The role of oxygen in the degradation of *p*-chlorophenol by Fenton system

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Abstract

The role of oxygen in the degradation pathway of 4-CP by Fenton system was investigated in this paper. The degradation of 4-CP, changes of Fenton reagent's concentration and formation of the intermediates in Fenton/O_2 system were respectively compared with those in Fenton/N_2 system. The result showed that both 4-CP degradation and COD_{cr} removal in Fenton/O_2 system were prior to those in Fenton/N_2 system. Investigation into the intermediates suggested that the presence of oxygen impeded the formation of 4-chlorocatechol and accelerated the production of organic acids such as maleic acid, fumaric acid, acetic acid and oxalic acid. Based on the changes of reaction substances and the intermediates, the degradation mechanism of 4-CP by Fenton system in the presence of O_2 was suggested. The dissolved oxygen competed against hydroxyl radical to react with *ortho-para*chlorohydroxyphenyl radical (ClHP$^\bullet$) producing *ortho-para*chlorophenolperoxyl radical (ClPP$^\bullet$) and impeding the generation of 4-chlorocatechol. In addition, the reaction of oxygen with (Cl)PP radical increased the extent of benzene ring cleavage, producing more aliphatic organic acids. This study makes clear the mechanism of Fenton/O_2 system and thus, it is helpful to establish the kinetic model and provide a good guide to the treatment of real wastewater.
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Keywords: Oxygen; Fenton system; 4-CP; Mechanism

1. Introduction

Phenolic compounds are common persistent organic contaminants, which show low biodegradability, posing serious risks to the environment once discharged into natural water. Some of the most toxic phenolic compounds are those chlorinated phenols, which are widely used as intermediates in the synthesis of the higher chlorinated congeners, certain dyes and pesticides [1]. Due to the recalcitrant nature of these phenolic compounds, the degradation rate by conventional biotreatment methods is too slow.

Available technologies to deal with phenolic compounds include the advanced oxidation processes (AOPs) [2–4]. Among the AOPs, Fenton system is one of the most attractive methods because Fenton reagent is easy to handle and environmentally benign [5]. Fenton reagent is the mixture of hydrogen peroxide and ferrous ion, which generates the very active hydroxyl radical

($^\bullet$OH) according to Eq. (1) [6].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^-, \quad k_1 = 51\,M^{-1}\,s^{-1} \tag{1}$$
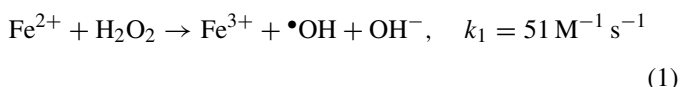
The contaminant (P) in the solution is attacked by hydroxyl radical as soon as $^\bullet$OH is generated, as described in Eq. (2).

$$^\bullet OH + P \xrightarrow{k_{^\bullet OH}} intermediates \tag{2}$$

Fenton reaction has been tested as a potential method for wastewater treatment [4,5,7,8]. However, the application of Fenton system to the treatment of real wastewater is limited due to the high cost of H_2O_2. It is well known that oxygen is a cheap oxidant, but its oxidation potential is too low to oxidize the organics by it. Some researches [9–12] have investigated the effect of oxygen on the degradation of the contaminant through using oxygen as carrier gas in Fenton and photo-Fenton systems. The studies of Kim et al. [9,10] suggested that the degradation rate of the organic pollutants in landfill leachate depended on the concentration of dissolved oxygen. Sun et al. [11] and Utset et al. [12] showed that oxygen took part in the mineralization of 2, 4-D and aniline in Fenton or photo-Fenton reaction, partially replacing

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H_2O_2, thus the input of H_2O_2 was reduced. The above researches indicated that oxygen played a positive role in the degradation of the refractory organics. However, the detailed effect of oxygen on the degradation pathway has not been especially discussed yet. Therefore, the objective of this paper is to investigate the role of oxygen in Fenton oxidation of *p*-chlorophenol (4-CP), a common chlorinated phenolic compound. Making clear the degradation mechanism of Fenton/O_2 system is helpful to establish the kinetic model and provide a good guide to the treatment of real wastewater.

In this paper, at first, 4-CP degradation and COD_{cr} removal in Fenton/O_2 system were respectively compared with those in Fenton/N_2 system to confirm the enhancement by oxygen. Secondly, changes of Fenton reagent's concentration in two systems were discussed, which explained the difference in 4-CP degradation by two systems. Thirdly, the aromatic intermediates and the aliphatic organic acids in two systems were identified and changes of their concentrations during the processes were especially measured. Differences in the changes of reaction substances and the formation of intermediates revealed the role of oxygen in the oxidation of 4-CP by Fenton system. Finally, a pathway was suggested to describe the oxidation of 4-CP in the presence of oxygen by Fenton system.

2. Materials and methods

2.1. Materials

4-CP, hydroquinone, catechol, acetic acid, oxalic acid, maleic acid, fumaric acid, $FeSO_4 \cdot 7H_2O$ and hydrogen peroxide (30%) were purchased from Hangzhou Huadong Medicine Group Co., Ltd., and 4-chlorocatechol from Tokyo Kasei Kogyo Co., Ltd. They were all of analytical grade. Deionized and doubly distilled water was used throughout this study.

2.2. Procedures and analysis

4-CP aqueous solution (1 L), which containing 1 mmol 4-CP, was added into a flask, which was put in a thermostatic bath ($T = 25\,^{\circ}C$). Ferrous ion was put into the solution after pH was adjusted to 3.0 by concentrated H_2SO_4. After O_2 or N_2 (a flow rate of $0.20\,m^3/h$) was bubbled for 10 min, hydrogen peroxide was added to initiate the reaction. The molar ratio of Fe^{2+} to H_2O_2 was chosen to be 1: 20 referring to the literatures [13,14]. The initial concentration of Fe^{2+} and H_2O_2 were 0.125 and 2.5 mM, respectively.

