Korean J. Chem. Eng., **25**(1), 46-52 (2008)

Degradation of 2-chlorophenol by Fenton and photo-Fenton processes

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(*Received 26 April 2007 • accepted 12 June 2007*)

Abstract−The photodegradation of a specific organic pollutant using the Fenton and the photo-Fenton processes has been examined in aqueous solution. The applications of the Fenton process and the photo-Fenton process to the degradation of 2-chlorophenol (2-CP) were investigated. The dependence on the following experimental conditions had been evaluated: initial pH (1.0-9.0), hydrogen peroxide (0.67-2 mM), ferrous ions (0.1-2 mM), initial concentration of 2-CP (0.1-2 mM). The optimal experimental conditions were 1 mM H_2O_2, 1 mM ferrous ion and pH 3.0. Under the optimal conditions, the degradation efficiency of 2-CP in the photo-Fenton process was enhanced 4% more than that of the Fenton process. Experimental results about the degradation of 2-CP show that UV irradiation improves the degradation efficiency of the Fenton process. The major intermediate formed during the degradation of 2-CP was *p*-benzoquinone.

Key words: Photo-fenton, Fenton, 2-Chlorophenol, Hydrogen Peroxide, UV

INTRODUCTION

Chlorophenols, found in aqueous systems and hazardous waste sites, exhibit a considerable water solubility, strong odor and taste, and high toxicity. Industrial activities, drinking water chlorination and partial degradation of phenoxy pesticides are the contributing sources of chlorophenols. As one of chlorophenols, 2-chlorophenol (2-CP) which is widely used in paper, pulp, pesticide, and herbicide industries, is a very toxic and poorly biodegradable pollutant. Also, 2-CP is one of the EPA (Environmental Protection Agency) priority pollutants. Trace toxic by-products such as PAHs, dioxins, and furans are frequently found in the incineration of 2-CP and considered carcinogens or mutagens.

There are several treatment alternatives available for treatment of chlorophenols. The biological oxidation process is the common option due in part to its cost-effectiveness and versatility in handling a wide variety of organic pollutants. But the biological treatment is effective only in low concentrations of the organics and has the generally long retention time. Thermal destruction, for example, incineration, is another effective choice for the treatment of wastes containing high concentrations of chlorophenols. However, this process has some disadvantages in that considerable energy is required to heat and vaporize the water mass before specific organic pollutants are destroyed and it can lead to the formation of new toxic organic materials. Activated carbon adsorption and air-steam stripping can be accepted for treatment of wastes containing chlorophenols, but activated carbon adsorption produces spent carbon as a waste by-product, and air-steam stripping creates an air pollutant problem.

Therefore, it is most favorable to examine destructive technologies for the treatment of toxic organic pollutants including chlorophenols, and advanced oxidation processes (AOPs) are possible technologies.

The photo-Fenton process, usually known as one of AOPs which are designed to generate hydroxyl radicals ($HO^•$), represents an attractive alternative for treatment or pretreatment of chlorophenols. The photo-Fenton process utilizes a combination of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in the presence of UV radiation. The first step of the process is the Fenton process, represented by Eq. (1).

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH^-+OH^• \tag{1}$$

In the presence of UV radiation, the ferric ions (Fe^{3+}) produced in the Fenton process are converted back to ferrous ions (Fe^{2+}), as known in Eq. (2), with formation of an additional equivalent of hydroxyl radical.

$$Fe^{3+}+H_2O \xrightarrow{h\nu} Fe^{2+}+H^++OH^• \tag{2}$$

The hydroxyl radicals formed in these two reactions react with organic species (RH) present in the system, promoting their oxidation, as indicated in Eq. (3).

$$OH^•+RH \rightarrow H_2O+R^• \tag{3}$$

The pH of the solution has a considerable influence on the reaction rate. At pH values higher than four, iron ions precipitate out of the solution in the form of hydroxides. The optimum pH for the photo-Fenton process is typically in the range of pH 3-3.5, where $Fe(OH)^{2+}$ is the predominant iron species present in the solution.

Many researchers have studied reaction intermediates of 2-CP in AOPs. Zhou et al. [7] reported that catechol and cyclopentadienecarboxylic acid were the only identified degradation products in aqueous solution at pH 7.1. Their results agree with those reported by Boule et al. (1987) who propose that cyclopentadienecarboxylic acid was primarily obtained from the 2-CP reaction and catechol is thought to arise from a water nucleophilic displacement of chloride from the singlet excited state of 2-CP. Rao et al. [11] reported that the presence of phenol, catechol, hydroxyhydroquinone, chlorohy-

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droquinone, 2-hydroxy benzaldehyde and [1,1-biphenyl]-2,2'-diol was revealed during photocatalytic oxidation of 2-CP. Jih-Gaw and Ying [12] found seven types of intermediates (4-chloro-1,3-benzendiol; 2-chloro-5-methyl-phenol; 2-chloro-6-methyl-phenol; 4-chloro-3-methyl-phenol; 2-chloro-*p*-hydroquinone; 2-chloro-*p*-benzoquinone; and 2,6-dichloro-2,5-cyclohexadiene-1,4-dione). Among them 2-chloro-*p*-benzoquinone was the major intermediate. Several authors also noted that chlorinated benzoquinone is the major intermediate during the decomposition of chlorophenols using chemical processes. In addition, Hongsang et al. [9] reported hydrochloric acid, trichloromethane, 2-amino-1-propanol, and ethyl ester were founded as intermediates and Jacek [8] reported pyrocatechol, 2-chloro-1,4-benzoquinone, 2-chlorohydroquinone, and maleic acid were formed as by-products during 2-CP degradation.

