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ScienceDirect
Journal of Environmental Sciences 2012, 24(3) 550–557
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Self-catalytic degradation of *ortho*-chlorophenol with Fenton's reagent studied by chemiluminescence

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Received 13 January 2011; revised 21 February 2011; accepted 14 March 2011

Abstract

The degradation of *ortho*-chlorophenol using Fenton's reagent was studied by chemiluminescence (CL). Without a special CL reagent, a weak CL emission from the mixture of ferrous ion and hydrogen peroxide was observed at room temperature. The CL intensity was increased by the addition of *ortho*-chlorophenol into the mixed solution. When the temperature was raised to 65°C, the CL intensity was enhanced strongly. The CL mechanisms for the system H_2O_2-Fe^{2+} with and without *ortho*-chlorophenol were studied by examining the CL spectrum, gas chromatography-mass spectrometry and electron spin resonance spectrum. The effects of various free radical scavengers, surfactants and fluorescence compounds on the CL intensity were also investigated. A self-catalytic oxidation mechanism was proposed. The results showed that singlet oxygen was the main emitter for the system H_2O_2-Fe^{2+}. The strong CL from the system H_2O_2-Fe^{2+}-*ortho*-chlorophenol was due to singlet oxygen and electronically excited quinone. The benzenediol-like intermediate product formed during the phenol oxidation process greatly promoted the Fenton's reaction and led to higher CL intensity. Chemiluninescence is a novel approach for the investigation of the oxidation of some organic pollutants by Fenton's reagent.

Key words: *ortho*-chlorophenol; Fenton' reagent; chemiluminescence; singlet oxygen

DOI: 10.1016/S1001-0742(10)60639-0

Introduction

Phenolic-type compounds are usually present in the wastewater generated from waste incineration, uncontrolled use of pesticides and herbicides, as well as some food processing industries. Several phenolic-type compounds have been listed among the 65 priority pollutants by the US EPA due to the fact that they do not readily degrade and pose a threat to human beings (Keith and Telliard, 1979). Therefore, removing these phenols or transforming them into biodegradable intermediates is a very urgent priority.

Chemical, biological and thermal treatments represent three different technologies to destroy phenols (Zazo et al., 2005). However, biological treatments can be easily affected by the conditions and are inconvenient to be applied to the degradation of high concentration of phenols (Eker and Kargi, 2006). Some hazardous compounds are emitted from thermal treatments (Benitez et al., 2000). Fortunately, an innovative technology named advanced oxidation processes (AOPs) is an interesting option to remove organic pollutants because of their strong oxidant power. Fenton's reagent, as one of the most important technologies among the AOPs, has been under development for more than a century since it was reported in 1894 (Fenton, 1894). It is a suite of reactions involving hydrogen peroxide and ferrous iron. A Fenton-like system (Cu^{2+}/H_2O_2) (Nieto-Juarez et al., 2010) and photo-Fenton (Pérez-Moya et al., 2007) also exhibit high efficiency for the degradation of organic pollutants. Recently, a new AOP, referred to as electro-Fenton, generates the H_2O_2 from the reduction of O_2 with an electrode. The H_2O_2 produced combines with ferrous ion to form Fenton's reagent (Brillas et al., 2009). In Fenton's reaction, H_2O_2 is decomposed by the catalysis of Fe^{2+} and gives rise to hydroxyl radical. Hydroxyl radical is highly reactive (E^{θ} = 2.8 V) and has great potential to oxidize numerous organic compounds. More and more attention has been focused on its possible application in wastewater detoxification, destruction of organic pollutants and biodegradability improvement of wastewater in recent decades (Kremer, 2003).

ortho-Chlorophenol has generated concern due to its high toxicity as well as the need for its removal from the environment. Its degradation by Fenton's reagent has been reported widely (Pignatello, 1992; Walling, 1998). Huang et al. (2001) examined the catalyzed decomposition of H_2O_2 and *ortho*-chlorophenol in the presence of different iron oxides in order to investigate the reaction of hydrogen peroxide and organics. The degradation of 2,4-dichlorophenol by Nafion-Fe in the presence of H_2O_2

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was studied by Sabhi and Kiwi (2001). Parameters influencing the reaction, such as pH, temperature, and ratio of oxidizer to substrate were investigated in some studies (Rivas et al., 2001; Elias and Waterhouse, 2010). However, the mechanism of phenol degradation is so complex that a deeper understanding of the degradation mechanism remains elusive.

The chemiluminescence (CL) process involves energy and electron transfer, which provides useful information on short-lived intermediates (Lin, 2004). In the present work, CL was utilized to study the process of *ortho*-chlorophenol degradation in order to gain valuable insight into the mechanism. The CL mechanisms for the system H_2O_2-Fe^{2+} and the system H_2O_2-Fe^{2+}-*ortho*-chlorophenol were studied by batch experiments, flow injection (FI), CL spectroscopy, gas chromatography-mass spectrometry (GC-MS) and electron spin resonance spectroscopy (ESR). The effects of various free radical scavengers, surfactants and fluorescence compounds on the CL intensity were also investigated. The proper mechanisms for the CL phenomena were revealed, which is of great significance for the understanding of Fenton's process.