At the given reaction time intervals, samples were taken out and analyzed. COD_{cr} was measured by the titrimetric method [15]. The interference of the residual H_2O_2 was eliminated by adding enzyme catalase [10] (from Worthington Biochemical Corporation) to the samples and the measurement was carried out after 12 h. Analysis of 4-CP and their intermediates was performed with a Knauer HPLC unit with a reversed phase C18 column and UV detector. For the measurement of 4-CP and the aromatic intermediates, the detecting wavelength was set at 278 nm, and mobile phase was prepared by methanol (A) and deionized water (containing 2‰ acetic acid) (B) in 52/48(v/v)

ratio. When analyzing the organic acids, the wavelength of UV detector was set at 210 nm and the mobile phase was the deionized water that contained 0.1 M KH_2PO_4 (pH was adjusted to 3.0 by concentrated H_3PO_4). A flow rate of $1.0\,mL\,min^{-1}$ was chosen. The potential reaction of the target by hydroxyl radical was prevented by adjusting pH of the sample at 10–11 by 6.0 M NaOH solution.

The H_2O_2 concentration was determined by the spectrophotometric analysis using the potassium titanium (IV) oxalate method ($\lambda = 400\,nm$, $\varepsilon = 935\,M^{-1}\,cm^{-1}$) [16]. In this method, the titanium (IV)-peroxide complex was formed and absorbed with a λ_{max} of about 400 nm. A solution of 0.1 M potassium titanium (IV) oxalate was mixed with the sample and the absorbance at 400 nm (A_1) was measured. Because the sample also absorbed a little at 400 nm and its absorbance was A_2, thus the real absorbance of the titanium (IV)-peroxide complex was $A_1 - A_2$.

The concentration of ferrous ion was measured by the *o*-phenanthroline colorimetric method ($\lambda = 510\,nm$, $\varepsilon = 1.1 \times 10^4\,M^{-1}\,cm^{-1}$) [17].

3. Results and discussion

3.1. Enhancement of 4-CP degradation and COD_{cr} removal by O_2 in Fenton system

The degradation of 4-CP and the removal of COD_{cr} in Fenton/O_2 and Fenton/N_2 systems are compared in Fig. 1(a) and (b). It showed that the degradation of 4-CP was faster and more complete when oxygen was used as carrier gas. Within the first 5 min, the degradation of 4-CP in two systems had no obvious difference. The residual 4-CP were 58% and 62% at 1 min, 17% and 15% at 5 min for Fenton/N_2 and Fenton/O_2 system, respectively. However, after 5 min, the degradation of 4-CP bubbled with O_2 was superior to that with N_2. Almost all 4-CP was degraded at 40 min in Fenton/O_2 system. In the absence of oxygen, the degradation of 4-CP halted at 15 min and there was still 10% 4-CP remaining in the solution.

Fig. 1(b) shows the presence of oxygen is benefit to the removal of COD_{cr}. In the presence of oxygen, COD_{cr} decreased continuously although the removal rate was much slower after 10 min, and only 52% COD_{cr} remained at 40 min. While in the absence of oxygen, COD_{cr} decreased quickly within the first 5 min and then it was hardly removed. When the reaction finished, there was 74% COD_{cr} left in the solution.

3.2. Difference in changes of Fenton reagent's concentration between Fenton/O_2 system and Fenton/N_2 system

In Fenton system, hydroxyl radicals are generated by the reaction of Fe^{2+} with H_2O_2. To some extent, changes of the concentration of Fe^{2+} and H_2O_2 could indicate the degradation of the contaminant. Changes of Fenton reagent's concentration in Fenton/O_2 and Fenton/N_2 systems are shown in Fig. 2(a) and (b). It could be seen that the concentrations of Fe^{2+} were both decreased rapidly in the first 1 min. There were only 75% and 59% ferrous ions at 1 min in Fenton/N_2 and Fenton/O_2
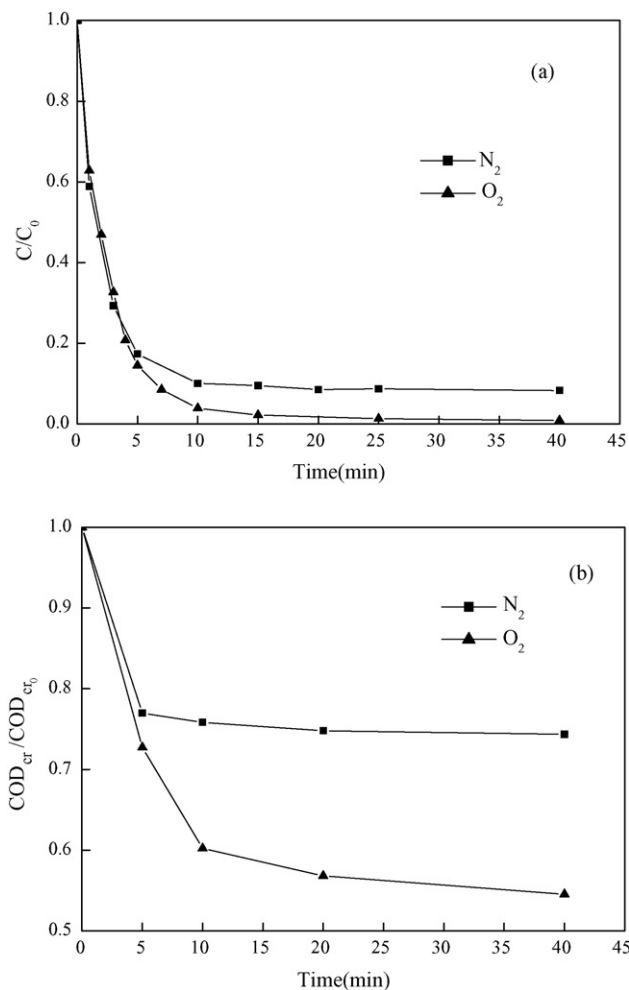
Fig. 1. Enhancement of 4-CP degradation (a) and COD_{cr} removal (b) by oxygen in Fenton system: $[4\text{-CP}]_0 = 1.0\,\text{mM}$, $[\text{Fe}^{2+}]_0 = 0.125\,\text{mM}$, $[\text{H}_2\text{O}_2]_0 = 2.50\,\text{mM}$, $Q_{(\text{O}_2\,\text{or}\,\text{N}_2)} = 0.20\,\text{m}^3/\text{h}$, $\text{pH}_0 = 3.0$ and $T = 25\,°\text{C}$.

