

Evidence against hydroxyl radical mechanism in photo-Fenton degradation of *p*-chlorophenol

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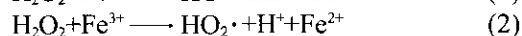
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Abstract: This paper provides evidence for the degradation of organic pollutant by the photo-Fenton complex mechanism. Both the complex oxidation and HO· oxidation mechanisms were verified by *p*-chlorophenol degradation, UV/Vis spectra analysis, and quantum yield. The hydroxyl radical involved in the photo-Fenton process can also be generated from the decomposition of H₂O₂, photolysis of Fe³⁺ and degradation of hydrated Fe(IV)-complex, excepting the traditional Fenton reaction.

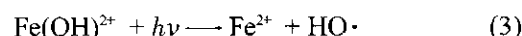
Keywords: photo-Fenton; *p*-chlorophenol; mechanism

Introduction

Advanced oxidation processes(AOPs) such as the Fenton process and photo-Fenton process have gained widespread attention for the treatment of various industrial wastewaters (Arslan and Balcioglu, 1999; Liao *et al.*, 2001). The high efficiency of these processes for organic pollutant degradation or mineralization is due to the generation of the hydroxyl radical(HO·), which has a high oxidation potential($E^0 = 2.80$ V) and can decompose organic compounds completely to water and carbon dioxide. In an acidic medium, the radical mechanism can be simplified as the following reactions in the Fenton process,



In the presence of UV light during the Fenton process, the photo-Fenton process forms, where the decomposition of the photo-active Fe(OH)²⁺ leads to the generation of the hydroxyl radicals and thus improves efficiency of the degradation (Sun and Pignatello, 1993).



However, even though the existence of hydroxyl radicals has been verified by spin-trapping experiments, sometimes, the radical mechanisms above still have been questioned. Such spin-trapping experiments are inconclusive because they can not rule out the existence of the nontrapped transient products. In addition, optical absorption measurements during the Fenton reaction proved the presence of complexes between Fe(III)/Fe(II) and H₂O₂ (Pignatello *et al.*, 1999; Arasasingham *et al.*, 1989). Consequently, many alternative mechanisms have been proposed (Kremer, 1985; Pignatello *et al.*, 1999; Bossmann *et al.*, 1998), among which an alternative mechanism has been established that complexes of Fe(II)/Fe(III) with organic ligands may react with per-

oxide or other oxidants to form the high-valent ferryl-ion. With the degradation of hydrated higher-valent iron-species, hydroxyl radicals can be generated concurrently as shown in the Equation (4):



This mechanism was also documented by our previous work of photo-Fenton degradation of ethanol and PVA, where hydroxyl radicals were deemed to be generated from split decomposition of H₂O₂, photolysis of Fe³⁺, and degradation of hydrated Fe(IV)-complex, but not by the traditional Fenton reaction (Lei *et al.*, 2003). Therefore, to validate such a modified mechanism, it may need to be tested with other kinds of wastewater, especially the widely present phenolic wastewater.

The object of this study was to discuss the photo-Fenton degradation mechanism using *p*-chlorophenol(PCP) as the model organic compound. PCP was chosen as the target pollutant because it is used widely as a preservative agent, a synthesis intermediate or as a raw material in many manufacturing processes. As a toxic and marginally biodegradable compound, it is difficult yet important to remove from the environment (Pera-Titus *et al.*, 2004).

1 Experimental

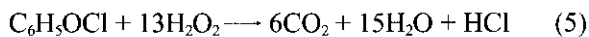
1.1 Materials

p-Chlorophenol, FeSO₄·7H₂O, FeCl₃·6H₂O, H₂O₂, H₂SO₄, NaOH, 1, 10-phenanthroline acetonitrile and potassium titanium(IV) oxalate were all analytical grade. Catalase was purchased from Worthington. Double-distilled quality water was used and all other chemicals were ACS grade.

1.2 Photoreactor and photodegradation procedure

All photodegradation experiments were carried out in a batch reactor, as shown in Fig.1. It consisted of a reservoir ($V=1.00$ L), and a flow-through annular

photoreactor ($V=0.30\text{ L}$) equipped with a mercury medium pressure lamp (Philips, GGZ 300) and a quartz filter. The initial concentration of chlorophenol solution was 125 mg/L , and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added into the solution before pH adjustment by concentrated H_2SO_4 . The stoichiometric amount of $\text{H}_2\text{O}_2 (Q_{th})$ required for total oxidation of phenol was calculated according to Equation (5).



The solution (1.0 L) was recirculated (5 L/h) by a pump (Masterflex), using cooling water at a constant temperature of 20°C . The *p*-chlorophenol solution was continuously purged in the reservoir with air throughout the degradation. At fixed intervals, samples were taken to measure residual phenol and chemical oxygen demand (COD). Residual H_2O_2 was consumed by the enzyme catalase to prevent interference with COD analysis.