In the present study, the degradation characteristics of 2-CP by the Fenton process and the photo-Fenton process were studied. The degradation efficiency of 2-CP in aqueous solution was investigated as a function of initial pH, Fenton reagent concentration and initial concentration of 2-CP. Also, reaction intermediates of 2-CP by Fenton process and photo-Fenton process were identified, respectively.

EXPERIMENTAL SECTION

1. Materials

2-CP was purchased from Junsei Chemical Co. (C_6H_4OHCl, ≥98.0% purity). Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, ≥99.0% purity) and hydrogen peroxide (H_2O_2, 30% purity), which were used as the source of hydroxyl radicals, were obtained from Sigma-Aldrich, Inc. and Junsei Chemical Co., respectively. Sodium nitrate ($NaNO_3$, 98.5% purity) used to control an ionic strength was purchased from Kanto Chemical Co. And nitric acid and sodium hydroxide solution, which were used to adjust the pH, were purchased from DC Chemical Co., Ltd. (HNO_3, 60% purity) and Yakuri Pure Chemicals Co., Ltd. (NaOH, ≥96% purity). Hexane used to extract 2-CP from the aqueous solution was obtained from Honeywell International Inc. (C_6H_{14}, ≥99.9% purity).

2. Experimental Procedure

The annular reactor (net volume of 1,000 mL) was an open Pyrex glass tube with double walls as shown in Fig. 1. The reactor was connected to a jacketed glass recirculation tank (volume of 1,500 mL) and fitted with a magnetic stirrer. The temperature of the solution was controlled by means of a thermostatic bath at 25 °C. The reactor was equipped with an Hg-vapor lamp (Sanko Denki Co., G15T8E, 15W power, maximum radiation at 306 nm in the range 280-360 nm) providing a radiation intensity of 8.59 $mWcm^{-2}$ (manufacturer's specification).

A solution (750 mL) containing 2-CP 3.9×10^{-4} M was introduced into the reactor. And the sodium nitrate concentration was adjusted to 5×10^{-2} M. The given amount of $FeSO_4$ solution that depended on the experimental conditions was added and well mixed with the solution before the hydrogen peroxide was added. The pH of the solution was maintained at 3.0 with nitric acid (1 M) and sodium hydroxide (1 M) and measured by the pH meter (Istek, Inc., Model 125PD). The time upon the hydrogen peroxide added was set as the reaction start time. At predetermined intervals, 5 mL samples were withdrawn from the solution and the 2-CP residues in the samples were immediately extracted with hexane.

3. Analysis

The 2-CP concentration was measured by means of GC (Agilent Technologies, 4890D), equipped with an electron capture detector (ECD) connected to an HP-5 column (J&W Scientific, 0.32 mm×30 m×0.25 μm). The carrier gas was nitrogen (N_2) with a constant flow rate and 2 μL samples were injected. 2-CP was quantitated by chromatographing standard samples of known concentrations and determining retention time and peak sizes. Intermediates of 2-CP were identified by GC-MS (Shimadzu Co., QP2010) equipped with a flame ionization detector (FID) which was connected to an AT-1000 column (Alltech, 0.32 mm×60 m×0.25 μm) and mass spectrometry.

RESULTS AND DISCUSSION

1. Preliminary Results for 2-CP Degradation

Fig. 2 shows that the evaporation has little effect on the removal of 2-CP in this experimental setup. During 120 minutes of UV ir-

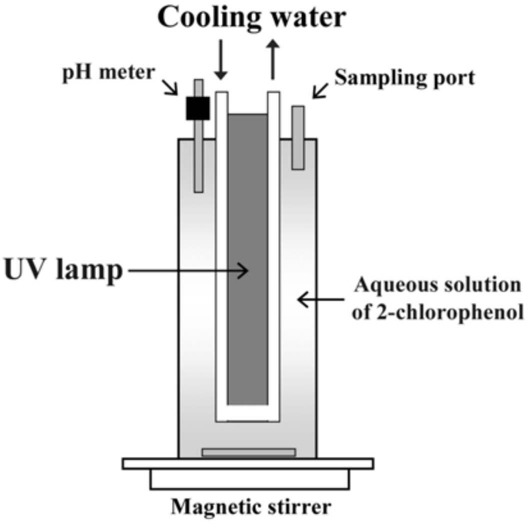

Fig. 1. Schematic diagram of reactor for the Fenton and photo-Fenton process.

