



# Photodecomposition of 4-chlorophenol by reactive oxygen species in UV/air system

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## ABSTRACT

In this article, the photo-degradation of 4-chlorophenol (4-CP) under UV irradiation was studied with focus on the photodecomposition of 4-CP by reactive oxygen species (ROS). 4-CP underwent much faster and more complete degradation in UV/air system than in UV/N<sub>2</sub> system. In UV/air system, the addition of *t*-butanol, a well-known •OH scavenger, significantly impeded the degradation of 4-CP. In the presence of *t*-butanol, the tendencies for the degradation of 4-CP and the formation of intermediates in UV/air system were very similar to those in UV/N<sub>2</sub> system. In UV/air system, 4-CP was degraded by two pathways, direct photolysis by absorbing the photons and the oxidation via •OH. The contribution of direct photolysis and the oxidation via •OH to 4-CP decomposition were 17.2% and 82.8%, respectively based on the apparent kinetic constants. Hydrogen peroxide, which could produce •OH through photolysis, was formed in UV/air system. It was shown that dissolved oxygen, organic matter in excited state and hydrogen ion are all necessary for the formation of hydrogen peroxide. The formation mechanism of H<sub>2</sub>O<sub>2</sub> was proposed based on experimental evidence.

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## 1. Introduction

Phenolic compounds, especially chlorinated phenols are persistent organic contaminants commonly found in the environment. These compounds are manufactured for a variety of applications such as the higher chlorinated congeners, certain dyes and pesticides [1]. Due to the recalcitrant nature of these phenolic compounds, conventional biological treatments are not effective [2].

Available technologies to deal with phenolic compounds include the advanced oxidation processes (AOPs) [3,4]. Among AOPs, the photo-degradation processes such as UV/Fe<sup>3+</sup>, UV/H<sub>2</sub>O<sub>2</sub> and UV/O<sub>3</sub> have shown great potential for the destruction of persistent organic contaminants including chlorophenols [5–9]. During these photo-degradation processes, the contaminants are degraded mainly by the attack of •OH radical produced via photoreaction of H<sub>2</sub>O<sub>2</sub>, Fe<sup>3+</sup> or O<sub>3</sub>. The other degradation pathway is by UV photolysis. Elucidation of the degradation of the contaminant under UV irradiation is key in understanding the mechanism of the photo-degradation processes including UV/Fe<sup>3+</sup>, UV/H<sub>2</sub>O<sub>2</sub> and UV/O<sub>3</sub>.

The fate of chlorophenols under UV irradiation has been studied, in particular on the effects of the operational parameters and the formation of degradation products [10–13]. Lipczynska-Kochany and Bolton [14] reported that *p*-benzoquinone was the primary product of 4-chlorophenol (4-CP) under UV irradiation, while Svetlichnyi et al. [15] observed that the main product is hydroquinone through the C–Cl bond cleavage and the decomposition of the intermediate ionic or radical forms. The photo-degradation rate of the chlorophenols depended on the concentration of dissolved oxygen, pH value, molecule structure, etc. The chlorophenol speciation (dissociated or undissociated) is determined by solution pH and various studies have demonstrated the impact of pH values and chlorophenol speciation (dissociated or undissociated) on the quantum yield for the photolysis of chlorophenols [16–19].

Previously, it has been demonstrated that some oxygen species are important oxidants for the photolysis of phenols [11,20]. During the degradation of phenol under UV irradiation, increasing oxygen concentration resulted in higher degradation and mineralization rates of phenol [11]. Furthermore, it has been suggested that the photodecomposition of organic matter may proceed via the direct photolysis involving energy and electron transfer after absorption of photons by organic matter, or via indirect (sensitized) processes, involving organic matter reactions with photochemically generated intermediates such as reactive oxygen species (ROS) [21,22]. ROS include free radicals (e.g., superoxide and hydroxyl radicals)

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and nonradical oxygen species (e.g., hydrogen peroxide and peroxynitrite) [23]. It has been known that the concentration of dissolved oxygen affects the photo-degradation process, thus the formation of ROS and the decomposition by ROS need to be investigated during the photo-degradation of chlorophenols under UV irradiation.

