

# The formation and influence of hydrogen peroxide during ozonation of *para*-chlorophenol

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Received 22 September 2005; received in revised form 15 July 2006; accepted 17 July 2006  
Available online 21 July 2006

## Abstract

Hydrogen peroxide was detected during the ozonation of *para*-chlorophenol (4-CP) in aqueous solutions. Its formation and influence on the reaction mechanism were examined. Semi-batch experiments showed that hydrogen peroxide was formed during the direct reaction between molecular ozone and 4-CP. The detected hydrogen peroxide could reach 12.3% of the initial mole concentration of 4-CP. Hydrogen peroxide reacts with ozone in neutral pH and leads to the appearance of the powerful oxidant, OH• radicals. An O<sub>3</sub>/OH• probe compound, succinate was then developed, and also included in the 4-CP solution matrix. The disappearance of succinate with time shows the amount of OH• radicals. With enough *tert*-butanol inhibiting the OH• radical oxidation, results showed that 4-CP was transformed to *para*-quinone by ozone, and subsequently destroyed to formic acid and oxalic acid. Without scavengers of inactivation the OH• radicals, 4-CP was destroyed to low molecular weight acid. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Ozone; OH• radical; Chlorophenol; Hydrogen peroxide

## 1. Introduction

Chlorinated aromatic compounds are class of widely used, toxic and refractory organic pollutants. Most of them are persistent organic pollutants (POPs). Chlorinated phenols are important subclass of them. Chlorinated phenolic compounds are generated from a number of industrial manufacturing processes. Aqueous effluents from many industrial operations, such as polymeric resin production, oil refining, petroleum, pesticide, paint, solvent, pharmaceuticals, wood preserving chemicals, coke-oven and pulp industries, contain chlorophenolic compounds [1,2]. Due to their high toxicity, recalcitrance, bioaccumulation, strong odor emission and persistence in environment and suspected carcinogen and mutagen to the living, chlorophenols (CPs) pose serious ecological problem as environmental pollutants. Their fate in the environment is of great concern. Chlorophenols have been listed as priority pollutants by China National Environmental Monitoring Centre and the U.S. Environmental Protection Agency [3].

The conventional treatment technologies for the removal of phenols and their derivatives from wastewater include biological treatment, the adsorption over activated carbon, air stripping and chemical oxidation. Chlorophenols are of strong toxicity and resistance to biological degradation, due to their aromatic ring structure and the existence of chloride in the ring. Activated carbon adsorption and air stripping still need a post treatment process to remove chlorophenols in another environment.

Ozonation has a good effect on the oxidation of refractory contaminants, due to its higher oxidation potential and the formed secondary oxidant, hydroxyl radicals (OH•) [4]. Most of the studies concerning the ozonation of CPs are focused on the degradation levels or the identification of some reaction by-products [5–7]. And in some cases, kinetic and mechanistic aspects of the ozonation of chlorophenols are proposed [1,8,9]. Hydrogen peroxide was detected during the ozonation of *para*-chlorophenol in our study. Hydrogen peroxide is a very important initiator, which may influence the ozonation process. Nevertheless, the description and investigation of hydrogen peroxide during the ozonation of *para*-chlorophenol are limited in literatures [8]. In order to make the most efficient use of the oxidant, more detailed information is necessary.

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The purpose of this paper is to investigate the simultaneous formation of hydrogen peroxide during the ozonation of *para*-chlorophenol, and especially the influence of the formed hydrogen peroxide on the reaction mechanism.