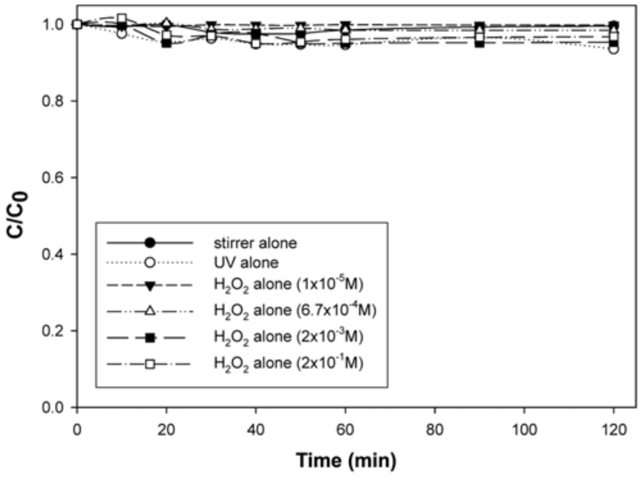

Fig. 2. Degradation of 2-CP with UV or H_2O_2 alone. Experimental conditions: $C_0=1\times10^{-3}$ M, $NaNO_3=5\times10^{-2}$ M.

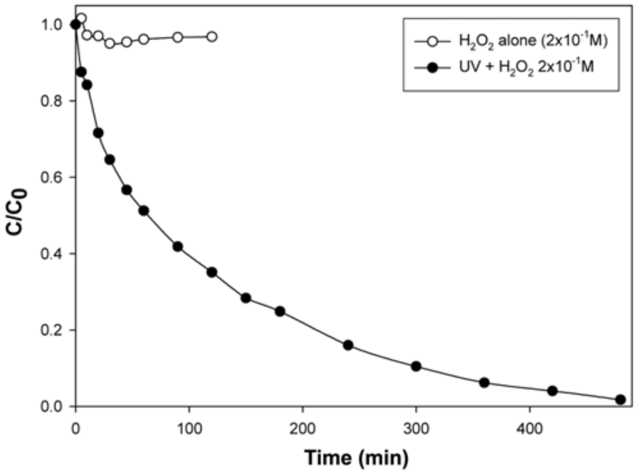

Fig. 3. Degradation of 2-CP by UV irradiation in the presence of H_2O_2. Experimental conditions: $C_0=1\times10^{-3}$ M, $NaNO_3=5\times10^{-2}$ M.

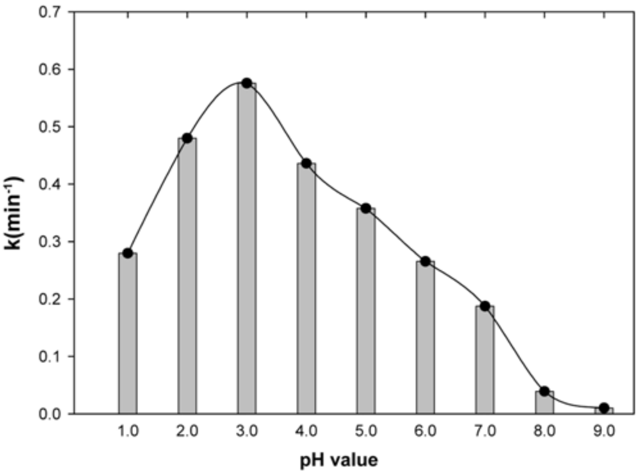

Fig. 5. Initial pH vs. rate constant (k). Experimental conditions: $C_0=1\times10^{-3}$ M, $H_2O_2=1\times10^{-3}$ M, $Fe^{2+}=1\times10^{-3}$ M, $NaNO_3=5\times10^{-2}$ M.

radiation with neither $FeSO_4$ nor H_2O_2 being added, approximately 7% of 2-CP was degraded. And little decrease in the 2-CP concentration was observed in the presence of H_2O_2 alone without UV irradiation. With the addition of 6.7×10^{-4} M, 2×10^{-3} M, and 2×10^{-1} M of H_2O_2, about 2%, 4%, and 5% of 2-CP were degraded in 60 minutes of irradiation, respectively. This indicates that H_2O_2 more than 2×10^{-3} M has negligible effect on the degradation of 2-CP.

Fig. 3 shows the effects of UV light and H_2O_2 on the degradation of 2-CP. The presence of both UV light (λ_{max}=306 nm) and H_2O_2 resulted in much larger removal of 2-CP than that of UV alone. In Fig. 3, over 65% and 98% of the initial concentrations of 2-CP were removed after 120 and 480 minutes of irradiation, respectively. With UV radiation, H_2O_2 can be degraded into hydroxyl radicals that are able to rapidly degrade the 2-CP in the water.

2. Degradation of 2-CP by the Fenton Process

The effect of initial pH on degradation of 2-CP in the Fenton process is shown in Fig. 4. The reaction rate has relatively higher values in the range of about 2.5 to 3.0 and rapidly decreases as pH becomes greater than 3.0, as shown in Fig. 5. In the basic condition (pH>8.0), 2-CP was little degraded by the Fenton process. It is reported that Fe^{2+} converts to Fe^{3+} at high pH values and then precipitates. As a result, it leads to the inhibition of the Fenton process. Among different values of pH chosen from 1.0 to 9.0, the largest removal efficiency of 2-CP was observed at pH 3.0. The optimum pH value agrees with other studies about the oxidation of various organic compounds. Sedlek and Andren (1991) reported the effect of initial pH on degradation of 2-CP in the Fenton process was explained by the formation of organometallic Complexes, which is favorable in the pH range of 2.0 to 4.0.