1 Materials and methods

1.1 Chemicals and solutions

All chemicals were of analytical grade. Water was purified using a Barnstead Nanopure system (18.3 MΩ·cm, Barnstead, Iowa, USA). $FeSO_4$ was purchased from Guan Hengye Fine Chemical Co., Ltd. (Hebei, China). $FeCl_2$, $FeCl_3$, $NH_4Fe(SO_4)_2$ and $(NH_4)_2Fe(SO_4)_2$ were from Beijing Chemical Reagent Company (Beijing, China). Hydrogen peroxide (Acros Organics, Belgium) was freshly prepared by the dilution of 35% H_2O_2. The ferric or ferrous solutions were prepared by dissolving ferric or ferrous salt in purified water spiked with an amount of sulfuric acid sufficient to avoid their hydrolyzation. A 0.01 mol/L stock solution of *ortho*-chlorophenol was obtained by diluting *ortho*-chlorophenol (Acros Organics, Belgium) with water. Glutathione (GSH), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6- tetramethyl-4-piperidone (TEMP) were purchased from Sigma-Aldrich (USA). Didodecyldimethylammonium bromide (DDDAB) was purchased from Kanto Chemical Co., INC. (Japan). Sodium dodecyl sulfate (SDS) and Tween-20 were from Beijing Chemical Reagent Company (Beijing, China). Dodecyltrimethylammonium bromide (DTAB), myristyltrimethyl-ammonium bromide (MTAB), cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) were bought from Xiamen Pioneer Technology INC. (Xiamen, China). 2-Methyl-6-(4-methoxyphenyl)-3,7-di-hydroimidazo [1, 2α] pyrazin-3-onehydrochloride (MCLA) was obtained from Tokyo Kasei Kogyo Co. (Tokyo, Japan).

1.2 Apparatus and procedure

Batch CL experiments were carried out in a BPCL luminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences, China) coupled with a PC 2000 computer. The signal was recorded by the computer equipped with a data-acquisition interface. The flow injection CL analyzer system used in this work is shown in Fig. 1. It consisted of two peristaltic pumps (SJ-1211, Atto, Japan), a 0.15-mL loop injector, a CL cell, and an ultra-weak luminescence analyzer (Model LF-800, Microtec Niti-On, Japan). Two peristaltic pumps were used to deliver all the solutions. The reagents were mixed in the CL cell which was placed close to the photomultiplier tube. The signal was recorded using an IBM-compatible computer, equipped with a data acquisition interface.

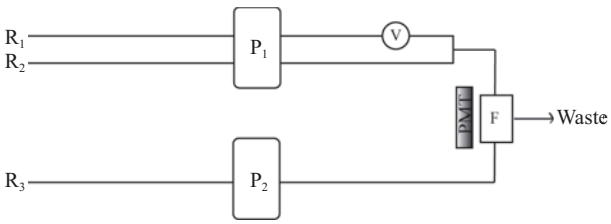

Fig. 1 Schematic diagram of the flow-injection CL system. P_1 and P_2: peristaltic pumps; V: six-way valve injector; F: flow cell; R_1, R_2, and R_3: solution delivering lines.

The CL emission spectra were measured using a FL-7000 spectrophotometer (Hitachi, Japan). A Bruker EPR ELEXSY 500 spectrometer was used to obtain the ESR spectra of radicals' spin-trapping adducts. The ESR signals were registered at microwave power 12.72 mW and modulation amplitude 2.00 G.

A Shimadzu GCMS-QP2010 (Shimadzu, Japan) system equipped with a DB-5MS capillary column (30 m long, 0.25 mm internal diameter, 0.1 μm film thickness) was used for the degradation products detection. Helium was used as carrier gas at a flow rate of 1.5 mL/min. One microliter sample was injected into the split/splitless inlet in splitless mode (splitless for 1 min, with total flow of 12.0 mL/min) at 220°C. The temperature of the GC-MS interface was 230°C. The oven temperature program started at 50°C for 2 min, increased to 200°C at 10°C /min, and then increased to 300°C at 40°C/min, which was maintained for 2 min. Full scan mode was used for data acquisition and analysis.

2 Results and discussion

2.1 Chemiluminescent kinetic study

The batch study was performed to provide details about the mechanism. As shown in Fig. 2A(a), CL emission with low intensity was observed with the mixing of H_2O_2 and ferrous solution. CL emission with a high value of 2.6×10^3 appeared when H_2O_2 was introduced into a solution containing both ferrous solution and *ortho*-chlorophenol, which indicated the significant influence of *ortho*-chlorophenol on the CL reaction (Fig. 2A(b)).