## 2. Experimental

### 2.1. Materials

*para*-Chlorophenol, *t*-butanol,  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  were analytical grade from Beijing Reagent Company. DPD (*N,N*-diethyl-*p*-phenylenediamine) and POD (horseradish peroxidase) were analytical grade from Merck. *para*-Chlorophenol solution was prepared in deionized water with a concentration of 20 mg/L (0.155 mM). Experiments were carried out in buffered and non-buffered solutions, where either phosphate buffer or 0.2 M NaOH was applied to adjust the pH value to 7.5, because pH 7.5 is one of the most common pH values in natural waters. The buffer was produced by blending 260 mM  $\text{KH}_2\text{PO}_4$  and 260 mM  $\text{Na}_2\text{HPO}_4$  with a ratio of 4:21 to make a buffer stock solution of pH 7.5. *t*-Butanol was chosen as an  $\text{OH}^\bullet$  radical scavenger. DPD and POD solutions were prepared according to the literature [10].

### 2.2. Experimental methods

Semi-batch tests were performed using a laboratory ozonation unit, equipped with an ozone generator, two ozone gas analyzers (BMT 961, BMT Messtechnik Berlin, Germany) and an ozone probe for liquid concentration determination (Orbisphere, Model 3202). The reactor volume was 2 L. The injected ozone gas with a concentration of 24 mg/L was flowed through the solutions at a flow rate of 27 L/h.

### 2.3. Analysis

*para*-Chlorophenol and *para*-quinone was monitored by HPLC (HP1100, Eclipse@XDB-C8 column) using eluent A (60% ethanol)/eluent B (40% pure water), UV-detection at 280 and 246 nm, respectively. DOC was measured using a TOC analyzer (Elementar High TOC). Oxalate, formate and succinate were analyzed by ion chromatography (Dionex DX 100, AS 14 column). UV absorbency measurements were accomplished using a Shimadzu UV-3100 model UV-vis-NIR recording spectrophotometer.

Hydrogen peroxide was measured by the DPD/POD method [10]. In the method of DPD/POD, DPD and POD are subsequently added to a sample.  $\text{H}_2\text{O}_2$  will oxidize POD to a higher valent state, which in turn oxidizes DPD to a pink coloured radical cation-DPD $^{\bullet+}$ . The colour can be measured by adsorption at 551 nm. Dissolved ozone can also oxidize DPD to pink DPD $^{\bullet+}$ . Agitation was used to quench the dissolved ozone selectively. Dissolved ozone normally can be removed after several minutes (it needs 10–30 min in the low pH range, such as pH 3–4) and the concentration of  $\text{H}_2\text{O}_2$  remains stable during this operation. Samples with dissolved ozone will be stirred until no pink colour appears before the

addition of POD. That means a total removal of dissolved ozone [11].

## 3. Results and discussions

### 3.1. Ozonation at initial pH 7.5 without buffer

NaOH was employed to adjust 0.155 mM 4-CP solution to pH 7.5. And the semi-batch ozonation experiment was performed. The depletion of 4-CP, DOC and the changes of pH are shown in Fig. 1. About 95% 4-CP was removed after 9 min reaction. At that time, the stoichiometric coefficient (mol ozone/mol 4-CP) was 6.8. However, only 26% DOC was reduced within the same period. This indicates that the attack of ozonation breaks 4-CP molecule to some intermediate products, instead of a direct mineralization. The value of pH decreased steadily down to 3.6 after 9 min. With further ozonation a pH of 3.25 was reached after 28 min.

In Fig. 2, the distributions of several identified intermediates are reported versus time. Formic acid ( $\text{p}K_{\text{a}}$  3.8) was detected after 3 min and increased linearly until 14 min. Oxalic acid ( $\text{p}K_{\text{a}1}$  1,  $\text{p}K_{\text{a}2}$  3.9) appeared after 9 min and went up smoothly. The dissociation of the generated small molecular weight organic acid might mainly contribute to the reduction of pH.