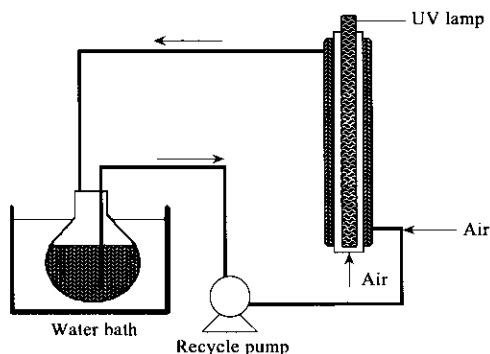


Fig.1 Photochemical batch reactor

1.3 Analytical methods

UV/Vis (8500 spectrophotometer, Techcomp) was used to measure the spectra of PCP solutions. Residual phenols and H_2O_2 concentration was determined with the 4-aminoantipyrine method and the potassium titanium(IV) oxalate method (Sellers, 1980).

COD analysis was carried out using a titrimetric method. Analysis of ferrous irons was conducted by the modified 1,10-phenanthroline colorimetric method at 510 nm .

2 Results and discussion

2.1 PCP degradation at reduced H_2O_2 addition

The effect of hydrogen peroxide on chlorophenol removal is shown in Fig.2. Although the PCP degradation rate increased with additional hydrogen peroxide, the difference was not significant. More than 90% of the chlorophenol could be decomposed within 2 min even under the addition of $0.25\text{ }Q_{th}\text{ H}_2\text{O}_2$. The chlorophenol degradation rate reached 97% within 5 min at the hydrogen peroxide addition of $0.5\text{ }Q_{th}$ and $1.0\text{ }Q_{th}$. This ensured that high degradation efficiency was obtained at the addition of less than $1.0\text{ }Q_{th}$

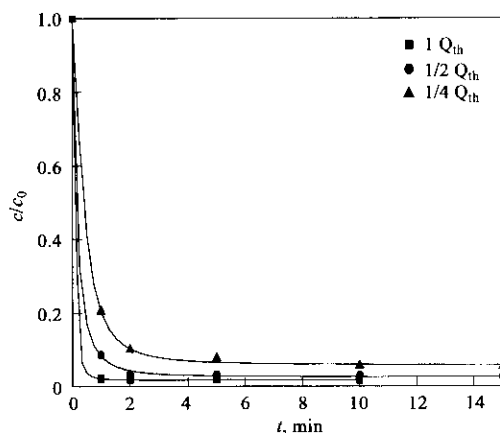


Fig.2 Effect of H_2O_2 on the degradation of *p*-chlorophenol

hydrogen peroxide.

Fig.3 shows *p*-chlorophenol degradation under reduced hydrogen peroxide addition. It was observed that the final removal of chlorophenol was less than 50% in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ process. However, with the assistance of UV radiation, the decomposition ratio of *p*-chlorophenol in the $\text{UV}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ process was almost the same as that in the photo-Fenton reaction, reaching around 90%. *p*-Chlorophenol degradation percentage in the $\text{UV}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ process was much high than that of the individual UV and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ degradation processes before 10 min, indicating synergetic effects existing in the photo-Fenton process.

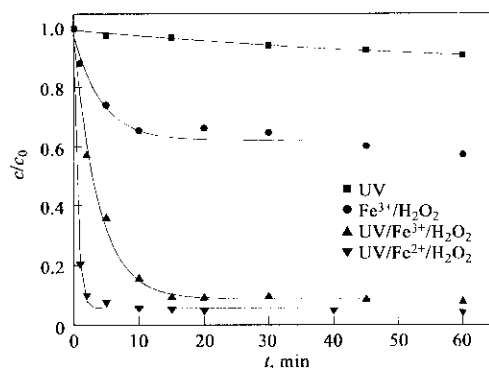


Fig.3 Degradation of *p*-chlorophenol
Conditions: $\text{H}_2\text{O}_2\text{ }0.25\text{ }Q_{th}$; $\text{Fe}^{2+}(\text{Fe}^{3+}) : \text{H}_2\text{O}_2 = 1:20$; 20°C ; $\text{pH } 3$

In UV-Fenton process, the intermediates were found to be hydroquinone and benzoquinone, which showed the existence of the traditional free radical mechanism. However, some phenomena involved in the photo-Fenton process were found not be explained by the classical hydroxyl radical mechanism.