The effect of different mixing orders of reagent solution on the CL dynamics was also investigated to get a deeper understanding of the CL character. If the ferrous solution was first mixed with H_2O_2, then *ortho*-chlorophenol was

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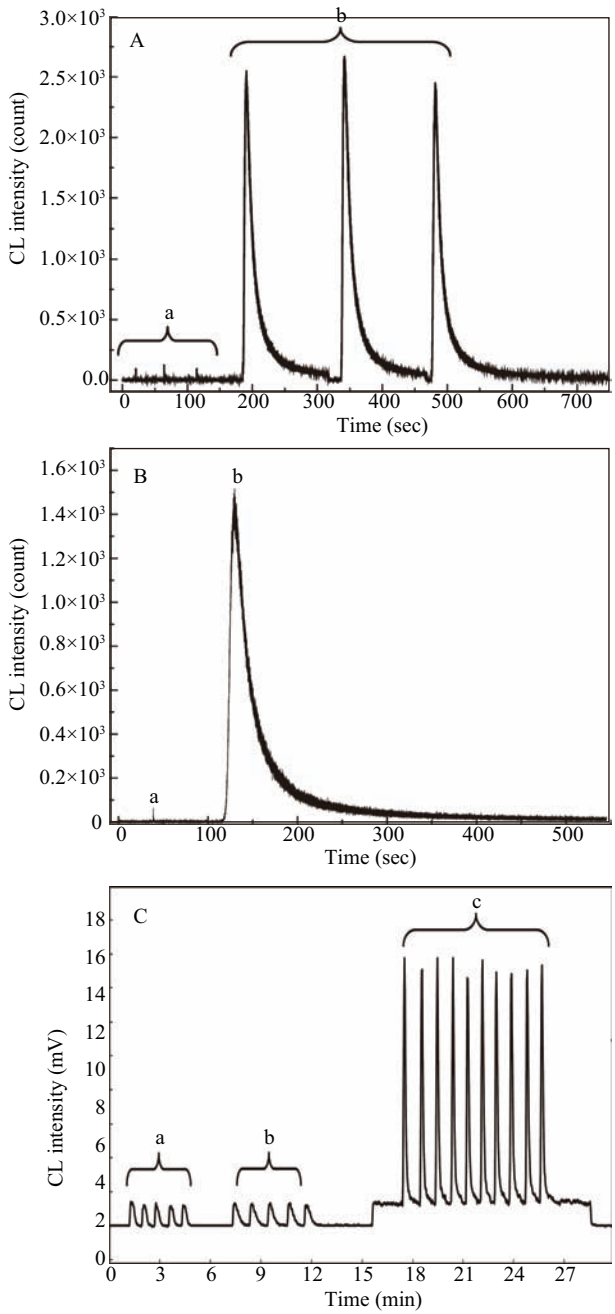


Fig. 2 Chemiluminescent (CL) signals for the batch system and flow injection. (A) batch CL signals with H_2O_2 injected into ferrous solution (a) and the mixture of ferrous solution and *ortho*-chlorophenol (b). (B) The kinetic spectra when *ortho*-chlorophenol was injected into the mixture of ferrous solution and H_2O_2. *ortho*-Chlorophenol: 1.0×10^{-3} mol/L; Fe^{2+}: 1.0×10^{-2} mol/L; H_2O_2: 1 mol/L. (C) The CL of the flow injection system. (a) H_2O_2 was injected through the six-valve injector into the ferrous solution; (b) Ferrous solution was injected through the six-valve injector into H_2O_2; (c) *ortho*-chlorophenol was injected through the six-valve injector to mix with the ferrous solution and H_2O_2. *ortho*-Chlorophenol: 5.0×10^{-4} mol/L; Fe^{2+}: 1.0×10^{-2} mol/L; H_2O_2: 1 mol/L.

added, CL with an intensity of 1.6×10^3 was detected (Fig. 2B(b)), which was higher than the emission of the Fe^{2+}-H_2O_2 system without *ortho*-chlorophenol (the insert in Fig. 2B(a)). However, the CL intensity in this case was much lower than that obtained by injecting H_2O_2 into the mixture of *ortho*-chlorophenol and ferrous solution (Fig. 2A(b). This was attributed to the consumption of H_2O_2 by the ferrous solution when they were mixed beforehand.

This CL phenomenon could be due to the formation of singlet oxygen ($^1O_2$) and electronically excited quinone. The mechanism is proposed as follows. The generation of hydroxyl radical through H_2O_2-Fe^{2+} is the initial step (Reaction (1)) (Walling, 1975). The resulting hydroxyl radical reacts with Fe^{3+} to produce $HO_2\cdot$ (Reaction (2)) (Walling, 1975).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH\cdot + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2\cdot + H^+ \quad (2)$$

$$Fe^{2+} + OH\cdot \longrightarrow OH^- \quad (3)$$

$HO_2\cdot$ decomposes to $\cdot O_2^-$(Reaction (4)) (Bielski et al., 1985). $\cdot O_2^-$ interacts with hydroxyl radical or $HO_2\cdot$ to produce singlet oxygen, which was one of the CL emitters during the CL reaction (Reactions (5) and (6)) (Khan and Kasha, 1970; Lin and Liu, 2008). The combination of $HO_2\cdot$ also generates singlet oxygen (Reaction (7)). When H_2O_2 and ferrous ion solution was mixed before the injection of *ortho*-chlorophenol, Fenton's reaction occurred. Thus the radical available for the organic compounds could be deduced. In this case, the CL intensity was not as strong as that obtained by injecting H_2O_2 into the mixture of *ortho*-chlorophenol and ferrous solution.