An important identified by-product during the ozonation of 4-CP solution was hydrogen peroxide. As shown in Fig. 3, rela-

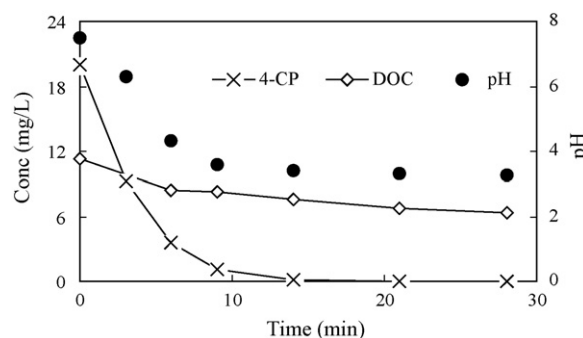


Fig. 1. The abatement of 4-CP, DOC and pH during the ozonation of 20 mg/L 4-CP without buffer. Initial pH was adjusted by NaOH to 7.5. Ozone flow rate, 0.65 g/h. Temperature,  $20 \pm 2$  °C.

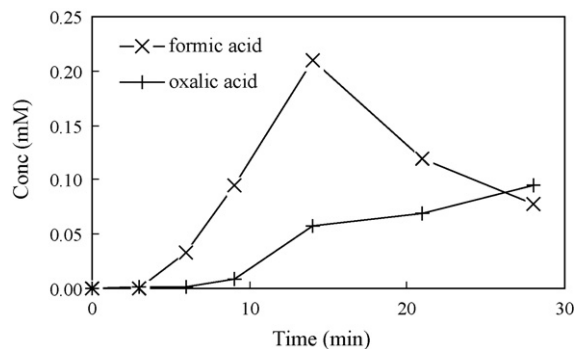


Fig. 2. Profiles of formic acid and oxalic acid during the ozonation of 0.155 mM 4-CP without buffer. Initial pH was adjusted by NaOH to 7.5. Ozone flow rate, 0.65 g/h. Temperature,  $20 \pm 2$  °C.

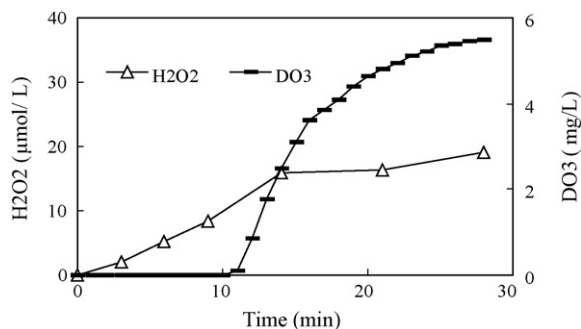


Fig. 3. The changes of  $\text{H}_2\text{O}_2$  and dissolved ozone during ozonation of 0.155 mM 4-CP without buffer. Initial pH was adjusted by NaOH to 7.5. Ozone flow rate, 0.65 g/h. Temperature,  $20 \pm 2^\circ\text{C}$ .

tively high amount of  $\text{H}_2\text{O}_2$  was detected. A value of  $19 \mu\text{M}$   $\text{H}_2\text{O}_2$  was found at the end of the ozonation, equivalent to 12.3% mole concentration of the initial 4-CP. Part of  $\text{H}_2\text{O}_2$  dissociate to  $\text{HO}_2^-$  at neutral pH ( $\text{p}K_a$  11.6), which can tremendously enhance ozone decompose to  $\text{OH}^\bullet$  radical [12]. In this process, both hydrogen peroxide and ozone were strongly consumed. Therefore, the simultaneously generated hydrogen peroxide should be higher than the real detected data in Fig. 3. This reaction also leads to the result that dissolved ozone remained 0 mg/L within the first 10 min. When hydrogen peroxide hardly dissociates to  $\text{HO}_2^-$  at low pH range, it does not react with ozone and then, the concentration of dissolved ozone quickly increases (Fig. 3).

$\text{HO}_2^-$  has a much higher promotion ability ( $k_{\text{O}_3/\text{HO}_2^-} = 2.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  [12]) compared with another common ozone decomposition initiator  $\text{OH}^-$  ( $k_{\text{O}_3/\text{OH}^-} = 70 \text{ M}^{-1} \text{ s}^{-1}$  [12]).  $\text{OH}^\bullet$  radicals are extremely powerful and non-specific oxidants, with standard reduction potentials of 2.8 V, compared to 2.07 V of ozone [3].