So far most researches have focused on direct photolysis of chlorophenols and limited data is available on the formation of ROS and the photodecomposition of chlorophenols by ROS under UV irradiation. In this study, the degradation of 4-chlorophenol (4-CP) under UV irradiation was investigated. A medium pressure mercury (Hg) lamp, which was widely applied in the photo-degradation processes, was the light source in present work. At first, the degradations of 4-CP under anaerobic (bubbling with  $N_2$ , called UV/ $N_2$  system) and aerobic (bubbling with air, called UV/air system) conditions were compared. Secondly, the oxidation of 4-CP by hydroxyl radical ( $\bullet OH$ ) was confirmed by the addition of *t*-butanol, a  $\bullet OH$  scavenger in UV/air system. The production of  $H_2O_2$ , which is readily photolyzed to produce  $\bullet OH$  under UV irradiation, was detected. And then the effects of dissolved oxygen, the input of 4-CP and pH value on the formation of  $H_2O_2$  were examined. Finally, the formation mechanism of  $H_2O_2$  in UV/air system was proposed. This study showed that  $H_2O_2$  was formed in 4-CP aerated solution under UV irradiation and the decomposition of 4-CP by ROS was significant. The study resulted in better understanding and provided more insight into the photo-degradation processes of chlorophenols under UV irradiation.

## 2. Materials and methods

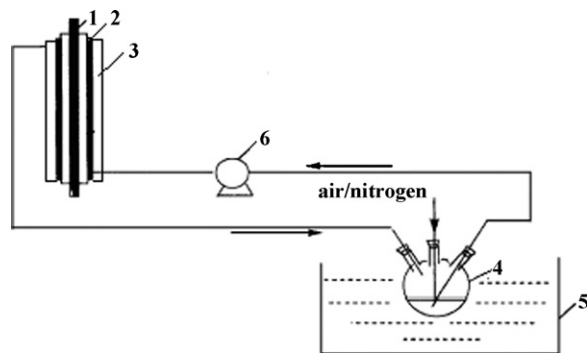
### 2.1. Materials

4-Chlorophenol (4-CP), hydroquinone, *p*-benzoquinone, *t*-butanol,  $H_2SO_4$  and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd, and 4-chlorocatechol was from Tokyo Kasei Kogyo Co., Ltd. These reagents were all of analytical grade. Deionized and doubly distilled water was used throughout this study.

### 2.2. Procedures and analysis

The schematic diagram of the experimental set-up used in the study is shown in Fig. 1.

The photoreactor is an annular quartz cylinder with a capacity of 0.56 L and a height of 200 mm, with inner and outer diameters of 40 mm and 50 mm, respectively. The water-cooled jacket out of the photoreactor is annular and made of quartz as well. The light source is configured in the axial center of the reactor, which



**Fig. 1.** Schematic diagram of photochemical reaction system experimental set-up: 1. lamp, 2. photoreactor, 3. water-cooled jacket, 4 flask, 5. thermostatic bath, and 6. pump.

is a medium pressure mercury lamp of 300 W (Philips). The lamp emits at various wavelengths ranging from 200 to 600 nm, mainly at 365 nm.

At first, 1.0 L aqueous solution of 4-CP at a desired concentration was prepared using a 4-CP stock solution and deionized water. The solution was put in a flask, which was immersed in a water bath. The reaction temperature was controlled at 35 °C ( $\pm 0.5$  °C) by circulating cooling water in the quartz jacket. Then the solution was bubbled with air or  $N_2$  ( $Q = 0.20 \text{ m}^3/\text{h}$ ) for 30 min before it was pumped into the photoreactor and the bubbling continued during the whole reaction. Solution pH was adjusted to the desired value with  $H_2SO_4$  solution ( $V_{H_2SO_4} : V_{\text{deionized water}} = 1 : 2$ ) or 1 M aqueous NaOH solution. After that, the solution was pumped from the flask into the photoreactor. When the solution flowed back into the flask, the reaction was initiated by turning on the lamp. At the desired time, the sample was withdrawn for analysis.