Fig. 6 shows the effect of the H_2O_2 concentration on degradation of 2-CP in the Fenton process. About 81.7% and 89.8% of 2-CP removal efficiencies were achieved when the H_2O_2 concentrations were 6.7×10^{-4} M and 1×10^{-3} M, respectively. The degradation efficiency of 2-CP increased with increasing of H_2O_2 dosage and reached

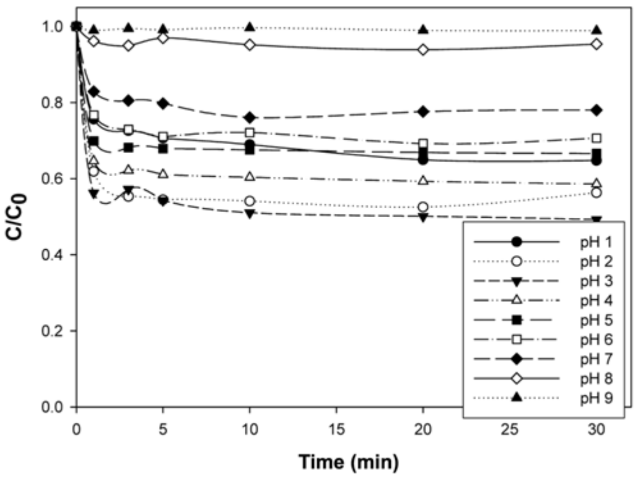

Fig. 4. Effect of the initial pH on degradation of 2-CP in the Fenton process. Experimental conditions: $C_0=1\times10^{-3}$ M, $H_2O_2=1\times10^{-3}$ M, $Fe^{2+}=1\times10^{-3}$ M, $NaNO_3=5\times10^{-2}$ M.

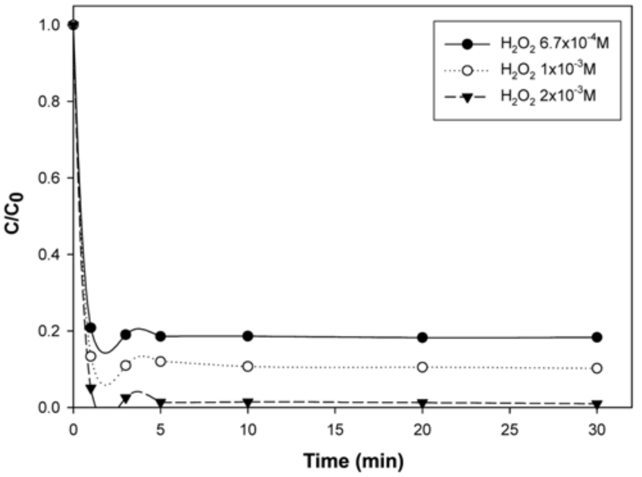

Fig. 6. Effect of the H_2O_2 concentration on degradation of 2-CP in the Fenton process. Experimental conditions: $C_0=3.9\times10^{-4}$ M, $Fe^{2+}=1\times10^{-3}$ M, pH=3.0, $NaNO_3=5\times10^{-2}$ M.

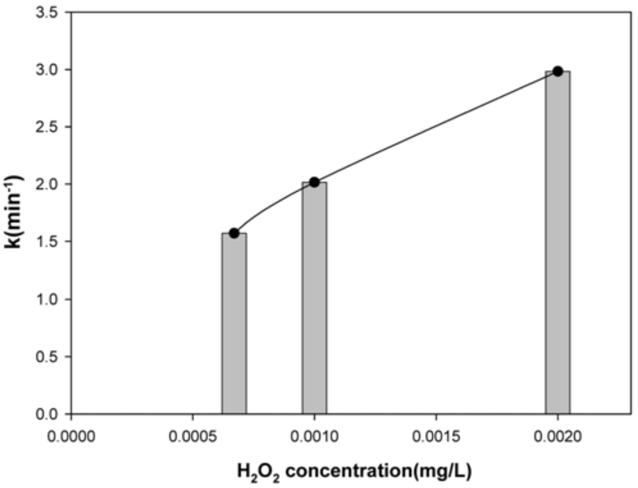

Fig. 7. H_2O_2 concentration vs. rate constant (k). Experimental conditions: C_0=3.9×10^{-4} M, Fe^{2+}=1×10^{-3} M, pH=3.0, $NaNO_3$=5×10^{-2} M.