### 3.2. Succinic acid used as an $\text{OH}^\bullet$ radical probe compound

In order to indirectly demonstrate the effect of the formed  $\text{OH}^\bullet$  radicals initiated by the intermediate product hydrogen peroxide, a hydroxyl radical probe compound was also included in the 4-CP solution. A hydroxyl radical probe compound reacts only with  $\text{OH}^\bullet$  radicals, and not significantly with ozone molecule. Moreover, the probe compound should not clearly promote ozone autodecomposition to  $\text{OH}^\bullet$  radicals [13,14]. Thus, the disappearance of the probe compound is an indirect measure of the  $\text{OH}^\bullet$  concentration.

Succinic acid (1 mM with pH 7.5 adjusted by NaOH) was degraded with ozonation and  $\text{O}_3/\text{H}_2\text{O}_2$ , respectively to evaluate a possibility to be the probe compound. An experiment was run in the presence of hydrogen peroxide to produce high load of  $\text{OH}^\bullet$  radicals. The combination of  $\text{H}_2\text{O}_2$  with ozone (input molar ratio = 1:2) reduced DOC obviously (Fig. 4). It means  $\text{OH}^\bullet$  radicals can react and destroy succinate. The reaction rate constant of  $\text{OH}^\bullet$  radical with succinic acid was reported as  $k_{\text{OH}^\bullet/\text{succ}} = 3.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  by Buxton et al. [15]. In the succinate solution without hydrogen peroxide, the DOC value remained stable during the 28 min ozonation (Fig. 4). The fur-

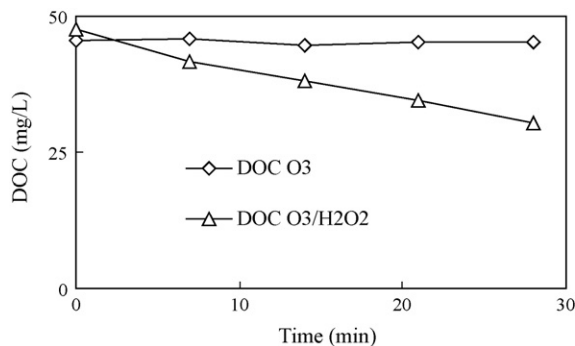


Fig. 4. DOC variation with time for 1 mM succinic acid solution when it is degraded with ozonation and  $\text{O}_3/\text{H}_2\text{O}_2$ . Initial pH was adjusted by NaOH to 7.5. Ozone flow rate, 0.65 g/h. Temperature,  $20 \pm 2^\circ\text{C}$ .

ther IC measurements of the samples demonstrated that almost all succinate were untouched. This agreed with the published data ( $k_{\text{O}_3/\text{succ}} = (3 \pm 1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  [16]) that succinate is of tough ozone resistance.

Taken these data in the experiment without additional hydrogen peroxide into consideration, succinate is not a strong promoter, and cannot enhance ozone decomposition to  $\text{OH}^\bullet$  radicals. Otherwise succinate would promote ozone decomposition to form a certain amount of  $\text{OH}^\bullet$  radicals, which could clearly degrade succinate. A chain reaction started. Then succinate would be reduced a lot during this process.

Succinic acid (0.85 mg/L) was spiked into the 0.155 mM 4-CP solution as the  $\text{OH}^\bullet$  radical probe compound. And the next ozonation experiment was conducted again under the same conditions. The succinate concentration is presented in Fig. 5. The decrease of succinate is obvious in the ozonation process. Fifty-eight percent succinate was degraded after 28 min. Because the loss of succinate in this solution is most likely by  $\text{OH}^\bullet$  radicals oxidation, this indicated that there was a strong generation of  $\text{OH}^\bullet$  radicals.