Analysis of 4-CP and the intermediates were performed with a Knauer HPLC unit with a reversed phase C18 column and UV detector. The detecting wavelength was set at 278 nm. The mobile phase was 52:48 (v/v) methanol and deionized water (containing 2% acetic acid) with a flow rate of 1.0 mL/min. The concentration of  $Cl^-$  was measured using an ion chromatography system (IC1000, Alltech, USA) with an anion column. The mobile phase was a solution of sodium bicarbonate and sodium carbonate with a flow rate of 1.0 mL/min.

The concentration of  $H_2O_2$  was determined by a spectrophotometric analysis using the potassium titanium (IV) oxalate method [24]. A solution of 0.1 M potassium titanium (IV) oxalate was mixed with the sample to form titanium (IV)-peroxide complex and then the absorbance at 400 nm ( $A_1$ ) was measured. Because the sample itself absorbed a little at 400 nm with an absorbance of  $A_2$ , the real absorbance of the titanium (IV)-peroxide complex was  $A_1 - A_2$ .

UV–Vis spectra were recorded with a Techcomp 8500 spectrometer. Dissolved oxygen (DO) was measured by a JPB-607 dissolved oxygen meter (Shanghai Precision & Scientific Instrument Co. Ltd.).

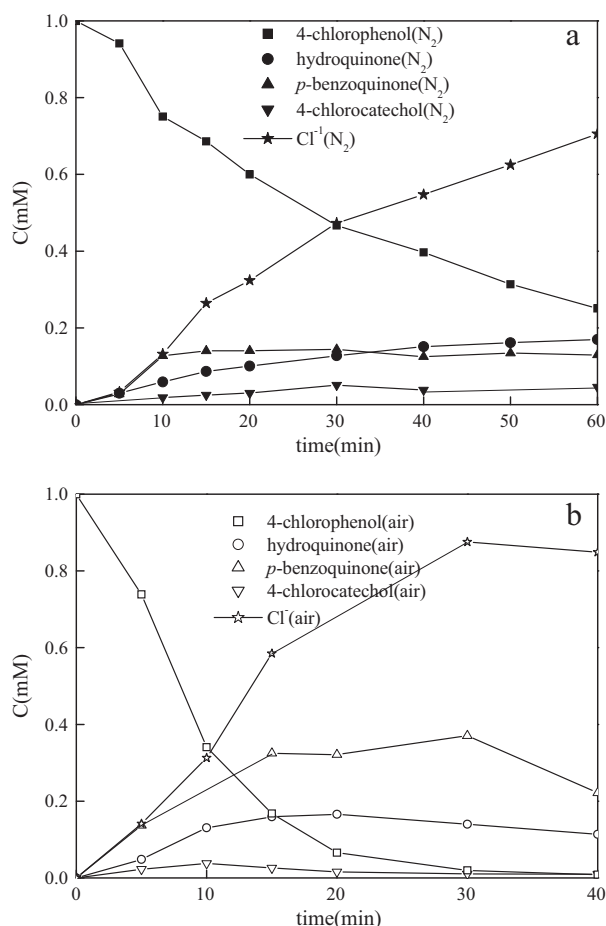
## 3. Results and discussion

### 3.1. Comparison of the degradation of 4-CP in UV/ $N_2$ and UV/air systems

The degradation of 4-CP and the formation of the intermediates in UV/ $N_2$  and UV/air systems are shown in Fig. 2(a) and (b), respectively. Bubbling with air gave the solution with a DO concentration of about 8 mg/L. While in UV/ $N_2$  system, nitrogen was purged for 30 min before the reaction initiation, resulting in a very low concentration of dissolved oxygen.