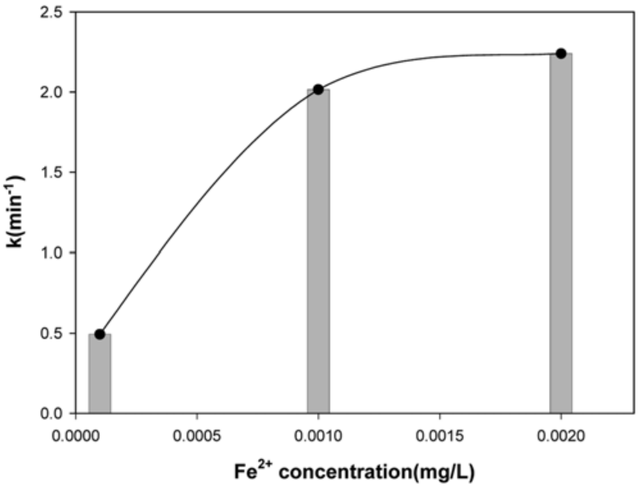

Fig. 9. Fe^{2+} concentration vs. rate constant (k). Experimental conditions: C_0=3.9×10^{-4} M, H_2O_2=1×10^{-3} M, pH=3.0, $NaNO_3$=5×10^{-2} M.

99.8% at H_2O_2 2×10^{-3} M. More addition of H_2O_2 produced more OH radicals and caused more 2-CP degradation following the reaction (Eq. (1)) mentioned before. The degradation efficiency of 2-CP did not increase further when the H_2O_2 concentration was above 2×10^{-3} M. This appears to due to the decomposition of H_2O_2 and the recombination of OH radicals at the high concentrations of H_2O_2. Furthermore, H_2O_2 can react with OH radicals as a scavenger. The optimal concentration of H_2O_2 for the degradation of 2-CP in the Fenton process was considered as 1×10^{-3} M. Fig. 7 shows the reaction rate rapidly increases with increasing of H_2O_2 concentration in the range of 6.7×10^{-4} M to 2×10^{-3} M.

In order to find the optimal amount of $FeSO_4 \cdot 7H_2O$ added in the solution, a set of tests was performed. Fig. 8 illustrates the degradation of 2-CP at pH 3 as a function of the ferrous ion concentration. About 42.8% of 2-CP was degraded when the ferrous ion concentration was 1×10^{-4} M. The degradation efficiency of 2-CP increased to 89.8% when ferrous ion 1×10^{-3} M was added. Increasing the ferrous ion concentration to 2×10^{-3} M had little effect on the degradation efficiency. The desirable concentration of ferrous ion in this study was chosen as 1×10^{-3} M. Fig. 9 shows the reaction rate rapidly increases with increasing of Fe^{2+} concentration in the range of 1×10^{-4} M to 1×10^{-3} M, then slightly increases beyond 1×10^{-3} M of Fe^{2+} concentration.

Fig. 10 shows the Fenton reaction of 2-CP under various initial concentrations of 2-CP at pH 3. At 2-CP 1×10^{-4} M, the oxidation led to more than 99.6% of the degradation efficiency of 2-CP after 5 minutes of oxidation and 89.8% of 2-CP had been degraded at 2-CP 3.9×10^{-4} M, whereas 50.8% and 24.7% of 2-CP had been degraded at 1×10^{-3} M and 2×10^{-3} M of 2-CP after the same time of oxidation, respectively. The degradation efficiency decreased with increasing of the initial concentration of 2-CP. Though the Fenton reaction of 2-CP appears to follow the first-order kinetics, the reac-

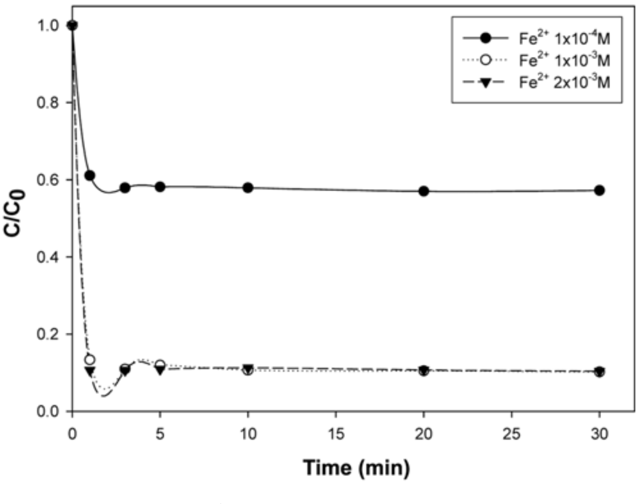

Fig. 8. Effect of the Fe^{2+} concentration on degradation of 2-CP in the Fenton process. Experimental conditions: C_0=3.9×10^{-4} M, H_2O_2=1×10^{-3} M, pH=3.0, $NaNO_3$=5×10^{-2} M.