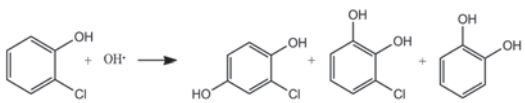
$$HO_2\cdot \longrightarrow \cdot O_2^- + H^+ \quad (4)$$

$$\cdot O_2^- + OH\cdot \longrightarrow {}^1O_2 + OH\cdot \quad (5)$$

$$\cdot O_2^- + HO_2\cdot \longrightarrow {}^1O_2 + HO_2\cdot \quad (6)$$

$$HO_2\cdot + HO_2\cdot \longrightarrow {}^1O_2 + H_2O_2 \quad (7)$$

The important role of *ortho*-chlorophenol in the CL can be explained by its reduction ability and the excited intermediates generated. The hydroxyl radical produced attacks the *ortho*-chlorophenol to form hydroquinone (Reaction (8)). Hydroquinone can quickly reduce ferric ion to ferrous ion and accelerate the Fenton's reaction (Reaction (9)) (Chen et al., 2002). A reaction between the semiquinone and hydroxyl radical would lead to the formation of electronically excited quinone with CL emission (Reaction (10)) (Brunmark, 1989; Brunmark and Cadenas, 1987).



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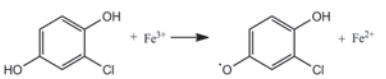

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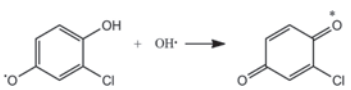

(10)

Photons were emitted rapidly from the CL reaction when a high concentration of ferrous ion was utilized. However, the CL signal was decreased with ferrous concentration higher than 0.1 mol/L. This was because ferrous

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ion could also further react with hydroxyl radical (Reaction (3)), which affected the reaction of hydroxyl radical with other species. The photon was emitted rather slowly from the reaction with a ferrous concentration of 1.0×10^{-3} mol/L. The result shows that the availability of free ferrous ion was critical to the production of hydroxyl radical and limited the decomposition of organic compounds. Although the reduction reaction could regenerate ferrous ion, the regeneration process was slow due to the slow reaction rate of Reaction (2) compared to that of Reaction (1) (0.001–0.01 $(mol/L)^{-1}$ sec^{-1} vs. 51 $(mol/L)^{-1}$ sec^{-1}) (Walling and Goosen, 1973). Thus, the kinetic dependence is shaped like a curve with low concentration of ferrous ion utilized.

The highest CL intensity was obtained with a pH value of 2.8. It was reported that the optimum pH value for *ortho*-chlorophenol degradation is between 3 and 4 (De et al., 1999). The CL intensity is thus presumed to be related to the degradation of chlorophenol.

2.2 CL-FI System

The solution-delivering lines R_1, R_2 and R_3 were for H_2O (carrier), H_2O_2, and ferrous solution, respectively (Fig. 1). The CL intensity arising from the mixing of H_2O_2 with ferrous solution was 1.5 mV, which was detected by the luminescence analyzer. The lines for H_2O_2 and ferrous solution could be interchanged, and the CL intensity observed was almost the same (Fig. 2C(b)). With the introduction of *ortho*-chlorophenol to the H_2O_2-Fe^{2+} system, a much stronger CL signal as high as 15 mV was recorded (Fig. 2C(c)), which further demonstrates the enhanced effect of *ortho*-chlorophenol on the CL from Fenton's reaction.

2.3 Influence of iron on CL

The CL intensity with the use of different iron salts was in the order of $(NH_4)_2Fe(SO_4)_2 \approx FeSO_4 > FeCl_2 > FeCl_3 > NH_4Fe(SO_4)_2$. This was because the ferric ion must react first with H_2O_2 to regenerate ferrous ion, which results in the generation of hydroxyl radical (see Reactions (1) and (2)). Because the reaction rate of Reaction (2) was 0.001–0.01 ($(mol/L)^{-1}$ sec^{-1}), which was much slower than the rate of Reaction (1), the ferrous ion was quickly consumed, but slowly regenerated, which brought on the slowing of the Fenton's reaction. As a result, $(NH_4)_2Fe(SO_4)_2$, which resulted in low background noise and high signal, was selected for further experiment.

2.4 Influence of temperature on CL

Values for the activation energy for Reaction (1) have been reported to be a few kilocalories. Little attention has been paid to the influence of temperature. In the present work, the effect of temperature on the reaction was studied. The CL intensity increased with increasing temperature when hydrogen peroxide was added to the mixture of ferrous ion solution and *ortho*-chlorophenol (Fig. 3). The increase of CL intensity can be explained by a greater production of hydroxyl radical at higher temperature, which is essential for the degradation of *ortho*-chlorophenol. A similar conclusion had been reported by Lopez et al. (2005), finding that 4-chloro-3-methyl phenol degradation was strongly influenced by temperature.