Most reduction of succinate occurred in the first 3 min. The reason was that only limited formic acid and oxalic acid were produced after 3 min ozonation. The pH value still remained in the neutral range (see Fig. 1). Thus the generated hydrogen peroxide could accelerate ozone decomposition to  $\text{OH}^\bullet$  radicals, which caused to the depletion of succinate. After 14 min

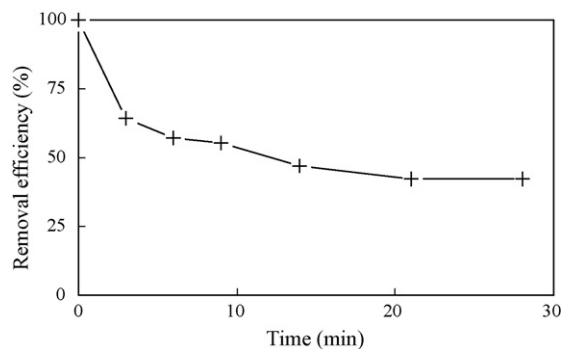


Fig. 5. Removal efficiency of succinic acid (initial concentration, 0.85 mg/L) during the ozonation of 20 mg/L 4-CP without buffer. Initial pH was adjusted by NaOH to 7.5. Ozone flow rate, 0.65 g/h. Temperature,  $20 \pm 2^\circ\text{C}$ .

ozonation, the accumulated intermediate organic acids resulted in the reduction of pH to the acid range of 3.4. The low pH of the solution prevented the dissociation of hydrogen peroxide to  $\text{HO}_2^-$ . Then  $\text{HO}_2^-$  cannot promote ozone decomposition to  $\text{OH}^\bullet$  radicals. Therefore succinate could not be further removed. And its concentration kept stable.

### 3.3. The formation of hydrogen peroxide and its influence on the reaction pathway

It is becoming clear that there are direct ozone reactions and indirect  $\text{OH}^\bullet$  radical reactions during the ozonation of 4-CP. And  $\text{OH}^\bullet$  radical reactions play an important role. However, it still remained unclear how 4-CP was destroyed and how hydrogen peroxide was generated. To clarify these points, it is necessary to discriminate between direct ozone reactions and  $\text{OH}^\bullet$  radical reactions. *t*-Butanol was then used as a scavenger in the next experiment. When the reaction rate of *t*-butanol with  $\text{OH}^\bullet$  is 10 times stronger than that of 4-CP with  $\text{OH}^\bullet$ , the  $\text{OH}^\bullet$  radical indirect reaction with 4-CP can be effect inhibited.

The reaction rate of *t*-butanol with hydroxyl radical =  $k_{\text{OH}/t\text{-buta}}[t\text{-buta}][\text{OH}^\bullet]$ .

The reaction rate of *p*-chlorophenol with hydroxyl radical =  $k_{\text{OH}/4\text{-CP}}[4\text{-CP}][\text{OH}^\bullet]$ , where  $k_{\text{OH}/t\text{-buta}}$  ( $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) and  $k_{\text{OH}/4\text{-CP}}$  ( $7.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) [15] are second order rate constants for the reaction of  $\text{OH}^\bullet$  radicals with *t*-butanol and 4-CP, respectively.

The concentration of *t*-butanol was determined using the expression [17]:

$$\begin{aligned} [t\text{-buta}] &= \frac{10 \times k_{\text{OH}/4\text{-CP}}[4\text{-CP}][\text{OH}^\bullet]}{k_{\text{OH}/t\text{-buta}}[\text{OH}^\bullet]} \\ &= \frac{10 \times k_{\text{OH}/4\text{-CP}}[4\text{-CP}]}{k_{\text{OH}/t\text{-buta}}} \end{aligned} \quad (1)$$

The employed 4-CP solution was 0.155 mM. Then the concentration of *t*-butanol should be 19.6 mM according to Eq. (1). In our experiments, a higher dosage of *t*-butanol (26.6 mM) was spiked to inhibit the indirect reaction so that the ozone direct reaction with 4-CP could be better isolated and investigated.