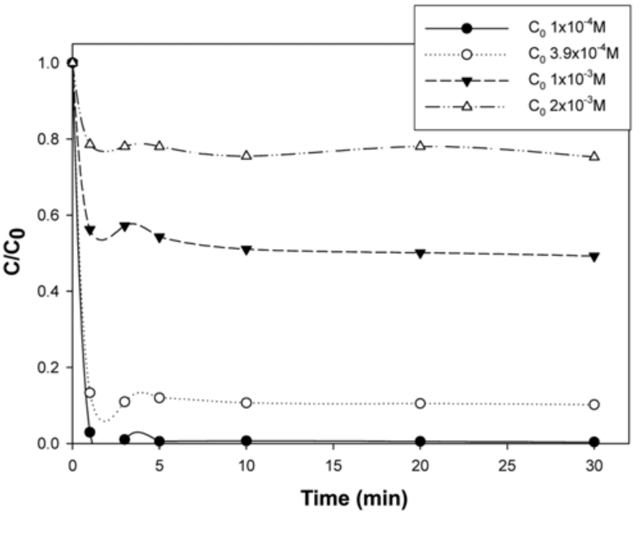

Fig. 10. Effect of the initial concentration of 2-CP on degradation of 2-CP in the Fenton process. Experimental conditions: H_2O_2=1×10^{-3} M, Fe^{2+}=1×10^{-3} M, pH=3.0, $NaNO_3$=5×10^{-2} M.

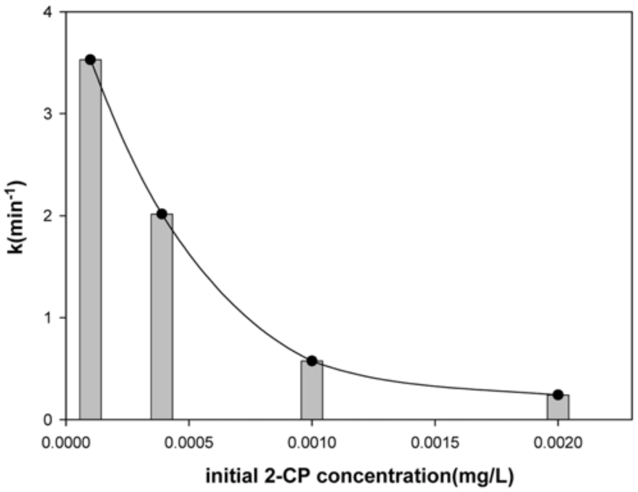

Fig. 11. Initial 2-CP concentration vs. rate constant (k). Experimental conditions: H_2O_2=1×10^{-3} M, Fe^{2+}=1×10^{-3} M, pH=3.0, $NaNO_3$=5×10^{-2} M.

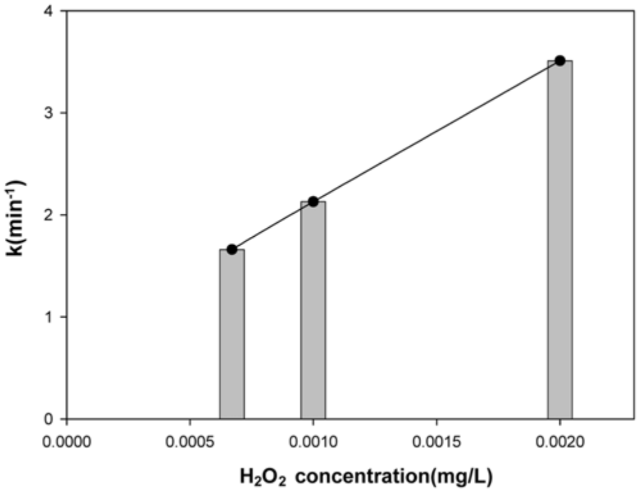

Fig. 13. H_2O_2 concentration vs. rate constant (k) in the photo-Fenton process. Experimental conditions: C_0=3.9×10^{-4} M, Fe^{2+}=1×10^{-3} M, pH=3.0, $NaNO_3$=5×10^{-2} M.

tion rate was found to be dependent on the initial concentration of 2-CP (Fig. 11). Because all steps of the 2-CP reaction have been taken to be first-order, with the definition of k, the reaction rate is written as the following Eq. (4).

$$\frac{dC}{dt} = -k\cdot C \tag{4}$$

Eq. (4) can be solved analytically and the solution substituted in the following equation.

$$C = C_O\cdot e^{-kt} \tag{5}$$

The first-order rate constant rapidly decreases from 3.53 min^{-1} to 0.58 min^{-1} in the range of 1×10^{-4} M to 1×10^{-3} M of 2-CP concentration, then slightly decreases beyond 1×10^{-3} M of 2-CP concentration.

3. Degradation of 2-CP by the Photo-Fenton Process

The photo-Fenton process was compared with the Fenton process. Fig. 12 shows the effect of the H_2O_2 concentration on degradation of 2-CP in the photo-Fenton process. Approximately 86.7% and 92.0% of 2-CP removal efficiencies were achieved when the H_2O_2 concentrations were 6.7×10^{-4} M and 1×10^{-3} M, respectively. The degradation efficiency of 2-CP increased with increasing of H_2O_2 and reached 99.0% when the H_2O_2 concentration increased to 2×10^{-3} M.

Fig. 13 shows the rate constant rapidly increases from 1.66 min^{-1} to 3.51 min^{-1} in the range of 6.7×10^{-4} M to 2×10^{-3} M of H_2O_2 concentration. These values were higher than those in the Fenton process.

