, the pathway of benzene for being photo-catalytically degraded is long and complex [36], which includes several intermediate processes, the direct reaction of benzene and electron hole pairs, the reaction of benzene and hydroxyl radical, and the polymerization of benzene.
2. The intermediate products of benzene vary and can be strongly adsorbed by the catalyst, leading them to be less reactive with the catalyst [36]. Thus, the competitive adsorptions of the intermediate products and the deactivated catalyst might be the main causes of the slow degradation of benzene [36,37]. Thus, as shown in Fig. 11b, the deactivation of TiO_2 in the photo-catalytic process may be the reason why the degradation of benzene did not fit the first-order reaction.
3. Another possible reason for the different kinetic degradation behaviors of formaldehyde and benzene might be that the optimal degradation conditions obtained with formaldehyde in the section on "Optimization experiments (OE) of photo-catalytic system" were not suitable for the degradation of benzene.

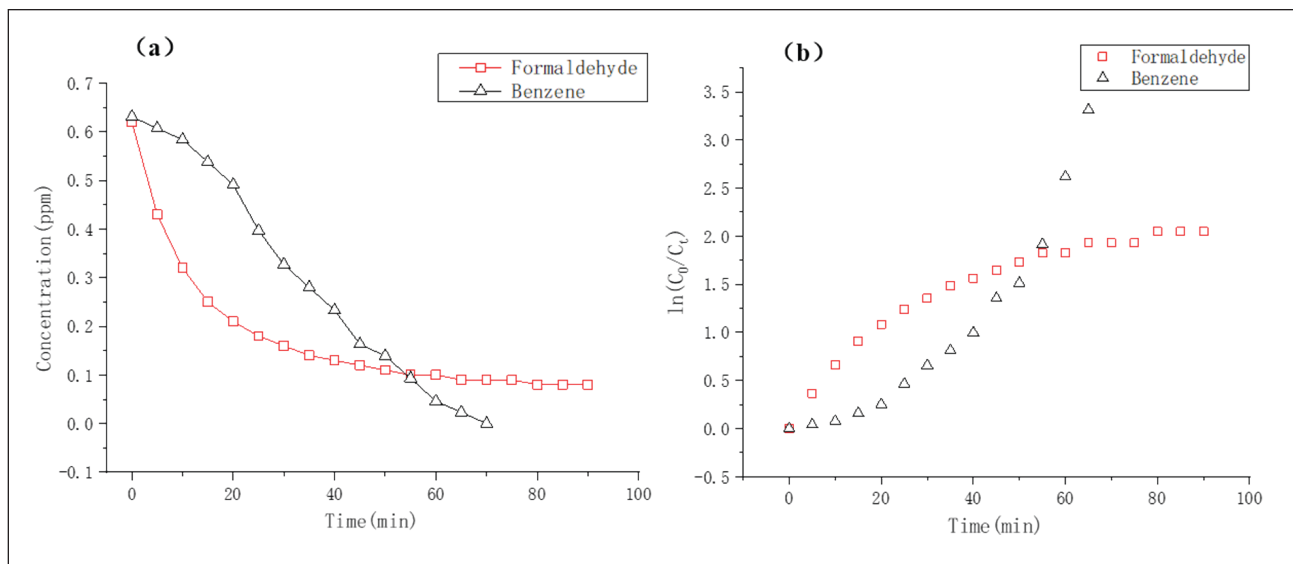
Mixture of formaldehyde and benzene as the target pollutant. In order to better simulate the actual gaseous conditions in paper mills, a mixture of formaldehyde and benzene was employed to evaluate the degradation performance of

the photo-catalytic reactor. The initial concentrations of both formaldehyde and benzene were about 0.625 ppm and the initial total concentration of the mixture was 1.25 ppm. The photo-catalytic degradation results for the mixture are given in **Fig. 12**.

The degradation of formaldehyde in the mixture, as plotted in Fig. 12a, decreased rapidly in the initial phase, but the rate gradually slowed, and became even slower than that of benzene, without being degraded completely in the end. The benzene concentration decreased relatively slowly in the initial stage and then dropped to near zero. Compared with the results in their pure forms (Fig. 11a), the reaction process of formaldehyde in the mixture was different; it took about two times longer to be degraded, while the degradation of benzene in the mixture was similar to that in its pure form.