Fig. 2. Changes of the concentrations of Fe^{2+} (a) and H_2O_2 (b) in Fenton/O_2 and Fenton/N_2 systems: $[4\text{-CP}]_0 = 1.0\,\text{mM}$, $[\text{Fe}^{2+}]_0 = 0.125\,\text{mM}$, $[\text{H}_2\text{O}_2]_0 = 2.50\,\text{mM}$, $Q_{(\text{O}_2\,\text{or}\,\text{N}_2)} = 0.20\,\text{m}^3/\text{h}$, $\text{pH}_0 = 3.0$ and $T = 25\,°\text{C}$.

system, respectively. Then, changes of the ferrous ion in two systems were different. Ferrous ion was effectively regenerated in Fenton/N_2 system. Fe^{2+} concentration increased after 1 min, reaching 90% of its initial concentration at 5 min, and then it almost unchanged. While in Fenton/O_2 system, increase in the concentration of Fe^{2+} was not obviously observed, for it ranged between 59% and 65% of the initial concentration after 1 min. Thus, the concentration of Fe^{2+} in Fenton/N_2 system kept at a higher level than that in Fenton/O_2 system during the degradation process.

In Fenton system, ferrous ion is oxidized to ferric ion by hydrogen peroxide, as shown in Eq. (1). In addition, ferric ion can be reduced to ferrous ion by hydrogen peroxide (Eq. (3)), which led to the regeneration of Fe^{2+}. However, the generation rate of Fe^{2+} is much lower than the consumption rate of Fe^{2+} [18,6]. Thus, the concentration of Fe^{2+} should be very low if there is no other substance to reduce Fe^{3+}. In our previous work [19], it was suggested that some hydroquinone-like intermediates of 4-CP such as 4-chlorocatechol, catechol and hydroquinone could reduce Fe^{3+} to Fe^{2+} quickly, as described in Eq. (4). Thus, the concentration of the hydroquinone-like
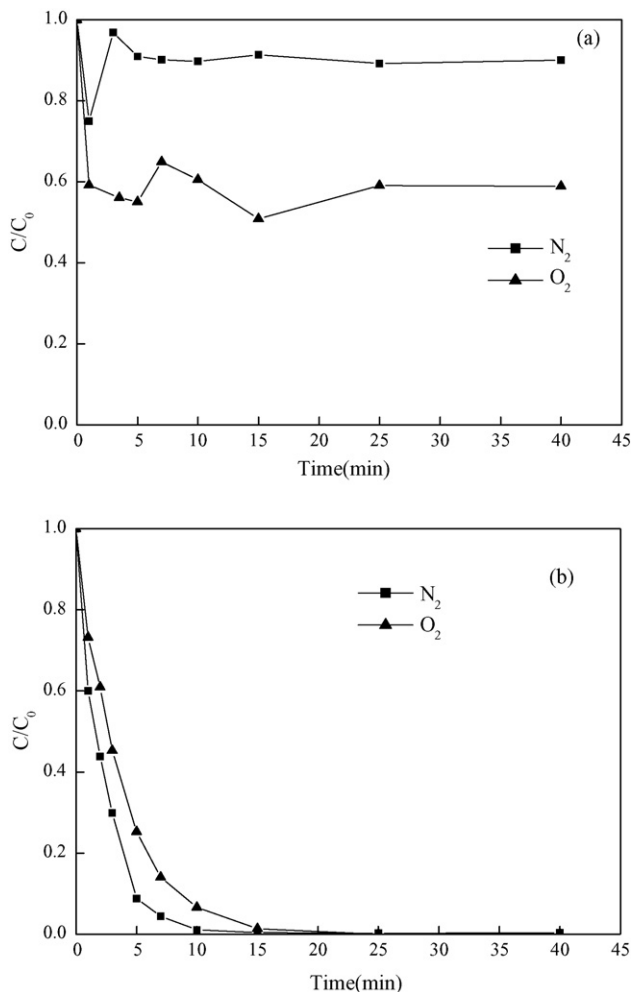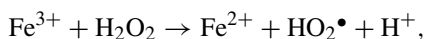
intermediates in Fenton/N_2 system was higher than that in Fenton/O_2 system because the concentration of Fe^{2+} was higher in Fenton/N_2 system. Formation of these intermediates in two systems was shown in Section 3.3 [18].