Fig. 14 shows the photo-Fenton reaction of 2-CP under various initial concentrations of 2-CP at pH 3. When the initial concentration of 2-CP was 1×10^{-4} M, more than 99.8% of 2-CP was degraded after 5 minutes of reaction time and 92.7% of 2-CP had been degraded at 2-CP 3.9×10^{-4} M, whereas only 53.6% and 28.1% of 2-

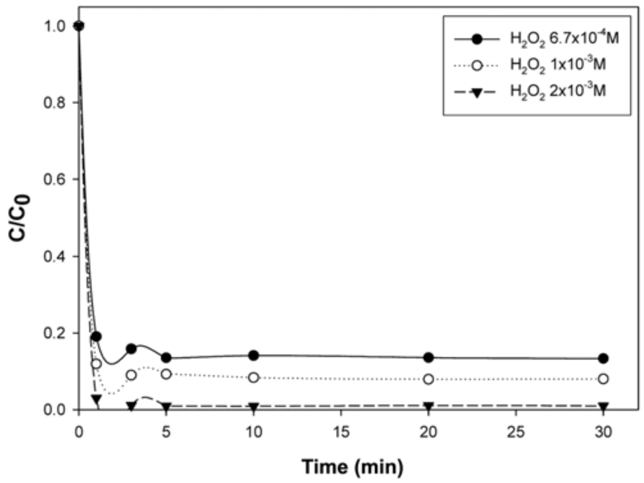

Fig. 12. Effect of the H_2O_2 concentration on degradation of 2-CP in the photo-Fenton process. Experimental conditions: C_0=3.9×10^{-4} M, Fe^{2+}=1×10^{-3} M, pH=3.0, $NaNO_3$=5×10^{-2} M.

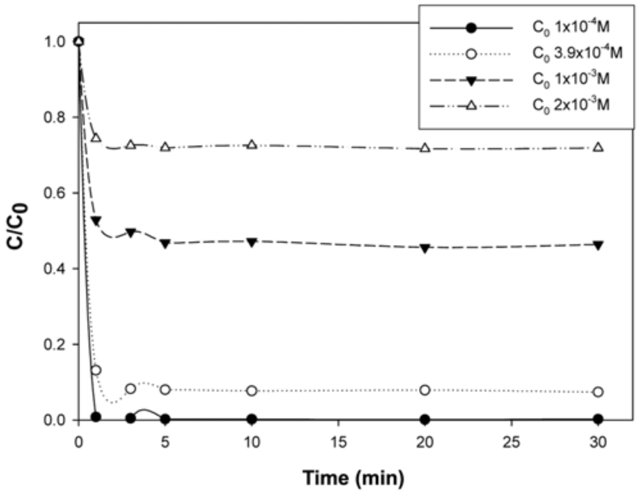

Fig. 14. Effect of the initial concentration of 2-CP on degradation of 2-CP in the photo-Fenton process. Experimental conditions: H_2O_2=1×10^{-3} M, Fe^{2+}=1×10^{-3} M, pH=3.0, $NaNO_3$=5×10^{-2} M.

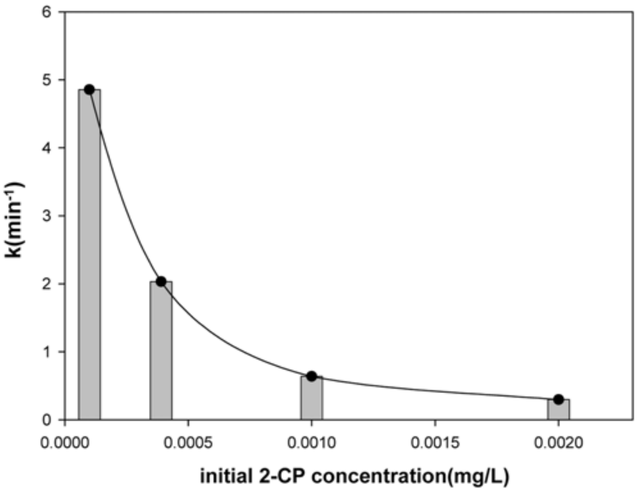

Fig. 15. Initial 2-CP concentration vs. rate constant (k) in the photo-Fenton process. Experimental conditions: $H_2O_2=1\times10^{-3}$ M, $Fe^{2+}=1\times10^{-3}$ M, pH=3.0, $NaNO_3=5\times10^{-2}$ M.

CP had been removed at 1×10^{-3} M and 2×10^{-3} M of 2-CP after the same time of reaction, respectively. The degradation efficiency decreased with increasing of the initial concentration of 2-CP as the results by the Fenton process, and the degradation efficiency of 2-CP in the photo-Fenton process was enhanced more 4% than that of the Fenton process. Fig. 15 shows the rate constant rapidly decreases from 4.85 min^{-1} to 0.64 min^{-1} in the range of 1×10^{-4} M to 1×10^{-3} M, then slightly decreases beyond 1×10^{-3} M of 2-CP concentration. As initial concentration of 2-CP increases, the reaction rate in the photo-Fenton process has higher values, even though the decreasing trend of 2-CP reaction rate in the photo-Fenton process is similar to that in the Fenton process under the same experimental conditions.