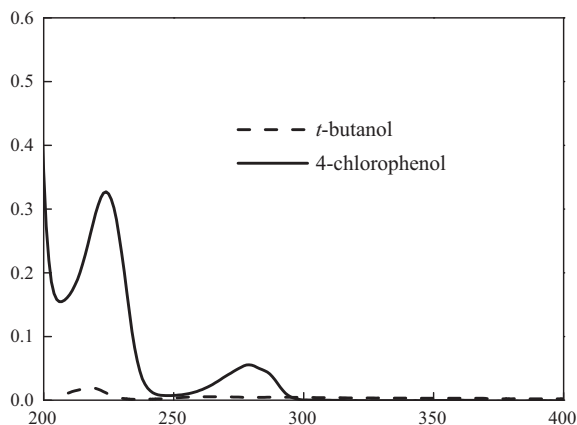
Fig. 2 shows that the degradation of 4-CP is much faster and more complete in UV/air system than that in UV/ $N_2$  system. Almost all 4-CP was eliminated from the solution after 40 min in UV/air system. While in UV/ $N_2$  system, only 64% of 4-CP was degraded after 40 min and about 25% of 4-CP remained in solution after 60 min.

Hydroquinone, *p*-benzoquinone and 4-chlorocatechol were the major intermediates formed during 4-CP degradation in UV/ $N_2$  system. In UV/ $N_2$  system, the concentration of *p*-benzoquinone reached 0.14 mM after 15 min of reaction and remained almost unchanged afterwards. Hydroquinone concentration increased fast within 30 min of reaction and then slowed down. After 60 min, hydroquinone concentration reached 0.17 mM in the solution. Only small amount of 4-chlorocatechol was formed, about 0.05 mM after 30 min of reaction. The comparison of 4-CP disappearance and the appearance of chloride ion confirmed that the chlorinated compound was generated in UV/ $N_2$  system. The generation of chlorinated compound of 3-chloro-1,4-benzenediol was also observed during the photolysis of 3-CP [12].

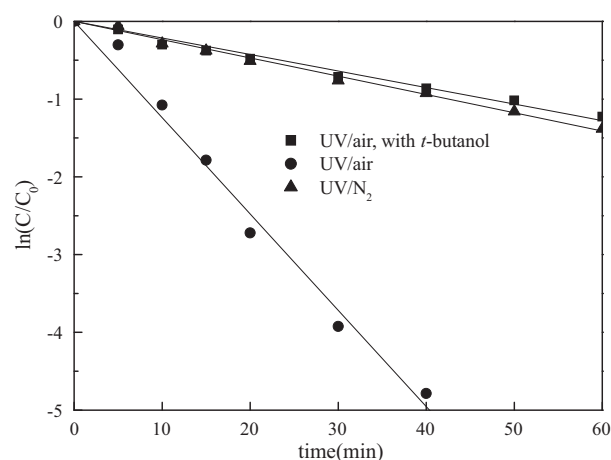


**Fig. 2.** Degradation of 4-CP and the formation of the intermediates in (a) UV/N<sub>2</sub> system and (b) UV/air system ([4-CP]<sub>0</sub> = 1 mM; pH<sub>0</sub> = 2.9; T = 35 °C; Q<sub>air/N<sub>2</sub></sub> = 0.20 m<sup>3</sup>/h).

Several differences are observed in the degradation in the two systems. In UV/air system, hydroquinone, *p*-benzoquinone and 4-chlorocatechol were also detected, however, the main product was *p*-benzoquinone. The concentration of *p*-benzoquinone reached a maximum of 0.37 mM after 30 min, which is much higher than that in UV/N<sub>2</sub> system. The concentration of hydroquinone increased to 0.16 mM after 20 min. Furthermore, the concentration of 4-chlorocatechol was much lower in UV/air system than that in UV/N<sub>2</sub> system. The formation of Cl<sup>-</sup> is also presented in Fig. 2(b), which



**Fig. 3.** UV-Vis spectra of 4-CP (1 mM) and *t*-butanol (10 mM).



**Fig. 4.** Observed kinetics of 4-CP degradation in the presence or absence of *t*-butanol by UV/air system ([4-CP]<sub>0</sub> = 1 mM; pH<sub>0</sub> = 2.9; T = 35 °C; Q<sub>air/N<sub>2</sub></sub> = 0.20 m<sup>3</sup>/h).

is quicker than that in UV/N<sub>2</sub> system. This was due to the quicker degradation of 4-CP and less formation of 4-chlorocatechol.