The next semi-batch experiment was run in the presence of 26.6 mM *t*-butanol. 4-CP decreased steadily to 3.1  $\mu\text{M}$  after 9 min, equivalent to 98% total elimination (Fig. 6). And the pH value reduced to 3.22 after 28 min (Fig. 6). These variances were similar to the experiment results without scavenger. The presence of *t*-butanol did not have a clear influence on the degradation of 4-CP. This indicates that the molecular ozone alone destroyed 4-CP. In this case, hydrogen peroxide was also detected (Fig. 7). The tendency and the maximum value of hydrogen peroxide were also similar to the results without scavenger. Therefore, the formation of hydrogen peroxide can be ascribed to the molecular ozone direct reaction with 4-CP. Since it has been reported that the reaction of ozone with the C=C double bond of olefin can lead to the formation of hydrogen peroxide [11,18,19]. It is proposed that  $\text{H}_2\text{O}_2$  was formed in the process of the double bond cleavage of 4-CP aromatic ring attacked by ozone.

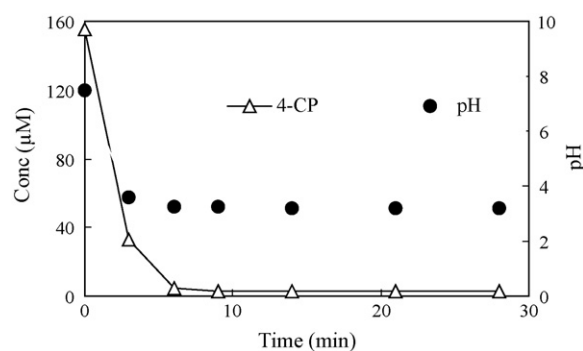


Fig. 6. The changes of 4-CP and pH during the ozonation of 0.155 mM 4-CP in the presence of 26.6 mM *t*-butanol. Initial pH was adjusted by NaOH to 7.5. Ozone flow rate, 0.65 g/h. Temperature,  $20 \pm 2^\circ\text{C}$ .

One interesting phenomenon in this experiment was the variance of colour during the ozonation. The initial colourless solution turned to be yellow within the first 3 min, and then it faded to be colourless again after 6 min. With enough inorganic scavenger bicarbonate instead of *t*-butanol, a similar variance of colour was observed. This excluded the interference of *t*-butanol. The yellow colour demonstrated a new emerged intermediate compound, and moreover a different mechanism than the experiment without scavenger. When DPD was added to the sample at 3 min, DPD was directly oxidized to the pink colour  $\text{DPD}^{\bullet+}$  by the yellow colour compound. It should be stressed that hydrogen peroxide itself cannot oxidize DPD to  $\text{DPD}^{\bullet+}$  without the catalysed oxidation of POD. This yellow substance probably was *para*-quinone while it can oxidize DPD. *para*-Quinone was also verified with a further HPLC analysis. This intermediate compound has been identified as intermediate product in the work of Trapido et al. [8], as well as in the research of Saulea and Brillas [20]. Again oxalic acid and formic acid were detected.

### 3.4. Ozonation at initial pH 7.5 with buffer

The pH value decreased to below 4 after a short time ozonation in the above experiments. However, the pH values of nature waters remain stable in the neutral range, because of

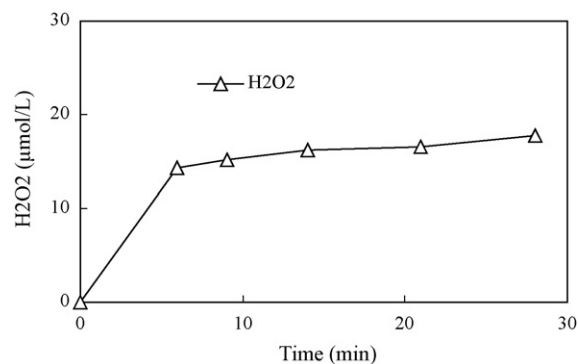


Fig. 7. The changes of  $\text{H}_2\text{O}_2$  during the ozonation of 0.155 mM 4-CP in the presence of 26.6 mM *t*-butanol. Initial pH was adjusted by NaOH to 7.5. Ozone flow rate, 0.65 g/h. Temperature,  $20 \pm 2^\circ\text{C}$ .