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^{\bullet} + \text{H}^+,$$
$$k_3 = 0.001\text{–}0.01\,\text{M}^{-1}\,\text{s}^{-1} \tag{3}$$

$$\text{Fe}^{2+} + \text{I} \rightarrow \text{Fe}^{3+} + \text{I}' \tag{4}$$

Fig. 2(b) shows that in Fenton/N_2 system, H_2O_2 is more rapidly consumed than that in Fenton/O_2 system. Before H_2O_2 was used up, the concentration of H_2O_2 in Fenton/O_2 system was about 15% higher than that in Fenton/N_2 system at the same time. In Fenton system, the consumption of H_2O_2 was mostly due to the reaction with Fe^{2+} and in consequence, more ferrous ion in the solution should lead to the faster consumption of hydrogen peroxide. Changes of Fe^{2+} and H_2O_2 show a coincidence in Fig. 2(a) and (b).

However, it was interesting to find that the faster consumption of H_2O_2 in Fenton/N_2 system did not enhance the degradation of

4-CP, as shown in Figs. 1(a) and 2(b). In addition, in Fenton/N_2 system, hydrogen peroxide was almost used up at 15 min, which led to the halt of 4-CP degradation and the COD_{cr} removal. While in Fenton/O_2 system, 4-CP and COD_{cr} both decreased slightly when almost no H_2O_2 in the solution. Thus, it might be concluded that there was another degradation way of 4-CP or its intermediates in the presence of oxygen [10], which was explained in Section 3.4.

3.3. Effect of oxygen on the intermediates of 4-CP by Fenton oxidation

Investigation into the formation of the intermediates is the key to reveal the mechanism of oxygen in Fenton system. In addition, the hydroquinone-like intermediates have a great influence on the Fe^{2+} concentration, and consequently, on the consumption of H_2O_2 and the degradation of 4-CP. Thus, formation of the intermediates during 4-CP degradation in two systems was analyzed.

The decomposition of contaminant in Fenton system was based on the attack of hydroxyl radical. Researches [20,21] suggested that during the degradation of aromatic compounds in Fenton system, hydroxyl radical attacked the benzene ring and the hydroxylated compounds were formed. Then the hydroxylated compounds were transformed to benzoquinone, which was subsequently oxidized to the aliphatic compounds such as organic acids by cleaving the benzene ring.

The intermediates of 4-CP during the degradation were identified and measured by HPLC analysis. They were divided into two types. One was the aromatic compound and the other was organic acid. The aromatic compounds such as 4-chlorocatechol, hydroquinone, catechol and benzoquinone were detected in both two systems. The evolution of these intermediates is shown in Fig. 3(a) and (b). In the two systems, the aromatic compounds, especially 4-chlorocatechol, were rapidly formed when the reaction was initiated. An obvious difference was the production of 4-chlorocatechol, while the formation of other aromatic intermediates had no distinct difference.

During Fenton/N_2 process, the concentration of 4-chlorocatechol reached 13.9 mg/L at 3 min and increased continuously to 33 mg/L at 10 min. Then it decreased to 32 mg/L at 15 min and afterwards almost unchanged. This might due to two reasons as followings. One was the exhaustion of H_2O_2 (seen in Fig. 2(b)) and 4-chlorocatechol was neither formed nor degraded by $\bullet$OH. The other was some organic acids such as oxalic acid might scavenge Fe^{3+} during the process [22] and formed the complex compound (ferrioxalate), which impeded the reaction between Fe^{3+} and 4-chlorocatechol. Therefore, the concentration of 4-chlorocatechol was unchanged after 15 min in Fenton/N_2 system. The concentrations of hydroquinone, catechol increased quickly within the first 1 min and then decreased. This was because when hydroquinone and catechol was formed from 4-CP, they transferred easily to quinone in sequence [20,21]. It could be seen from Fig. 3(a) that benzoquinone increased rapidly at the beginning of the reaction and its concentration reached the maximum at 3 min. In Fenton/O_2
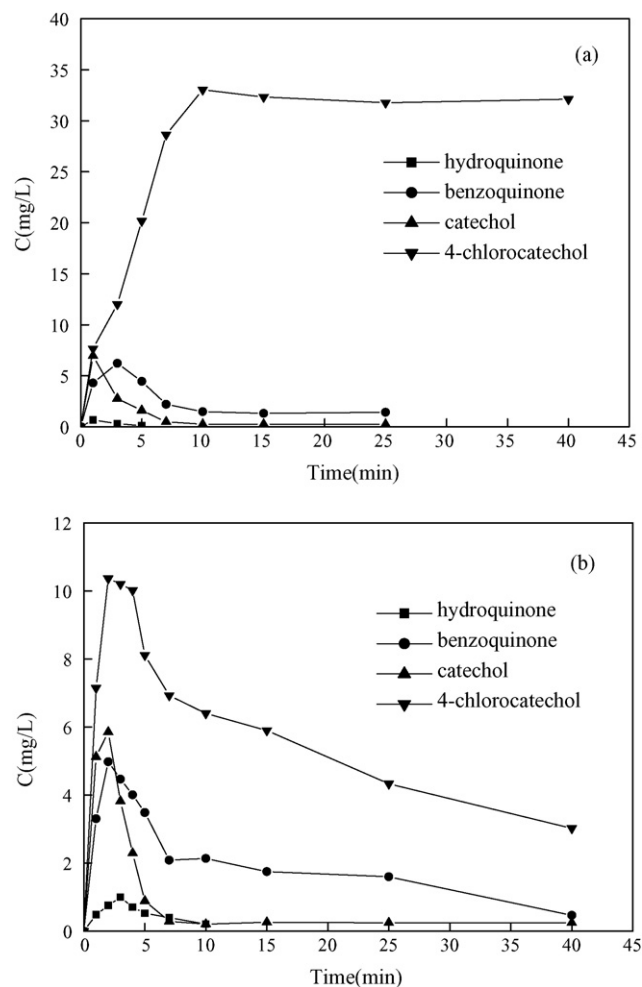