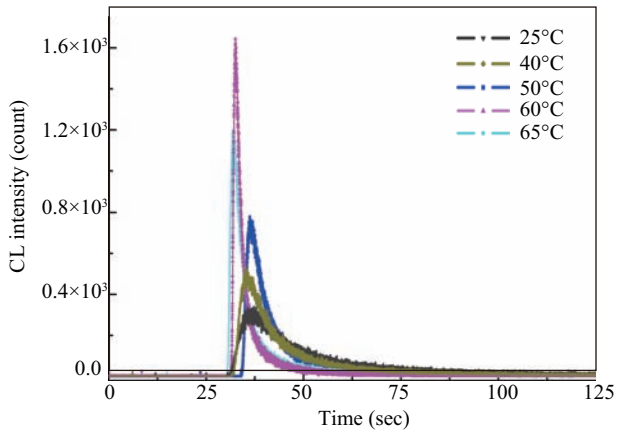

Fig. 3 Effect of temperature on the CL when hydrogen peroxide was added to the mixture of ferrous ion solution and *ortho*-chlorophenol. *ortho*-chlorophenol, 5.0×10^{-4} mol/L; Fe^{2+}, 1.0×10^{-2} mol/L; H_2O_2, 1 mol/L.

2.5 Effect of radical scavengers on CL

In the system containing metal, the introduction of hydrogen peroxide initiated a number of radical type reactions. To obtain further insight into the mechanism of the CL system, the effects of some radical scavengers on the CL intensity were studied. Several organic solutions, i.e., methanol (Rodríguez et al., 2001), ethanol, propanol, and *tert*-butanol (Chen and Pignatello, 1997; Rivas et al., 2001; Du et al., 2006), were reported to prevent the potential reactions of hydroxyl radical. In the present work, it was found that organic solutions acting as radical scavengers had an inhibiting effect on the CL of the system Fe^{2+}-H_2O_2-*ortho*-chlorophenol. Some other organic compounds including acetonitrile, CH_3Cl and cyclohexane had little effect on the CL intensity. Among all the organic compounds, *tert*-butanol inhibited the CL intensity the most, consistent with its highest reactivity towards hydroxyl radical.

Inhibited CL was observed when thiourea or maninitol, two important scavengers towards hydroxyl radical (Liang et al., 2008), was introduced into the CL reaction, which further confirmed the participation of the hydroxyl radical in the CL reaction.

Formate caused the intensity to increase up to 10.1-fold at a concentration of 1.0 mol/L. Formate ion reacted with hydroxyl radical and then with $\cdot O_2$ to form $\cdot O_2^-$ radical, which doubled the efficiency of $\cdot O_2^-$ generation and enhanced the CL (Lin and Yamada, 1999).

Sodium azide was claimed to be a quencher of singlet oxygen (Reaction (11)) (Lunar et al., 2000). When sodium azide at the concentration of 1.0×10^{-3} to 0.1 mol/L was added into the system, the CL intensity decreased greatly (Wang et al., 2007).

$$N_3^- + {}^1O_2 \longrightarrow N_3^- + {}^3O_2 \quad (11)$$

The iron ions are the center of Fenton's reaction. Many ligands such as PO_4^{3-} and malonic acid were added into

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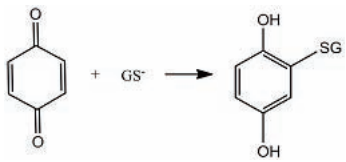
the reaction. Both of them showed a significant effect on the CL reaction.

2.6 Effect of MCLA and GSH on CL intensity

MCLA was chosen as a probe for superoxide anion, due to its high sensitivity towards superoxide anions under neutral and acidic conditions (Hosaka et al., 1999). The CL intensity increased with the concentration of MCLA, which indicated the presence of superoxide anion in the system.

Quinones are reported to undergo 1,4-reductive addition by SH-containing compounds (Reaction (12)). Brunmark had found that glutathione had a quenching effect on the photoemission resulting from the reaction of H_2O_2 and *para*-benzoquinone (Brunmark, 1989; Brunmark and Cadenas, 1987). When the concentration of glutathione increased to 1.0×10^{-2} mol/L, the CL peak was decreased. It could be postulated that the peak resulting from the excited states of quinone was affected by the addition of glutathione, which indicated the generation of excited quinine-like intermediates in the system H_2O_2-Fe^{2+}-*ortho*-chlorophenol.



(12)

2.7 ESR-spin trapping method

In order to check for the presence of hydroxyl radical, the ESR method was performed. DMPO reacts with free radicals at its double bond and converts to DMPO-radical adducts with hyperfine splitting (Kim and Metcalfe, 2007; Cheng et al., 2003). As shown in Fig. 4A, when DMPO was added to the system Fe^{2+}-H_2O_2-*ortho*-chlorophenol, the ESR spectra showed a four-line signal, with a peak ratio of 1:2:2:1 and hyperfine coupling constant (α_N = 15.0 G, α_H =15.0 G), which was well-matched with the spectrum of the DMPO-OH adduct.