In UV/N<sub>2</sub> system, no reactive oxygen species could be generated and thus the decomposition of 4-CP by ROS could not happen. As shown in Fig. 3, the absorption of 4-CP in the region of 200–300 nm is obvious and the absorption peak appeared at 278 nm. Because the emission spectrum of Hg lamp overlaps the absorption spectrum of 4-CP, energy supplied by the lamp could be absorbed by 4-CP, which then was passed to its excited state and underwent further reactions to other intermediates.

The degradation of 4-CP was enhanced by the presence of the dissolved oxygen. As oxygen could not react with 4-CP directly, it was concluded that during the degradation of 4-CP under UV irradiation, oxygen should participate in some photochemical reactions to form the reactive oxygen species.

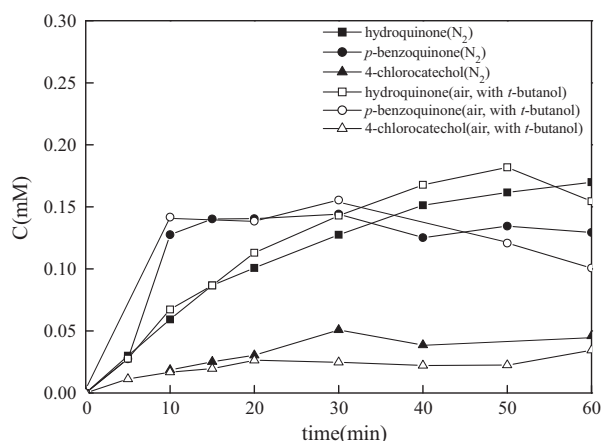
### 3.2. Two degradation ways of 4-chlorophenol under UV irradiation

It has been reported that the photo-induced transformation of reactive oxygen species such as superoxide radical (O<sub>2</sub><sup>•-</sup>), hydroperoxyl radicals (HO<sub>2</sub><sup>•</sup>) and hydroxyl radicals (•OH) took place in the photo-degradation of organic matters [25,26].

To determine whether the reactive oxygen species were formed during the degradation of 4-CP in UV/air system, *t*-butanol (10 mM), a well-known •OH radical scavenger was added into 4-CP solution. As shown in Fig. 4, the presence of *t*-butanol significantly impeded the degradation of 4-CP. In UV/air system, the degradation of 4-CP in the presence or absence of *t*-butanol both followed the pseudo-first-order kinetics well. In the presence of *t*-butanol, the apparent reaction rate constant was  $2.13 \times 10^{-2} \text{ min}^{-1}$ , which was much smaller than that in the absence of *t*-butanol, i.e.,  $12.4 \times 10^{-2} \text{ min}^{-1}$ .

It was interesting that with the addition of *t*-butanol, the degradation of 4-CP and the formation of intermediates in UV/air system were almost the same as those in UV/N<sub>2</sub> systems, as shown in Figs. 4 and 5. As 4-CP was destructed only by direct photolysis in UV/N<sub>2</sub> system, the degradation of 4-CP in UV/air system in the presence of *t*-butanol could only occur via direct photolysis.

*t*-Butanol is a well-known •OH scavenger, with a reaction rate constant with •OH as high as  $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [27]. The absorption of *t*-butanol is minimal in the range of 200–400 nm (Fig. 3), which is the main absorption region of 4-CP. Thus, it was concluded that the depression in 4-CP degradation by the addition of *t*-butanol was due to the competition of *t*-butanol against 4-CP to react with •OH



**Fig. 5.** Formation of the intermediate products in UV/air (in the presence of *t*-butanol) and UV/N<sub>2</sub> systems ([4-CP]<sub>0</sub> = 1 mM; pH<sub>0</sub> = 2.9; T = 35 °C; Q<sub>air/N<sub>2</sub></sub> = 0.20 m<sup>3</sup>/h).

Thus, it could be deduced that in UV/air system, 4-CP was destructed via two pathways. One is the direct photolysis, the other is the oxidation via •OH. The hydroxyl radical with a strong oxidation potential of 2.80 V, reacts rapidly with most organic compounds with second order rate constants in the range of 10<sup>9</sup>–10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> [27]. According to the apparent rate constants in the presence or absence of *t*-butanol, the contribution of direct photolysis and oxidation via •OH to 4-CP decomposition was calculated as 17.2% and 82.8%, respectively. This suggested that the oxidation via •OH of 4-CP is the primary decomposition pathway of 4-CP in UV/air system under the experimental conditions.

