

# Heterogeneous and homogeneous photocatalytic degradation of chlorophenols in aqueous titanium dioxide and ferrous ion

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**Abstract** Photocatalytic degradation of 100 mg/l chlorophenols was studied using  $\text{TiO}_2$  and Fenton reagent as catalysts. 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol were selected as the target compounds. Results showed that direct photolysis of chlorophenols was faster than that in the  $\text{TiO}_2$ -amended system. The photodegradation of 2CP followed a first-order rate relationship and the rate constants were  $0.022$  and  $0.0103 \text{ min}^{-1}$  in direct photolysis and  $\text{TiO}_2/\text{UV}$  systems, respectively. The apparent-first-order reaction rate for decomposition of 4-chlorophenol was higher than that for 2-chlorophenol and 2,4-dichlorophenol under acidic conditions, while 2,4-dichlorophenol was higher than 2-chlorophenol and 4-chlorophenol in an alkaline medium. Both the  $\text{TiO}_2$  catalyst system and direct photolysis process were faster in basic medium than acidic and neutral medium processes. The Fenton system is excellent for the degradation of chlorophenols and its activity has become low in high pH medium.

**Keywords** Photodegradation; photocatalyst; chlorophenols; Fenton reagent; first-order rate constants

## Introduction

Chlorinated compounds present in aqueous systems have caused severe environmental problems. Chlorophenols, such as 2-chlorophenol (2CP), 4-chlorophenol (4CP) and 2,4-dichlorophenol (DCP) represent important water pollutants and have been promulgated as priority pollutants by US EPA since 1976. Most chlorophenols are released into the environment in wastewater from the plastic and pesticide chemical industries. Although the toxicity of chlorophenols to mammals and aquatic organisms is classified as moderate, chlorophenols have strong organoleptic effect and their taste threshold is 0.1 ppb. A great deal of toxic and bio-resistant organochlorine compounds in aqueous systems should be transformed into harmless species. These compounds can be decomposed or oxidized using chemical, photochemical and biological processes. However, the biological processes need longer retention time and are not applicable to high concentrations of pollutants. The chemical methods are additive processes, which are high cost and increase the dissolved solid content in the effluent.

Photochemical techniques have been identified as promising methods for the decomposition of toxic chemicals. It is known that photochemical processes can be applied as heterogeneous or homogeneous systems. In heterogeneous systems, the utilization of an aqueous suspension of  $\text{TiO}_2$  illuminated by near-UV light to photodegrade organic compounds has been well established (Doong and Chang, 1998). The photoexcitation of a semiconductor promotes valence band electrons into the conduction band leaving free electron holes. However, the recombination of electrons and holes hampers the photocatalytic reaction process. In homogeneous systems,  $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{O}_2$  mixing with  $\text{Fe}^{2+}$  (Fenton reagent) have been identified as another efficient technique for the degradation of hazardous wastes, like PCBs, chlorinated herbicide and chlorophenols (Pignatello and Chapa, 1994, Pignatello and Sun, 1995). Typically, high-valent ions, such as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are used in combination with hydrogen peroxide to generate OH radicals that can attack organic

compounds. However, the comparison between heterogeneous and homogeneous systems on the degradation of chlorophenols has received less attention.

The purpose of the present work is to compare the photodegradation efficiency of chlorophenols using  $\text{TiO}_2$  as a heterogeneous system and Fenton's reagent as a homogeneous system. 2-chlorophenol (2CP), 4-chlorophenol (4CP) and 2,4-dichlorophenol (DCP) were selected as the target compounds. The effect of the catalyst, pH values, wavelengths and concentration of ferrous ion were evaluated. Apparent first-order rate constant ( $k_{\text{obs}}$ ) was used to describe the degradation behavior of chlorophenols under various conditions. Moreover, the mineralization and intermediates for the degradation of 2-CP is discussed.

## Materials and method

### Chemicals

The chlorophenols used in this study, 2CP, 4CP and DCP were purchased from Sowa Chemical Inc. (>99.0%, Tokyo, Japan). Titanium oxide ( $\text{TiO}_2$ ) (99.9%, power) was taken as a catalyst in the heterogeneous system. Acetonitrile (99.97%, TEDIA HPLC / SPECTRO grade) was obtained from Tedia Co., Inc. (Fairfield, OH, USA). Hydrogen peroxide (33–35%) was obtained from Showa Chemical Inc. Deionized distilled water (Millipore Co., Bedford, Mass., USA) was used to prepare all of the chemical solutions. All other reagents were analytical grade and were used without further treatment.