For the detection of singlet oxygen, an indirect method by ESR spin-trapping with TEMP was employed. 2,2,6,6-tetramethyl-4-piperidone can react with singlet oxygen to give the adduct 4-oxo-TEMPO (Lion et al., 1976). TEMP mixing with Fe^{2+}-H_2O_2 resulted in an ESR spectrum presenting a three-line signal, which was well in accordance with the spectrum of 4-oxo-TEMPO (Fig. 4B). The three-line signal for the system Fe^{2+}-H_2O_2-*ortho*-chlorophenol showed that a lower concentration of singlet oxygen was produced (Fig. 4B) in the presence of *ortho*-chlorophenol. This could be due to the consumption of hydroxyl radical in the process of the formation of hydroquinone. The enhanced CL intensity for *ortho*-chlorophenol was due to the excited quinone.

2.8 Investigation of CL reaction products by GC-MS

The degradation products were characterized with GC coupled to MS to further investigate the CL reaction. Intermediate compounds, including 2-chloro-1,4-benzoquinone,

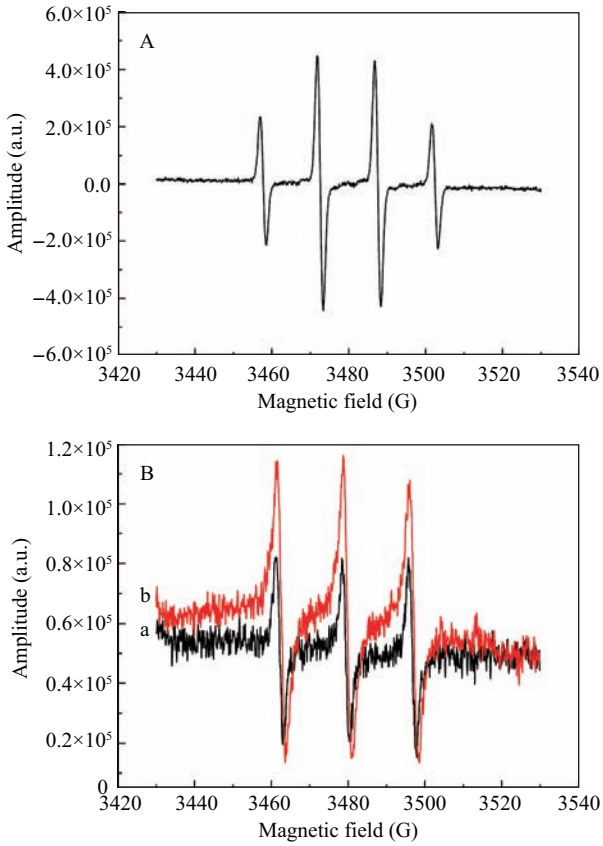


Fig. 4 (A) ESR spectrum of DMPO/·OH produced by mixing DMPO with Fe^{2+}-H_2O_2-*ortho*-chlorophenol; (B) ESR spectrum of TEMP/$^1O_2$ produced by mixing TEMP with and Fe^{2+}-H_2O_2-*ortho*-chlorophenol (a) and Fe^{2+}-H_2O_2 (b). Reactions were carried out at room temperature in phosphate buffer (0.1 mol/L, pH 7.0). The reaction mixture contained 2.5×10^{-2} mol/L DMPO, 2.5×10^{-3} mol/L Fe^{2+}, 0.25 mol/L H_2O_2 and 2.5×10^{-4} mol/L *ortho*-chlorophenol.

2-chlorobenzene-1,4-diol and 3-chlorobenzene-1,2-diol, were found in the reaction processes (Fig. 5). Although –OH group and –Cl groups are both *ortho* and *para* orientation in *ortho*-chlorophenol, the substitution depends on the orienting power of the –OH group due to its predominant role. Hence, the main substituted products were 2-chlorobenzene-1,4-diol and 3-chlorobenzene-1,2-diol. The detected compounds have been reported to

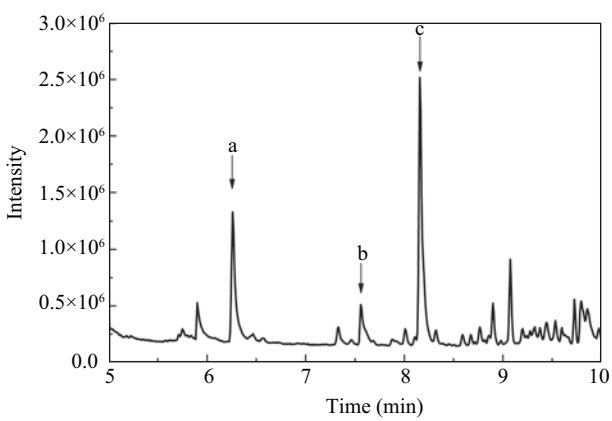


Fig. 5 GC chromatogram of the GC-MS determination of the degraded intermediates in the Fenton's oxidation of *ortho*-chlorophenol. Peak a: 2-chloro-1,4-benzoquinone; Peak b: 2-chlorobenzene-1,4-diol; Peak c: 3-chlorobenzene-1,2-diol.