The degradation mechanism of 4-CP by •OH attack has been extensively studied [28–30]. In our previous work, the role of oxygen during the degradation of 4-CP by •OH has been investigated in detail [31,32]. Dissolved oxygen could hinder the generation of 4-chlorocatechol, which explained the lower concentration of 4-chlorocatechol in UV/air system than that in UV/N<sub>2</sub> system. In addition, hydroquinone possesses a reducing capacity and readily reacts with oxygen to form *p*-benzoquinone [33], which might lead to the higher concentration of *p*-benzoquinone in UV/air system.

### 3.3. Formation of hydrogen peroxide during the process

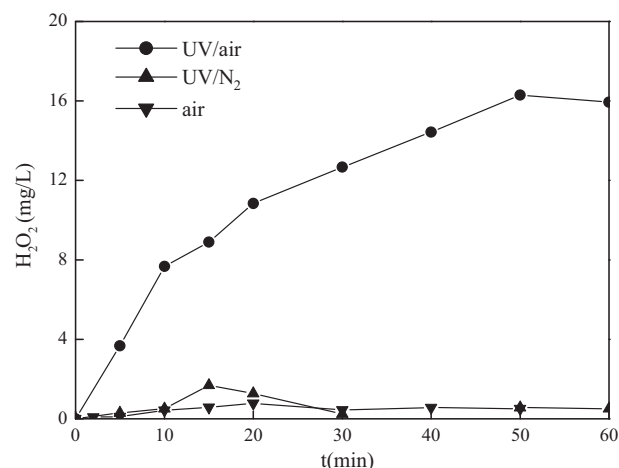
The formation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was detected, which can photolyze into •OH under UV irradiation. Previous study has shown that during photo-degradation of naphthalene [34], tannic acid and gallic acid [35] in an aqueous solution, the production of H<sub>2</sub>O<sub>2</sub> was also observed. In freshwater, marine and atmospheric environments, H<sub>2</sub>O<sub>2</sub> has been shown to form from the interaction of sunlight and light-absorbing substances [36–38].

Fig. 6 shows the formation of H<sub>2</sub>O<sub>2</sub> in UV/air and UV/N<sub>2</sub> systems, as well as in aerated solution of 4-CP without UV irradiation. In UV/air system, H<sub>2</sub>O<sub>2</sub> was formed quickly once the reaction was initiated. The concentration of H<sub>2</sub>O<sub>2</sub> increased steadily with the reaction time, reaching 16.3 mg/L after 50 min. However, no H<sub>2</sub>O<sub>2</sub> was produced in UV/N<sub>2</sub> system or in aerated solution of 4-CP without UV irradiation. This indicated that the dissolved oxygen and UV irradiation were both necessary for the formation of H<sub>2</sub>O<sub>2</sub>.

To better understand the formation mechanism of H<sub>2</sub>O<sub>2</sub>, the effects of 4-CP input and solution pH on H<sub>2</sub>O<sub>2</sub> formation were investigated.

#### 3.3.1. Effect of 4-CP input on the formation of hydrogen peroxide

The effect of the initial concentration of 4-CP on the formation of hydrogen peroxide is shown in Fig. 7. A control experiment of

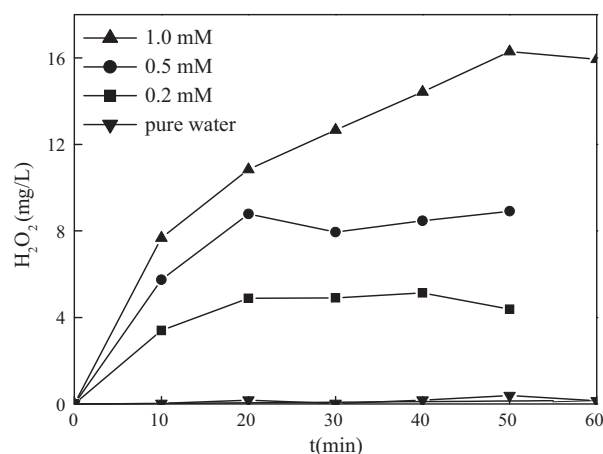


**Fig. 6.** Formation of hydrogen peroxide in various systems ([4-CP]<sub>0</sub> = 1 mM; pH<sub>0</sub> = 2.9; T = 35 °C; Q<sub>air/N<sub>2</sub></sub> = 0.20 m<sup>3</sup>/h).