2.2 PCP degradation at H_2O_2 addition twice

In order to investigate the mechanism of the Fenton reaction, the same dosages of *p*-chlorophenol and hydrogen peroxide were added 20—30 min later into the solution for the second time after the decomposition of the first batch of chlorophenol by photo-Fenton. The results of the different processes

are shown in Fig.4. Surprisingly that *p*-chlorophenol degradation rate for the second run was almost as fast as the first run in the UV/Fenton reaction. Based on the free radical mechanism, Fe(II) would have been converted to Fe(III) completely after the Fenton reaction was finished and thus the Fe(II) concentration would be low. Therefore, when hydrogen peroxide was introduced into the solution for the second time, the reaction would be similar to that of the Fenton-like reaction ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$). According to the results showed in Fig.3, *p*-chlorophenol degradation rate in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ would be much slower than that in $\text{UV}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$, and the final degradation content would be smaller than half of the value in $\text{UV}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$. This fact is inconsistent with the classical hydroxyl radical mechanism, indicating that another mechanism should also be acting in the process. The phenomenon also implied that Fe(III) would be transformed into Fe(II) quickly with UV radiation and H_2O_2 addition, because

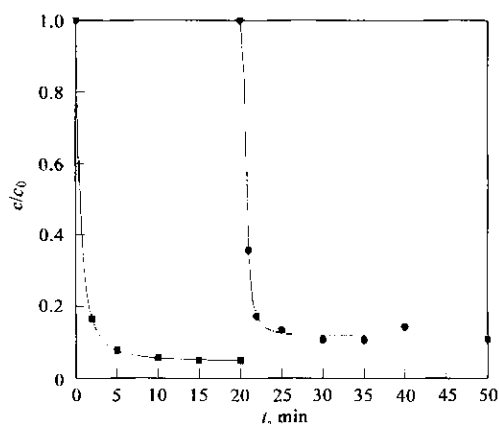


Fig.4 Degradation of PCP with 4-CP and H_2O_2 added twice
Conditions: H_2O_2 0.25 Q_{00} ; Fe^{3+} (Fe^{II}) : H_2O_2 = 1:20; 20°C; pH 3

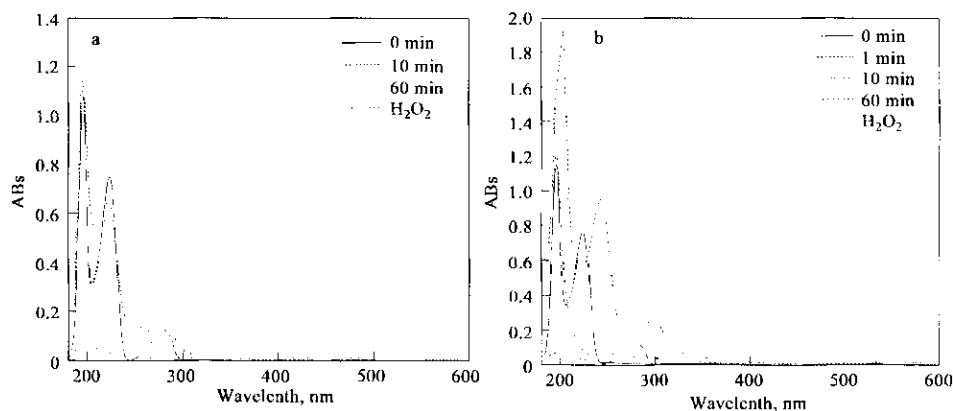


Fig.5 UV-spectra of *p*-chlorophenol degradation by $\text{UV}/\text{H}_2\text{O}_2$ (a) and photo-Fenton(b)
Conditions: a. H_2O_2 0.25 Q_{00} , 4-CP of 125 mg/L; b. H_2O_2 0.25 Q_{00} , 4-CP of 125 mg/L, Fe^{3+} : H_2O_2 (1:20)

henol were irradiated by UV. This indicated that the complex is associated with hydrogen peroxide. This observation agrees with the complex reaction as shown in Eq. (4), in which the hydroxyl radical was generated to decompose *p*-chlorophenol. Photolysis of

the rate of Fenton-like reaction was usually slower than that of the Fenton reaction.

2.3 Comparison of UV/Vis spectra between photo-Fenton and $\text{UV}/\text{H}_2\text{O}_2$

To support the complex mechanism, UV/Vis spectra of the reaction mixture during the $\text{UV}/\text{H}_2\text{O}_2$ and photo-Fenton degradation of *p*-chlorophenol are shown in Fig.5. In view of the $\text{UV}/\text{H}_2\text{O}_2$ process as a typical hydroxyl radical reaction, its spectra change in *p*-chlorophenol degradation was investigated for comparison with that of photo-Fenton process. As shown in Fig.5a, the addition of H_2O_2 in *p*-chlorophenol solution did not change the spectral character peak of *p*-chlorophenol at 196 nm, 224 nm, or 279 nm. No complex with high absorbance was formed in this process. The characteristic absorption peaks at 224 nm and 279 nm gradually disappeared due to the generation of hydroxyl radical.