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be involved in the redox cycle of iron (Chen and Pignatello, 1997; Duesterberg and Waite, 2007; Iwahashi et al., 1989). With oxidation by ferric ion and hydroxyl radical, 2-chlorobenzene-1,4-diol converted to 2-chloro-1,4-benzoquinone (Chen and Pignatello, 1997). 3-Chlorobenzene-1,2-diol was not changed to 3-chloro-1,2-benzoquinone. This might be due to its low concentration or its short lifetime.

2.9 Investigation of *ortho*-chlorophenol degradation by fluorescence spectrophotometry and CL emission spectra

The fluorescence method was utilized to monitor the degradation of *ortho*-chlorophenol under the Fenton's reagent treatment. The maximum excitation and emission wavelength of *ortho*-chlorophenol was 251 and 302 nm, respectively. The mixing of ferrous solution and *ortho*-chlorophenol resulted in little change in the fluorescence intensities of *ortho*-chlorophenol. With the injection of H_2O_2 into the mixture of *ortho*-chlorophenol and ferrous solution, the fluorescence intensities reduced with increasing mixing time, which strongly demonstrated the degradation of *ortho*-chlorophenol under the oxidation of Fenton's reagent (Fig. 6).

The CL spectrum of the system was also examined using fluorescence spectrophotometry to investigate the CL-emitting species. The emission spectrum of the system is characterized by a broad band at 480–540 nm centered around 500 nm, which is presumed to arise from electronically excited quinone and singlet oxygen (Brunmark and Cadenas, 1987; Lin and Yamada, 1999). The presence of rhodamine 6G in the system H_2O_2-Fe^{2+}-*ortho*-chlorophenol caused the maximum emission wavelength to shift from 500 to 555 nm, which was the maximum emitting wavelength for rhodamine 6G (Fig. 7, line b). The CL intensity located around 500 nm was reduced, which strongly demonstrated energy transfer from an excited intermediate that was a weak emitter to a fluorescent compound with a high quantum yield (Magde et al., 1999).

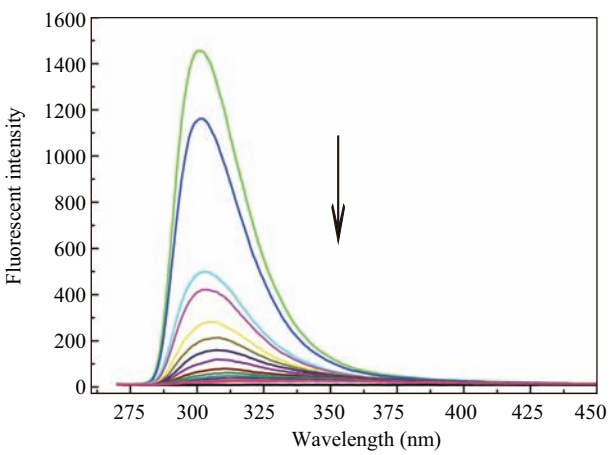

Fig. 6 Degradation of *ortho*-chlorophenol investigated by fluorescence spectrum with increasing time (along arrow direction). *Ortho*-chlorophenol, 3.5×10^{-5} mol/L; Fe^{2+}, 2.5×10^{-4} mol/L; H_2O_2, 1.0×10^{-4} mol/L.

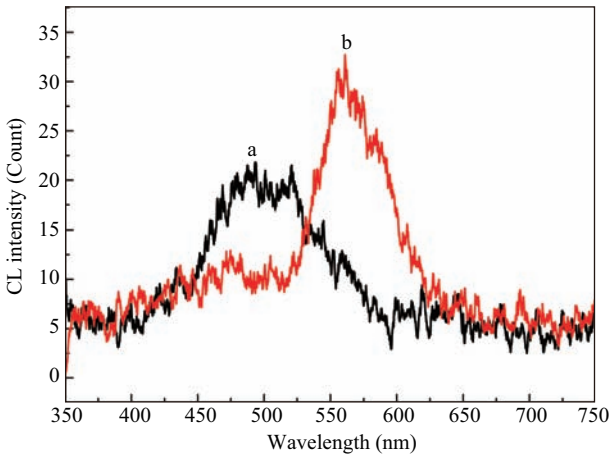

Fig. 7 CL spectrum distribution for the system H_2O_2-Fe^{2+}-*ortho*-chlorophenol (a) and the system H_2O_2-Fe^{2+}-*ortho*-chlorophenol-rhodamine 6G (b). *ortho*-chlorophenol, 1.0×10^{-3} mol/L; Fe^{2+}, 1.0×10^{-2} mol/L; H_2O_2, 1 mol/L; rhodamine 6G, 1.0×10^{-4} mol/L.