Fig. 3. Comparison of the formation of aromatic intermediates in Fenton/N_2 (a) and Fenton/O_2 (b) systems: [4-CP]$_0$ = 1.0 mM, [Fe^{2+}]$_0$ = 0.125 mM, [H_2O_2]$_0$ = 2.50 mM, $Q_{(O_2\ or\ N_2)}$ = 0.20 m^3/h, pH$_0$ = 3.0 and T = 25 °C.

system, all aromatic compounds reached the maximum concentration in 5 min and then their concentrations decreased. For 4-chlorocatechol, its concentration came to a peak of 10.4 mg/L at 2 min, and then decreased to 6.9 mg/L at 7 min and 3.0 mg/L at 40 min. It was shown that 4-chlorocatechol formed in Fenton/O_2 system was much lower than that in Fenton/N_2 system. Therefore, oxygen in the solution may impede the generation of 4-chlorocatechol or accelerate the decomposition of 4-chlorocatechol.

In addition, formation of the hydroquinone-like intermediates was coincident with the changes of Fe^{2+} concentration in two Fenton processes, as shown in Fig. 2(a). The hydroquinone-like intermediates generated in Fenton/N_2 system were more than those in Fenton/O_2 system. Because the hydroquinone-like intermediates reduced Fe^{3+} to Fe^{2+} quickly (Eq. (4)), the concentration of Fe^{2+} in the absence of oxygen was higher than that in the presence of oxygen.

Compared with the retention time of the standard substances, the organic acids such as maleic acid, fumaric acid, oxalic acid and acetic acid were identified as the ring-open intermediates in Fenton/O_2 and Fenton/N_2 system. The formation of these
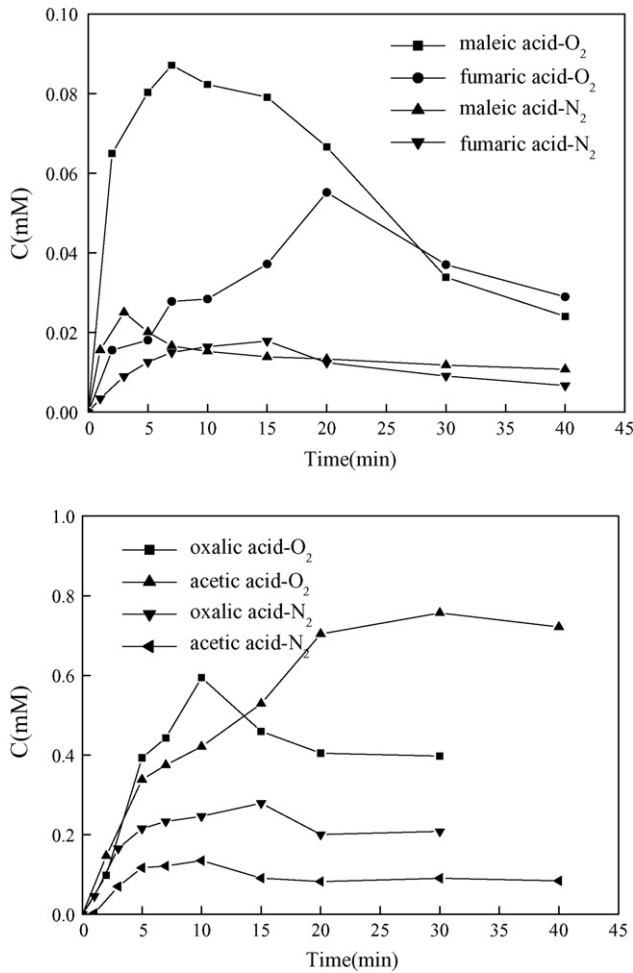
Fig. 4. Comparison of the formation of organic acids in Fenton/O_2 and Fenton/N_2 systems: [4-CP]$_0$ = 1.0 mM, [Fe^{2+}]$_0$ = 0.125 mM, [H$_2$O$_2$]$_0$ = 2.50 mM, $Q_{(O_2 \text{ or } N_2)}$ = 0.20 m^3/h, pH$_0$ = 3.0 and T = 25 °C.

organic acids during the processes is shown in Fig. 4. It was found that the concentrations of the organic acids in Fenton/O_2 system were all higher than those in Fenton/N_2 system. For example, maleic acid in Fenton/O_2 system increased quickly at the first 7 min, achieving the peak concentration of 0.086 mM at 7 min. Since then, the concentration of maleic acid decreased slowly and its concentration was 0.028 mM at 40 min. While in Fenton/N_2 system, after maleic acid attained the maximum concentration i.e., 0.025 mM at 3 min, its concentration decreased within 15 min and then it kept almost unchangeable. The comparison of other organic acids had the similar result to that of maleic acid.

Thus, the comparison of the intermediates generated in the two systems showed that oxygen played an important role in the oxidation of 4-CP by Fenton system. When the solution was bubbled with oxygen, the concentration of the toxic intermediate, 4-chlorocatechol, was much lower, while a larger extent of the aromatic substances cleaved the ring to form the organic acids. Therefore, a higher degree of the oxidation of the intermediates was happened in Fenton/O_2 system, explaining the more COD$_{cr}$ removal (Fig. 1(b)). This was very important to the treatment of the toxic and refractory contaminant.