UV/pure water/air was designed, in which an acid aqueous solution without any organic substance was irradiated and bubbled with air. The formation rate of hydrogen peroxide was promoted by increasing the concentration of organics in the solution (including 4-CP and the intermediates). After 20 min, the concentrations of hydrogen peroxide were 4.89, 8.79 and 10.8 mg/L when the initial concentrations of 4-CP were 0.2, 0.5 and 1.0 mM, respectively. No formation of hydrogen peroxide was detected in control experiment of UV/pure water/air. Thus, it appeared that organic matter was required for the formation of H<sub>2</sub>O<sub>2</sub>. The result was consistent with a previously reported study that showed that the rate of H<sub>2</sub>O<sub>2</sub> accumulation was related to the concentration of light-absorbing organic substances [39].

#### 3.3.2. Effect of pH on the formation of hydrogen peroxide

The formation of H<sub>2</sub>O<sub>2</sub> during 4-CP photolysis in UV/air system at different pH values is shown in Fig. 8. The formation of H<sub>2</sub>O<sub>2</sub> was clearly accelerated by decreasing the pH values of the solution. After 20 min, the concentrations of hydrogen peroxide were 2.49, 6.56, 7.80 and 10.8 mg/L at pH of 9.6, 7.3, 5.3 and 2.9, respectively. At each pH value, the profile of H<sub>2</sub>O<sub>2</sub> formation was similar, of which it increased steadily to a maximum and then decreased. After 50 min, the concentrations of hydrogen peroxide were 2.73, 6.98, 8.60 and 16.3 mg/L at pH of 9.6, 7.3 and 2.9, respectively. The notable difference among the reaction solutions at various pH



**Fig. 7.** Effect of the input of 4-CP on the formation of hydrogen peroxide in UV/air system (pH<sub>0</sub> = 2.9; T = 35 °C; Q<sub>air</sub> = 0.20 m<sup>3</sup>/h).



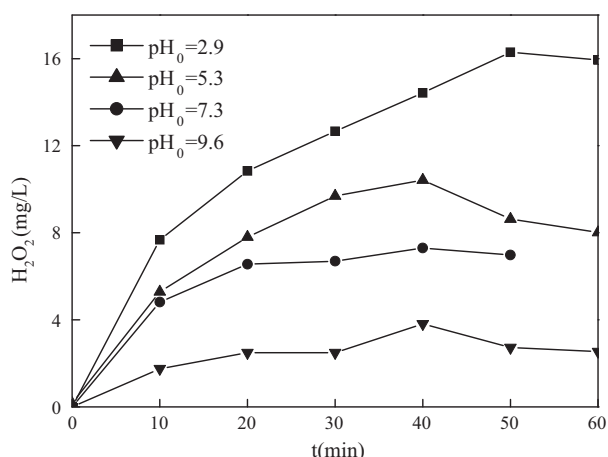
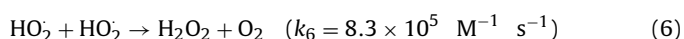
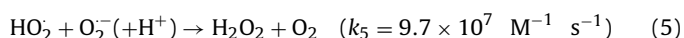
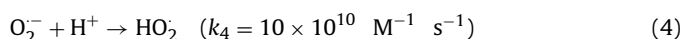
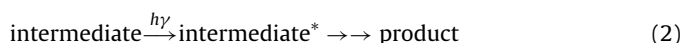


Fig. 8. Effect of pH value on the formation of hydrogen peroxide in UV/air system ( $[4\text{-CP}]_0 = 1 \text{ mM}$ ;  $T = 35^\circ \text{C}$ ;  $Q_{\text{air}} = 0.20 \text{ m}^3/\text{h}$ ).

values is concentration of hydrogen ion. This indicated that the concentration of hydrogen ion is another key factor for the formation of hydrogen peroxide.