2.10 Possible mechanism for CL reaction

Based on the above results, the mechanism of the CL emission for the system H_2O_2-Fe^{2+} with and without *ortho*-chlorophenol is presented in Fig. 8. The mixing of H_2O_2 and ferrous solution generated hydroxyl radical (Reaction (1)), which reacted with Fe^{3+} to produce HO_2 (Reaction (2)). $HO_2\cdot$ decomposed to $\cdot O_2^-$. The $\cdot O_2^-$ interacted with hydroxyl radical or $HO_2\cdot$ to produce singlet oxygen, which was one of the CL emitters during the CL reaction (Reactions (5) and (6)). Singlet oxygen was also produced from the combination of $HO_2\cdot$ (Reaction (7)). Investigation of the effects of different radical scavengers (thiourea, formate, sodium azide) on the CL system indicated that hydroxyl radical, singlet oxygen and superoxide anion were involved in the CL reaction. The ESR spectra further confirmed the presence of hydroxyl radical and singlet oxygen in the system H_2O_2-Fe^{2+}.

Cationic surfactants, such as DTAB, MTAB, CTAB, CTAC, and DDDAB enhanced the CL signal to some extent. This could be explained by the fact that the $\cdot O_2^-$ was concentrated around the positive micelle surface, which was beneficial for the formation of singlet oxygen, leading to stronger CL intensity. Furthermore, micelles might provide a protected environment for the exited singlet state. The 56-fold enhancement effect of MCLA on the CL intensity confirmed the participation of superoxide anion in the CL reaction.

The reaction between *p*-benzoquinone and H_2O_2 yielded excited triplet 2-hydroxy-*p*-benzoquinone, the decay of which was accompanied by photo-emission. A similar process is involved in the oxidation of semiquinone by hydroxyl radical leading to the formation of the electronically excited quinone (He et al., 2006; Lasovsky et al., 2007). Hence, the reason for the enhanced CL of the H_2O_2-Fe^{2+} system with *ortho*-chlorophenol was the formation of electronically excited quinone (Reaction (10) in Fig. 8). The decay of the excited triplet quinone to the ground state was accompanied by photoemission with maximal intensity at 480–540 nm, which is in accordance with the CL distribution spectrum for the system H_2O_2-Fe^{2+}-*ortho*-

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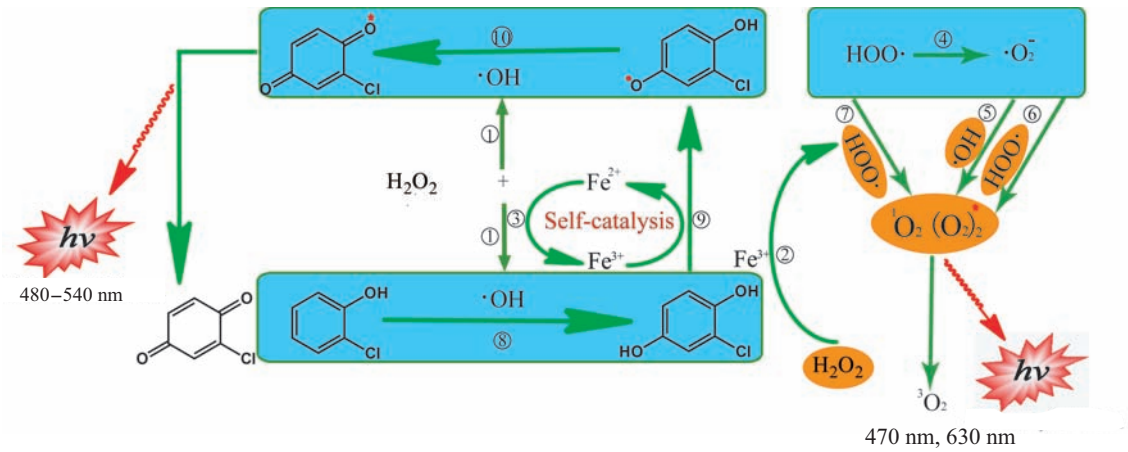

Fig. 8 A possible mechanism for the self-catalyzed CL of *ortho*-chlorophenol with the oxidation of Fenton's reagent.

chlorophenol centered at 500 nm (Khan and Kasha, 1970).

3 Conclusions

ortho-Chlorophenol has an enhancement effect on the CL arising from the mixture of ferrous ion and hydrogen peroxide. The effect of free radical scavengers demonstrated the presence of hydroxyl radical and electronically excited quinone. ESR spectrum results confirmed the presence of hydroxyl radical and singlet oxygen in both systems. The CL spectrum and the reaction product determination demonstrated that both singlet oxygen and electronically excited quinone were the main emitters of the system H_2O_2-Fe^{2+}-*ortho*-chlorophenol. The CL method is an interesting approach for the investigation of the oxidation of *ortho*-chlorophenol by Fenton' reagent. Research on the application of the CL method is in progress in our laboratory.

Acknowledgments

This work was supported by the National Key Technology R & D Program of China (No. 2007AA09210107) .

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