### Apparatus and instrument

Photochemical degradation experiments were carried out in a hollow cylindrical photo-reactor equipped with a water jacket (Quartz or Pyrex). A 100 W medium pressure mercury lamp (ACE glass Inc., NJ, USA) was used for the irradiation. Batch experiments were conducted at  $25 \pm 1^\circ\text{C}$ . Aliquots (10 mL) were withdrawn from the solution at various time intervals for analysis after removal of  $\text{TiO}_2$  by centrifugation at 14000 rev/min for 10 min. A standard experiment involved the addition of 100 mg of chlorophenols to 1L deionized distilled water. For the heterogeneous system, titanium dioxide was used as the photocatalyst. After  $\text{TiO}_2$  was added into the suspension, the sample was sonicated for 20 min to obtain a good dispersion. The solution was magnetically stirred and purged with air for 30 min at a rate of 50 ml/min and equilibrated in the dark for 10 min prior to illumination to maintain the oxygenated condition. For the heterogeneous system, Fenton's reagent was prepared by mixing 290 mg/l  $\text{H}_2\text{O}_2$  and 50 mg/l  $\text{Fe}^{2+}$ . Immediately after the addition of the hydrogen peroxide, the light was turned on. Samples were withdrawn at different time intervals and analyzed followed by centrifugation. All of the experiments were buffered with phosphate buffer solutions to yield pH values ranging from 2.0 to 12.5.

### Analytical procedures

The samples were determined using high performance liquid chromatography (HPLC) equipped with a 510 pump and 486 variable wavelength UV detector. A Supelcosil LC-18 column (15 cm $\times$ 0.46 mm $\times$ 5.0  $\mu\text{m}$ ) was employed for determining the chlorophenols and the metabolites. The mobile phase was a mixture of 70:30:0.1 acetonitrile : water: phosphoric acid (v/v). The elute was delivered at a rate of 1.0 mL/min and the wavelength for detection was 254 nm. The chlorophenol concentrations were determined using calibration graph methods and the peak areas were used to calculate concentrations. The oxygen concentration was measured during irradiation using an oxygen-sensitive membrane electrode, which is capable of detecting accurately oxygen levels up to 0.5 mg/L. The concentration of ferrous iron was determined using ferrozine methods. Ferric ion was first reduced to ferrous ion using ascorbic acid as the reducing agent and then analyzed with the ferrozine method (Doong and Chang, 1998). Total organic carbon (TOC) concentration of

the supernatants was analyzed by a model 700 TOC analyzer (O. I. Corporation, Texas) after filtering the liquid with a 0.45  $\mu\text{m}$  cellulose nitrate membrane filter.

## Results and discussion

### Effect of semiconductors on the photodegradation of 2CP

In order to compare the direct photolysis and photocatalytic activity of  $\text{TiO}_2$ , experiments with and without the addition of  $\text{TiO}_2$  were carried out. Figure 1 illustrates the photodegradation of 2CP in dark reaction, direct photolysis, and UV/ $\text{TiO}_2$  systems. Results showed no obvious degradation of the 2CP after 6 h in darkness. Nearly complete degradation of the original 2CP was accomplished within 210 min under direct photolysis. The photocatalytic process follows an apparent first-order rate reaction. The first-order rate constant ( $k_{\text{obs}}$ ), calculating for the disappearance of 2CP from linear regression analysis of  $\ln(C/C_0)$  versus time, was  $0.022 \text{ min}^{-1}$  for direct photolysis. The addition of 1 g/L  $\text{TiO}_2$  decreased the degradation efficiency and an irradiation time of 360 min was needed for the complete decomposition of 2CP. The rate constant was  $0.0103 \text{ min}^{-1}$  for the UV/ $\text{TiO}_2$  system. This result proves the sensitivity of 2CP to direct photolysis and the effect of UV is greater than that of  $\text{TiO}_2$  for the degradation of 2CP under neutral conditions (pH 7.1).