### 3.3.3. Formation mechanism of hydrogen peroxide

In summary, dissolved oxygen, the organic matter, UV irradiation and hydrogen ion are all involved in the formation of hydrogen peroxide during 4-CP degradation in UV/air system. Based on these results, the formation mechanism of hydrogen peroxide was suggested. Firstly, the molecule of 4-CP absorbs the photos and transfers itself to excited state, as described in Eq. (1). This has been confirmed by 4-CP degradation in UV/N<sub>2</sub> system, which is shown in Fig. 2. The intermediate could transform to its excited state too (Eq. (2)). It has been suggested previously that the excited state of organics is active and it can reduce the dissolved oxygen to form superoxide radical-ion ( $\text{O}_2^{\bullet-}$ ) (Eq. (3)) [40–43]. It is commonly realized that in nature water, absorption of ultraviolet radiation by dissolved organic matter (DOM) generates an excited triplet state, which reacts with molecular oxygen to form superoxide radical-ion [37,39].  $\text{O}_2^{\bullet-}$  associated with the hydrogen ion ( $\text{H}^+$ ) to form conjugated acid of the hydroperoxyl radical ( $\text{HO}_2^{\bullet}$ ) (Eq. (4)) [44]. Then  $\text{H}_2\text{O}_2$  was produced via the dismutation of  $\text{HO}_2^{\bullet}$  (Eq. (5)) or the interaction of  $\text{HO}_2^{\bullet}$  with  $\text{O}_2^{\bullet-}$  (Eq. (6)) [44]. Eqs. (4) and (5) show that the increment of hydrogen ion can enhance the formation of  $\text{HO}_2^{\bullet}$  and  $\text{H}_2\text{O}_2$ . This explains the higher concentration of  $\text{H}_2\text{O}_2$  at lower pH value. It is noted that at neutral and alkaline solutions, the disproportionation of  $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$  is not the only way to produce hydrogen peroxide. It was reported that  $\text{H}_2\text{O}_2$  was formed when alkaline solutions of benzene diols were exposed to air or oxygen (thermal reaction) [35]. While at pH 6.0 or below, this thermal reaction was normally negligible. Since benzene diols such as 4-chlorocatechol and hydroquinone were the intermediates during the photodecomposition of 4-CP, the thermal reaction of these benzene diols with oxygen was another way to generate  $\text{H}_2\text{O}_2$  at neutral and alkaline solutions.



## 4. Conclusion

1. The degradation of 4-CP was much faster and more complete in UV/air system than that in UV/N<sub>2</sub> system. Near complete elimination of 4-CP was achieved after 40 min in UV/air system, while more than 25% of 4-CP remained after 60 min in UV/N<sub>2</sub> system. Hydroquinone, benzoquinone and 4-chlorocatechol were detected in both UV/N<sub>2</sub> and UV/air systems but at different concentrations.
2. In the presence of *t*-butanol, the degradation of 4-CP and the formation of intermediates in UV/air system were almost the same as those in UV/N<sub>2</sub> system. In UV/air system, 4-CP was degraded via two pathways of direct photolysis and oxidation by  $\bullet\text{OH}$ . The contributions of direct photolysis and the oxidation by  $\bullet\text{OH}$  to the decomposition of 4-CP were 17.2% and 82.8%, respectively.
3. Hydrogen peroxide, the source of  $\bullet\text{OH}$ , was formed during the degradation of 4-CP in UV/air system. The formation of  $\text{H}_2\text{O}_2$  was depended on dissolved oxygen, organic matter, UV irradiation and hydrogen ion.
4. The formation mechanism of hydrogen peroxide was proposed as follows: the electron transfers from the excited state of organic matters (4-CP or its intermediates) to the dissolved oxygen to form superoxide radical-ion ( $\text{O}_2^{\bullet-}$ ). Then  $\text{HO}_2^{\bullet}$ , i.e., the conjugated acid of  $\text{O}_2^{\bullet-}$ , undergoes disproportionation to yield  $\text{H}_2\text{O}_2$ .

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