4. Identification of Reaction Intermediates

Fig. 16 shows gas chromatogram from GC/MS analysis of the 2-CP reaction products. Under the experimental conditions, three reaction intermediates were found: 3-hydroxy propionic acid, *p*-benzoquinone, and malonic acid. Among them the major intermediates was *p*-benzoquinone.

This analysis of reaction intermediates leads to the proposed reaction pathways describing the Fenton reaction of 2-CP in aqueous solution. Fig. 17 shows one of the possible reaction pathways involving hydroxyl radicals. The Fenton reaction is brought about by hydroxyl radicals, which can react with the organic species in the solution. The hydroxyl phenyl radical is generated by the abstraction of a Cl^{-}, leading to a peroxy radical which can disproportionate to hydroquinone and *p*-benzoquinone. The hydroxyl phenyl radical reacts with a hydroxyl radical, then is converted to 1,2-benzenediol. The next reactions lead to formation of oxylated products such as *p*-benzoquinone. The subsequent cleavage of the *p*-benzoquinone results in the formation of 3-hydroxy propionic acid which further oxidizes into malonic acid. The malonic acid is then converted to acetic acid and carbon dioxide as the end products.

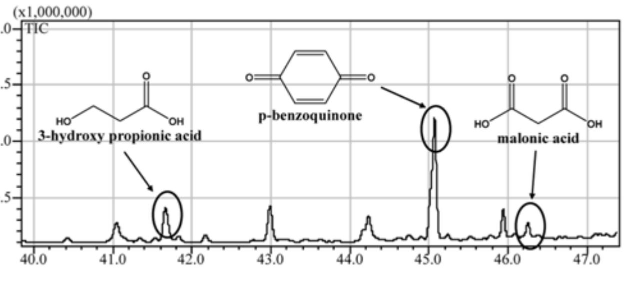

Fig. 16. Gas chromatogram from GC/MS analysis of the 2-CP reaction products. Experimental conditions: $C_0=3.9\times10^{-4}$ M, $H_2O_2=\times10^{-3}$ M, $Fe^{2+}=1\times10^{-3}$ M, pH=3.0, $NaNO_3=5\times10^{-2}$ M.

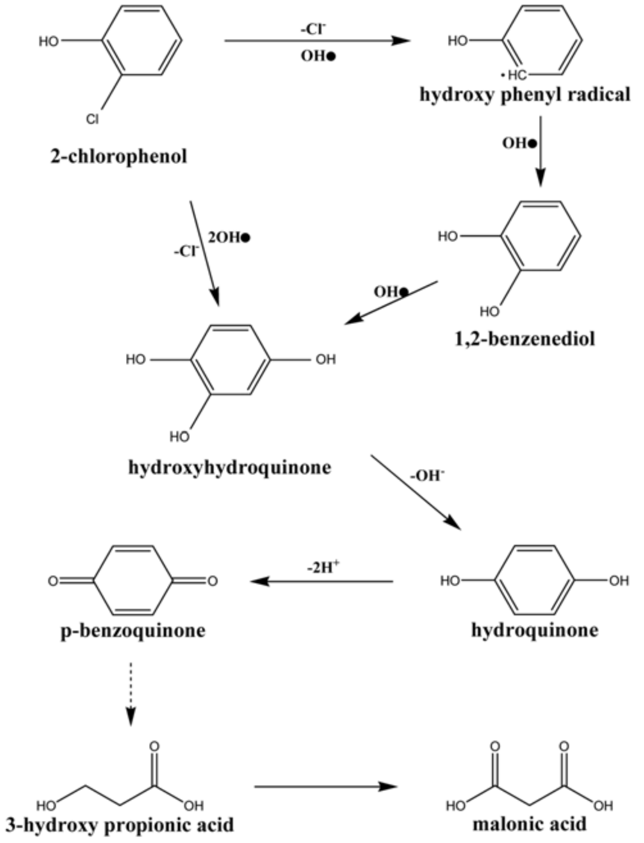

Fig. 17. A proposed reaction pathway of 2-CP degradation involving hydroxyl radicals.

CONCLUSIONS

The results showed that degradation of 2-CP with UV alone (λ_{max} =306 nm) was more efficient than that of 2-CP with H_2O_2 alone. In the traditional Fenton process, optimal experimental conditions are H_2O_2 1×10^{-3} M, ferrous ion 1×10^{-3} M, and pH 3.0. Also, the experimental results showed that the degradation efficiency was inversely proportional to the initial concentration of 2-CP. As a result, in the optimized experimental conditions, the UV irradiation with high intensity enhanced the degradation efficiency of 2-CP in the Fenton process, that is, the photo-Fenton process was more efficient than the traditional Fenton process for the degradation of 2-CP in aqueous solutions. Under the experimental conditions, three reaction intermediates were found: 3-hydroxy propionic acid, *p*-benzoquinone, and malonic acid.

NOMENCLATURE

k : rate constant [$\min^{-1}$]
λ_{max} : maximum wavelength of the UV lamp [nm]
C : final concentration of 2-CP [mg/L]
C_0 : initial concentration of 2-CP [mg/L]

AKNOWLEDGMENT

This research work was supported by the Korea Meteorological Administration Research and Development Program under Grant CATER 2006-2101.

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