3.4. Reaction mechanism of oxygen in the degradation of 4-CP by Fenton system

According to the experiment data and the discussion above, the acceleration role of oxygen in the degradation of 4-CP by Fenton system was summarized as follows:

(a) In the presence of oxygen, 4-CP degradation was enhanced, indicating there was another pathway for the degradation of 4-CP or its intermediates.
(b) In Fenton/O_2 system, the aromatic intermediate, 4-chlorocatechol, was produced less than in Fenton/N_2 system, while more aromatic was ring-cleaved and more aliphatic organic acid was generated.

Based on these conclusions, the participation of oxygen in the degradation of 4-CP by Fenton system was suggested.

In Fenton system, hydroxyl radical was generated when hydrogen peroxide was added to initiate the reaction. During the oxidation of the organic species, the addition to a double bond or a hydrogen extraction was assumed to be the first step of the •OH attack [23]. The attack of hydroxyl radical on 4-CP was directed by the hydroxyl group, which was a stronger *ortho/para* director than chlorine. Under the influence of these directors, hydroxyl radical preferred to attack the *ortho* position of the hydroxyl group, as expressed in Eq. (5). This oxidation process was extremely fast as its rate constant was as high as 10^7 to 10^{10}(mol^{-1} s^{-1})[24]. The hydroxyl radical abstracted a hydrogen atom from 4-CP yielding a 4-chlorohydroxycyclohexadienyl radical (ClHP• radical). Also, formation of the dechlorinated product, hydroquinone, was possible when •OH attack occurred at the chloro position of 4-CP [25]. (Eq. (6)):


$$(5)$$

$$(6)$$
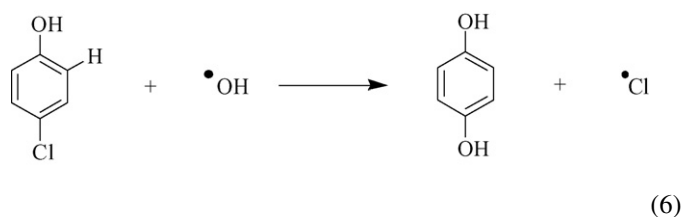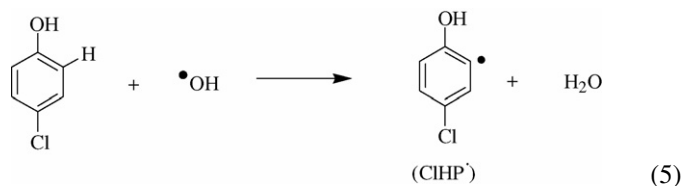
In the absence of oxygen, hydroxyl radical reacted with ClHP• radical, producing 4-chlorocatechol, as described in Eq. (7). When hydroxyl radical attacked at the chloro position of 4-chlorocatechol, catechol was formed by the dechlorination of 4-chlorocatechol. Researches [20,21] suggested that hydroquinone and catechol transferred easily to quinone, which was

oxidized to organic acid by cleaving the benzene ring:

(7)
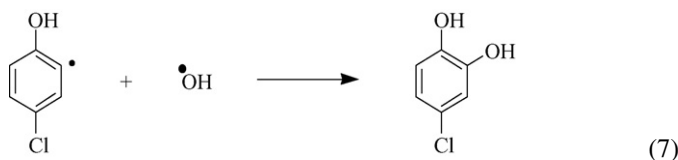
In the presence of O_2, the experimental result showed that 4-chlorocatechol was less produced than that in the absence of oxygen. Moreover, the literatures [11,23,25] reported that organic radicals would yield peroxyl radical by addition of molecular oxygen. Thus, it was supposed that ClHP• radical in solution gave rise to *ortho*-parachlorophenolperoxyl radicals (ClPP• radical) by reaction with the dissolved oxygen, as described in Eq. (8). Therefore, the generation of 4-chlorocatechol was hindered, which explained why the concentration of 4-chlorocatechol in Fenton/O_2 system was lower than that in Fenton/N_2 system:

(CIPP•) (8)
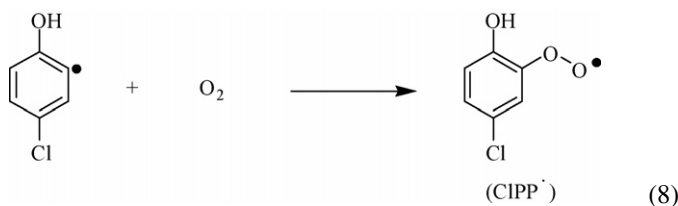
To verify the presumption that O_2 in solution could compete with •OH to reaction with ClHP• radical, the following experiment (called system A) was carried out. At first, 4-CP solution was bubbled with nitrogen during Fenton process. After 5 min, the carrier gas was changed to oxygen. The degradation of 4-CP and formation of 4-chlorocatechol were compared with those in Fenton/N_2 system, as shown in Fig. 5. During the first 5 min, the degradation of 4-CP and formation of 4-chlorocatechol were very similar in these two systems. While after 5 min, the degradation of 4-CP in system A was a little faster than that in Fenton/N_2 system. At 10 min, the residual ratios of 4-CP were 8.3% and 12.0% for system A and Fenton/N_2 system, respectively. And after hydrogen peroxide was exhausted (15 min), the concentration of 4-CP in system A even decreased to 4.5% at 60 min, while no degradation of 4-CP was observed after 15 min in Fenton/N_2 system. The formation of 4-chlorocatechol in system A was close to that in Fenton/N_2 system during the first 5 min, while it became much slower than that in Fenton/N_2 system after 5 min. At the end of the reaction, the concentration of 4-chlorocatechol in Fenton/N_2 system and system A was 32 and 18 mg/L, respectively. The result of this experiment suggested that the addition of oxygen hindered the generation of 4-chlorocatechol. Thus, it was concluded that dissolved oxygen could compete against hydroxyl radical to react with ClHP• radical.