Furthermore, owing to the different degradation behavior of formaldehyde in the mixture, as shown in Fig. 12b, the previously observed linear correlation between $\ln \frac{C_0}{C_t}$ and the reaction time, t , for formaldehyde in its pure form (Fig. 11b) became nonlinear, which revealed that the photo-catalytic kinetics of formaldehyde in the mixture no longer belonged to the first-order reaction.

This degradation phenomena for the mixture could be explained as due to the presence of the hydroxyl group that is an electron-donor functional group in formaldehyde [38]. The adsorption ability of formaldehyde on the catalyst is greater than that of benzene. Hence, in the initial stage of the photo-catalytic oxidation, formaldehyde was adsorbed on the TiO_2 and degraded preferentially. With the formaldehyde concentration decreased, the adsorption and degradation of benzene gradually became dominant in the mixture, and the competitive adsorptions of the intermediate products of benzene impeded the further degradation of formaldehyde in the mixture. Another possible explanation may be that aldehyde substances, intermediate products of benzene [36,39], influenced the



12. Comparison of the photo-catalytic degradation profiles of formaldehyde and benzene in the mixed forms with the same initial concentration: (a) evolutions of concentration with time, and b) correlations of $\ln(C_0/C_t)$ with time.

formaldehyde sensor and caused it to deliver a signal that might not represent the real concentration of formaldehyde.

The photo-catalytic experiment results in the “Degradation performance of the photo-catalytic reactor” section indicated that when employing formaldehyde, benzene, and their mixtures as representative gaseous pollutants in paper mills, the developed photo-catalytic reactor was capable of degrading the test gasses. These bench scale results suggest the possibility that a photo-catalytic reactor could be used to purify gaseous pollutants in the ambient air of paper mills.

CONCLUSION

Analytical results of ambient air in five pulp and paper mills showed formaldehyde and TVOC (including benzene series) to be the two main gaseous pollutants. A photo-catalytic reactor system with TiO_2 was developed and tested to degrade these gaseous pollutants. After having conducted blank and optimization studies on the reactor, studies were undertaken with the reactor by applying formaldehyde, benzene, and their mixtures as the target gasses. The following points were concluded from the study:

1. Both formaldehyde and benzene could be completely photo-catalytic degraded, but the complete degradation time for benzene was almost four times longer than that for formaldehyde, which revealed the difficult degradation of benzene.
2. The photo-catalytic degradation rate of formaldehyde increased with initial concentration, and its degradation could be modeled as a first-order reaction. Reaction rate constants were similar and independent of the initial concentration. On the contrary, the degradation rate of benzene had no relationship with initial concentration, and its photo-catalytic degradation did not conform to the first-order kinetics reaction.

3. The photo-catalytic reaction process of formaldehyde in the mixture was different; it took about two times longer to be degraded than in its pure form, and related kinetics were no longer first-order. However, the photo-catalytic degradation of benzene in the mixture was almost the same as in pure form.

These study results demonstrated that the photo-catalytic reactor could degrade formaldehyde and benzene. **TJ**

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ABOUT THE AUTHORS

We chose to research this topic because analysis of gaseous pollutants in paper mills has been scarce for some time, and few studies have dealt with degrading treatment of gaseous pollutants in mills. In the past few years, we have performed systematic research on the main composition of gaseous pollutants from paper mills. This work introduces a photo-catalytic degradation system for dealing with these pollutants.

The most difficult aspect of this research was finding a way to conduct the degradation experiments for the papermaking gaseous pollutants in the laboratory. Therefore, we developed feasible photo-catalytic degradation equipment so we could degrade and observe the evolution of the main types of polluted gas. When we applied formaldehyde, benzene, and their mixtures as the target pollutants, the photo-catalytic reactor system we developed had excellent degradation performance for

these pollutants. It was interesting to find that the degradation behaviors of formaldehyde and benzene are different in their pure forms and that they may affect each other in their mixing form during the degradation process.

This study will raise awareness around the serious gaseous pollution in the paper industry, and the photo-catalytic degradation technology introduced here can help paper mills control the emission of polluting gases. Our subsequent research will study the photo-catalytic degradations of other gaseous pollutants and realize their practical application in paper mills.

Tong is a post-doctoral student, Li is a doctoral student, Chen is associate professor, and Shen is professor at the State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China. Email Shen at ppwhshen@scut.edu.cn.



Tong



Li



Chen



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