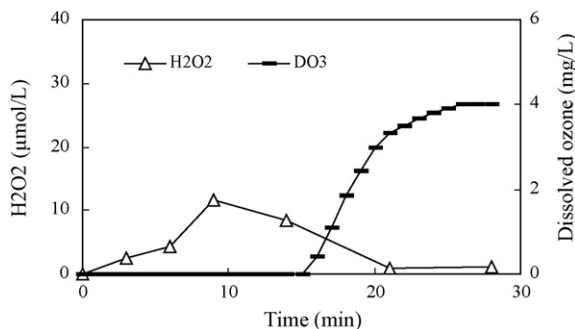


Fig. 8. The changes of H<sub>2</sub>O<sub>2</sub> and dissolved ozone during the ozonation of 0.155 mM 4-CP in the presence of 6.5 mM phosphate buffer. Initial pH was adjusted by phosphate buffer to 7.5. Ozone flow rate, 0.65 g/h. Temperature, 20 ± 2 °C.

the existence of inorganic and organic buffer agents. Phosphate buffer (6.5 mM) was then used in another experiment to control pH at 7.5. This experiment was then carried out under the same conditions (initial 4-CP concentration, ozone dosage).

As it is shown in Fig. 8, 4-CP was quickly removed, and hydrogen peroxide was also detected. Its concentration reached a maximum value of 11.7 μM at 9 min, and decreased afterwards to near 0 μM at 21 min. In this neutral pH range, the generated hydrogen peroxide tremendously reacted with ozone. Consequently, hydrogen peroxide and ozone were both greatly consumed. Almost all generated hydrogen peroxide was used up at 21 min. A strong formation of OH• radicals then can be predicted and expected in this experiment.

Low concentration of the dissolved ozone (about 0 mg/L) indicates a high reaction rate of ozone. The dissolved ozone appeared at 10 min (Fig. 3) and 15 min (Fig. 8), respectively. This difference can be mainly ascribed to the pH variation in these two experiments. In Fig. 3 (Section 3.1), the pH value reduced to about 3.5 at 10 min. The generated hydrogen peroxide hardly reacted with ozone at such low pH range and then the dissolved ozone accumulated and could be detected. In Fig. 8, a high reaction rate of hydrogen peroxide with ozone always occurred at the constant pH of 7.5. Dissolved ozone appeared at 15 min until the disappearance of hydrogen peroxide.

#### 4. Conclusions

This research has investigated the ozonation of *para*-chlorophenol with the simultaneous formation of hydrogen peroxide. Ozonation experiments show that the attack of molecular ozone on the double bonds of the aromatic ring of 4-CP leads to the formation of hydrogen peroxide, which subsequently partly deprotonates to HO<sub>2</sub><sup>-</sup> at the neutral pH range. The ion HO<sub>2</sub><sup>-</sup> greatly promotes ozone decomposition to OH• radicals. Succinic acid was developed as an OH• radical probe compound. The disappearance of this probe compound verified the existence of OH• radical, and its distribution with time.

The new formed OH• radicals will influence the reaction mechanism due to its powerful oxidizing ability. Without scav-

engers inactivating the OH• radicals, the generated OH• radicals and ozone degrade 4-CP together to small molecular weight organic compounds. With *t*-butanol sufficiently inhibiting the indirect reaction of OH• radicals with 4-CP, the direct reaction of molecular ozone with 4-CP firstly produces an intermediate organic compound, *para*-quinone. It will be further destroyed to formic acid, oxalic acid and some other organic substances.

#### Acknowledgments

The authors are grateful to the precious comments presented by anonymous reviewers. This work is supported by the Chinese Postdoc Fund and the National Natural Science Foundation of China (Grant no. 50325824), which are greatly acknowledged.

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