It was questionable that whether bubbling oxygen into the solution would keep the degradation of 4-CP when hydrogen peroxide was exhausted in Fenton/N_2 system. In the following experiment (called system B), the solution was bubbled with nitrogen before H_2O_2 was used up (15 min). At 15 min, oxygen was bubbled into the system. Fig. 5(a) and (b) suggested that the degradation of 4-CP and the generation of 4-chlorocatechol
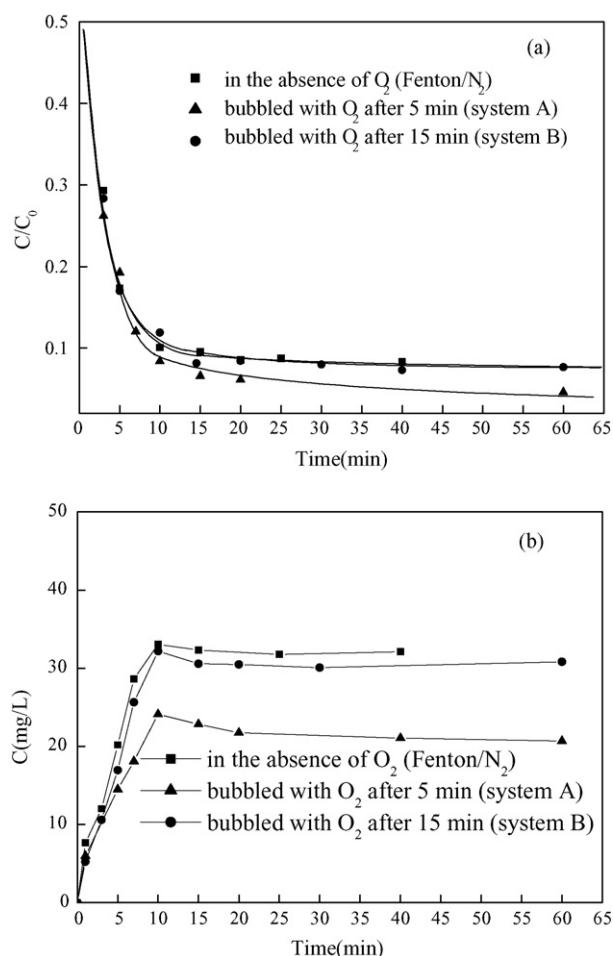

Fig. 5. Comparison of 4-CP degradation (a) and 4-chlorocatechol generation (b) in three Fenton systems: Fenton/N_2 system (bubbling with nitrogen during the whole process); system A (bubbling with nitrogen within the first 5 min and then bubbling with oxygen); system B (bubbling with nitrogen within the first 15 min and then bubbling with oxygen); [4-CP]$_0$ = 1.0 mM, [Fe^{2+}]$_0$ = 0.125 mM, [H_2O_2]$_0$ = 2.50 mM, $Q_{(O_2 \text{ or } N_2)}$ = 0.20 m^3/h, pH$_0$ = 3.0 and T = 25 °C.

were both close to those in Fenton/N_2 system. Eq. (8) suggested that the action of O_2 required the existence of ClHP• radical in solution. Because ClHP• radical was first produced by the occurrence of Fenton reaction and the radical would die out quickly, therefore oxygen could enhance the degradation only when oxygen was bubbled before hydrogen peroxide was depleted.