From the figure above, it can be deduced that the UV/Vis spectra of *p*-chlorophenol during the photo-Fenton reaction would be similar to that of the $\text{UV}/\text{H}_2\text{O}_2$ process supposing UV/Fenton process was a hydroxyl radical reaction. However, we get an unexpected result from Fig.5b. It is noteworthy that *p*-chlorophenol's characteristic absorption peaks increased compared to the results of *p*-chlorophenol degradation during the $\text{UV}/\text{H}_2\text{O}_2$ process. A bathochromic shift was also observed while the reaction was progressing. A complex was formed in this process with high absorption at the range from 180 nm to 400 nm. This observation was distinct from the degradation of *p*-chlorophenol in the $\text{UV}/\text{H}_2\text{O}_2$ process. Further experiments confirmed that no complex was found when Fe(III)/Fe(II) and *p*-chlorop-

H_2O_2 should be also existent in the photo-Fenton process, as hydroxyl radicals came from the split decomposition of hydrogen peroxide under UV radiation and decomposition of hydrated Fe(IV)-complex but not the traditional Fenton reaction.

2.4 Quantum yield

Quantum yield is an important parameter in the photochemical reaction. In the photo-Fenton reaction, the efficiency-determining step consists of the photochemical generation of Fe²⁺ or hydrated iron-complexes via electron transfer oxidation of organic ligands. In the present work, ferric oxalate was used as the chemical actinometer and the production of Fe(II) in three different photochemical systems are demonstrated in Fig.6.

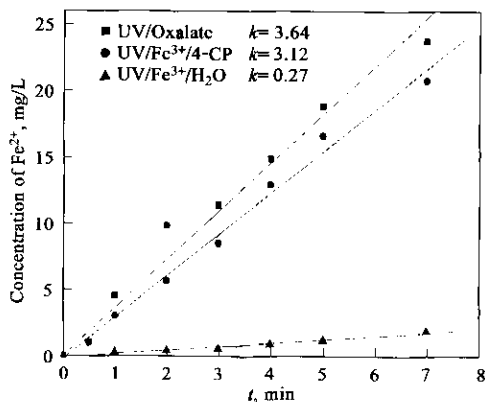


Fig.6 Concentration of Fe²⁺ generated in different systems
Conditions: Fe³⁺ 5.19 × 10⁻⁴ mol/L; 4-CP 125 mg/L; 20°C; pH 3

Table 1 shows apparent quantum yield of Fe(II) production calculated according to the standard equation used under monochromatic irradiation(Braun *et al.*, 1991).

$$\Phi(\text{Fe(II)}) = \frac{dn/dt}{P_a} \quad (6)$$

where P_a is the rate of photons absorbed, Einstein/(L · s); and dn/dt is the rate of Fe²⁺ formation, mol/(L · s).

Table 1 $\Phi(\text{Fe}^{2+})$ of Fe³⁺/H₂C₂O₄, Fe³⁺/4-CP, Fe³⁺/H₂O systems

Photolyzed system	$C_{\text{Fe}^{3+}}$, mol/L	dn/dt	$\Phi(\text{Fe}^{2+})$
Fe ³⁺ /H ₂ C ₂ O ₄	5.19×10^{-4}	3.64	1.14
Fe ³⁺ /4-CP	5.19×10^{-4}	3.12	0.977
Fe ³⁺ /H ₂ O	5.19×10^{-4}	0.27	0.085

Note: $\Phi(\text{Fe}^{2+})$ of Fe³⁺/H₂C₂O₄ system is 1.14 of standard reference (Bossmann *et al.*, 1998)

It is well known that the photolysis of the complex formed between Fe(III) and oxalate lead to a complete reduction of Fe (III) to Fe (II). As shown in Fig.6 and Table 1, the apparent quantum yield for the photo-reduction of Fe³⁺ by *p*-chlorophenol ($\Phi(\text{Fe}^{2+}) = 0.977$) was surprisingly high while that for Fe³⁺/H₂O ($\Phi(\text{Fe}^{2+}) = 0.085$) was quite low. The quantum yield results confirmed that *p*-chlorophenol, which was able to serve as a ligand in iron complexes and processed a suitable oxidation potential, could undergo an efficient inner-sphere electron transfer to the electronically excited Fe(III) leading to Fe(II) formation. Since an inner-sphere electron transfer was impossible

according to the free radical theory, the complex mechanism can be also supported thermodynamically.

3 Conclusions

The degradation of *p*-chlorophenol by the photo-Fenton mechanism in the presence of low hydrogen peroxide addition was investigated. The process exhibited synergetic effects, and high *p*-chlorophenol degradation could be achieved with only 1/4 Q_{th} H₂O₂ addition. The existence of the complex reaction was proved by UV/Vis spectra and quantum yields. *p*-Chlorophenol was most likely degraded through both a complex reaction and the traditional radical mechanism.

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