In the presence of oxygen, oxygen competed against •OH to react with ClHP• radical, which impeded the formation of 4-chlorocatechol. Therefore, it led to the lower concentration of Fe^{2+} and slower consumption of H_2O_2 in Fenton/O_2 system (Fig. 2). But the degradation of 4-CP in Fenton/O_2 system was not slower than that in Fenton/N_2 system. The reason could be that most of ClHP• reacted with O_2 quickly in Fenton/O_2 system and •OH was less consumed for the reaction with ClHP•. This caused more •OH to degrade 4-CP in Fenton/O_2 system. Therefore, within the first 5 min, the degradation of 4-CP was similar in the two systems. After 5 min, the remaining H_2O_2 was greater than that in Fenton/N_2 system, which led to the quicker degradation of 4-CP.
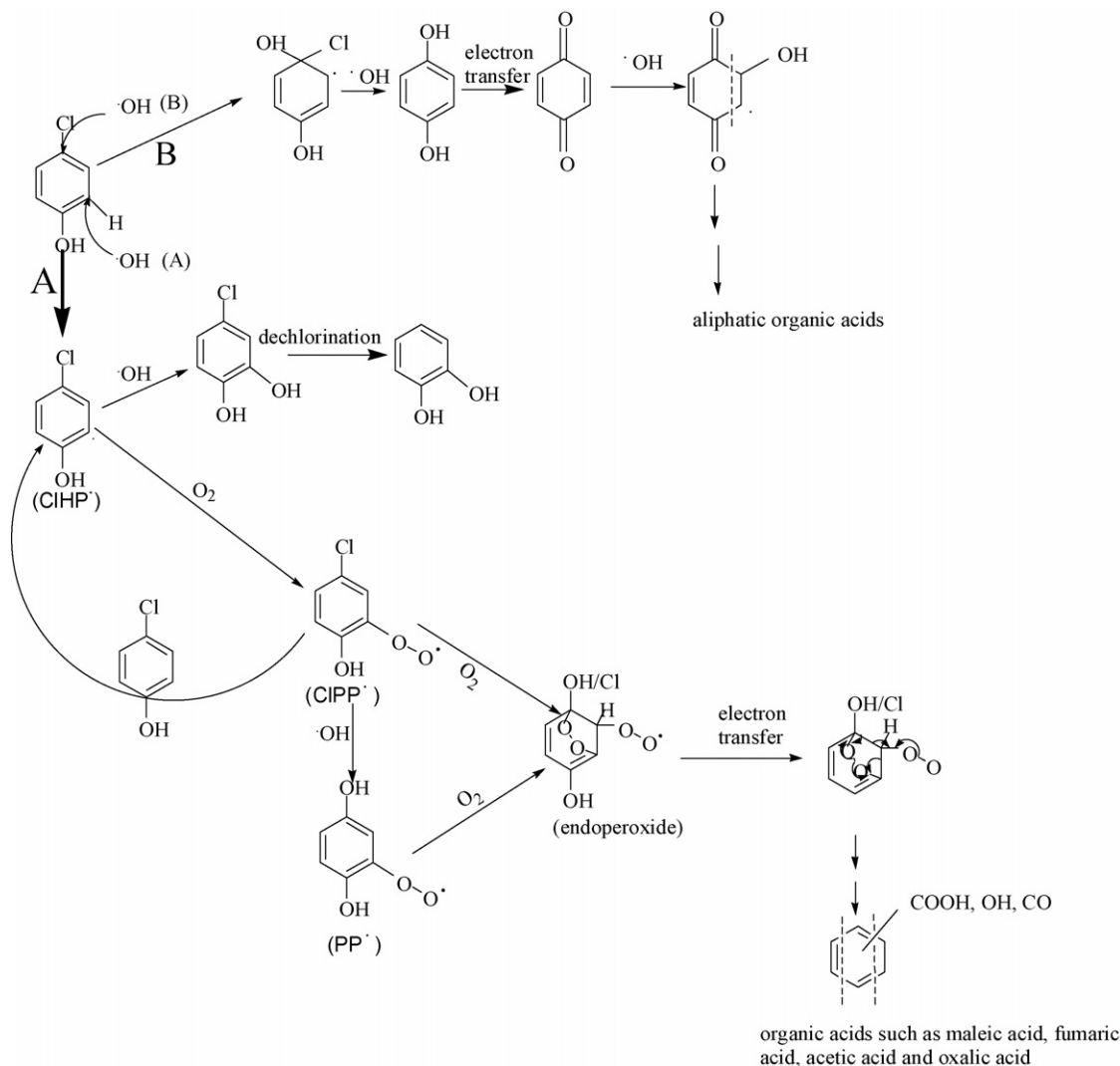
Fig. 6. Reaction mechanism of oxygen during the oxidation of 4-CP by Fenton system.

ClPP[•] radical could participate in another series of reactions. (1). According to the review [23], the organic peroxyl radical (RO$_2$[•]) could abstract a hydrogen atom from the organics (RH). Therefore, it was supposed that ClPP[•] radical reacted with 4-CP and gave birth to ClHP[•] radical again. Thus, 4-CP could be degraded through another way, which explained the enhancement of 4-CP degradation in Fenton/O$_2$ system well. (2) ClPP[•] radical could be dechlorinated and changed to PP[•] radical. Then ClPP[•] or PP[•] radical formed endoperoxide by scavenge of oxygen and cyclization. The literature [26] reported that the endoperoxide was very instable and electron transfer happened in it, which led to ring cleavage. The aliphatic substance was oxidized, producing the aliphatic organic acids such as maleic acid, fumaric acid, acetic acid and oxalic acid. Therefore, in the presence of oxygen, there were two pathways to generate the organic acids. One was the cleavage of endoperoxide, which was generated by the reaction of (Cl)PP[•] radical with oxygen. The other was the cleavage of quinone by attack of hydroxyl radical, which also took place in Fenton/N$_2$ system. That accounted

for the more organic acids in Fenton/O$_2$ system. Mechanism of 4-CP oxidation in the presence of oxygen by Fenton system was described in Fig. 6.

4. Conclusion

1. 4-CP degradation and CODcr removal were both enhanced by oxygen. At the end of the reaction, all 4-CP in Fenton/O$_2$ system was degraded while about 10% 4-CP remained in Fenton/N$_2$ system. The CODcr removal was 48% and 26% in Fenton/O$_2$ and Fenton/N$_2$ system, respectively.
2. The higher concentration of ferrous ion in Fenton/N$_2$ system was due to the effective reduction of 4-chlorocatechol, which was massively formed in the absence of oxygen. The more Fe^{2+} in Fenton/N$_2$ system caused the quicker consumption of H$_2$O$_2$ and the depletion of H$_2$O$_2$ resulted in the halt of the degradation in Fenton/N$_2$ system.
3. The intermediates generated in two systems were both divided into two species. One was the aromatic substance

including hydroquinone, catechol, 4-chlorocatechol and benzoquinone. The other was the organic acid such as maleic acid, fumaric acid, oxalic acid, acetic acid and formic acid. Much more 4-chlorocatechol was produced in Fenton/N_2 system. This was because in Fenton/O_2 system, oxygen competed against hydroxyl radical for the reaction with ClHP$^\bullet$ radical, producing ClPP$^\bullet$ radical and impeding the generation of 4-chlorocatechol.

4. In Fenton/O_2 system, another way to cleave benzene ring was provided by the reaction of oxygen with (Cl)PP$^\bullet$ radical, thus accelerated the formation of aliphatic organic acids. The concentrations of the organic acids in Fenton/O_2 system were over twice than that in Fenton/N_2 system.

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