The decrease in degradation efficiency of 2CP in a  $\text{TiO}_2$ -amended system may be due to the low adsorption amount of 2CP on the surface of  $\text{TiO}_2$  under the experimental conditions. Several researches have demonstrated that the photodecomposition rates of pollutants are influenced by the active site and the photo absorption of the catalyst used. Although Al-Sayyed *et al.* (1991) depicted that the decomposition rate of 4CP increased linearly with the amount of  $\text{TiO}_2$  added, Ku *et al.* (1996) reported that the rate constant of 2CP decreased with increasing  $\text{TiO}_2$  amounts for loading above 0.1 g/L under alkali conditions. Recently, Leyva *et al.* (1998) reported that the photocatalytic effect of  $\text{TiO}_2$  was greater than the direct photolysis effect in the degradation of 4CP and the best decomposition was produced in the presence of 0.2 g/L  $\text{TiO}_2$ . To elucidate the effect of semiconductors, experiments with the addition of different dosages of  $\text{TiO}_2$  were also performed. Little effect by the  $\text{TiO}_2$  dosage on the photodegradation of 2CP was observed. As depicted in Figure 1, the decomposition slightly increased when the  $\text{TiO}_2$  amount decreased from 1 g/L to 0.5 g/L. Doong and Chang (1997) depicted that the addition of

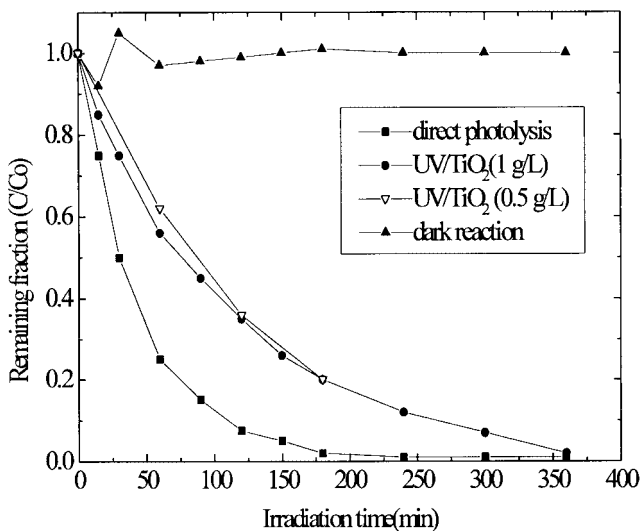
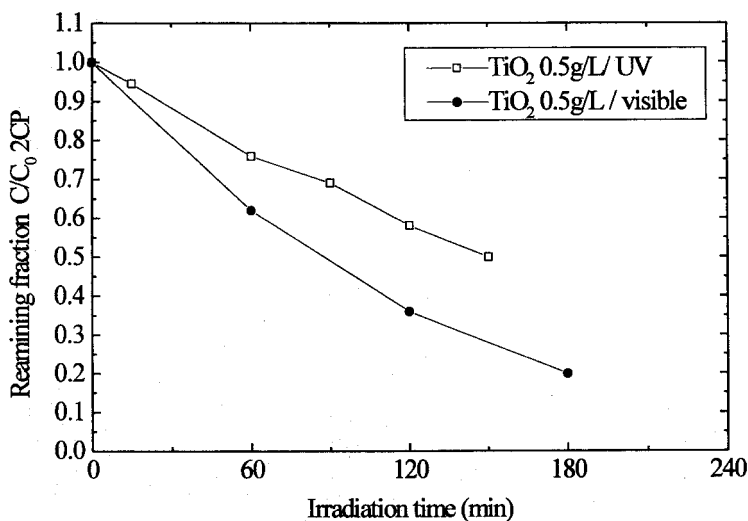


Figure 1 Effect of direct photolysis and amount of  $\text{TiO}_2$  on degradation of 2CP in UV/ $\text{TiO}_2$  system



**Figure 2** Effect of wavelength on the photodegradation of 2CP in the presence of TiO<sub>2</sub> (0.5 gL<sup>-1</sup>)

TiO<sub>2</sub> had little effect on the enhancement of the photodegradation rate of readily degradable pesticides. This implies that 2CP is a readily degradable compound and the photodegradation was mainly attributed to the direct photolysis.

#### Effect of wavelength on the photodegradation of 2CP

To evaluate the effect of wavelength on the photodegradation of 2CP, a pyrex reactor was used instead of a quartz reactor. Figure 2 illustrates the photodegradation of 2CP using various wavelengths of incident light. The degradation efficiency was lowered from 70% to 50% within 150 min when a pyrex reactor was used to cut off UV and near UV (under 320 nm). The  $k_{\text{obs}}$  was also decreased from 0.0038 min<sup>-1</sup> to 0.002 min<sup>-1</sup>. The bond energy of aryl-Cl is 97 kcal/mole, which corresponds to the wavelength of 294 nm. Therefore, a pyrex reactor will hamper the direct photolysis reaction. When TiO<sub>2</sub> was added, the semiconductor absorbed light, which encompasses energy higher than the corresponding band gap (3.1 eV) and electron/hole pairs were generated on the surface of TiO<sub>2</sub>. The hole was then trapped by a surface hydroxyl group to yield hydroxyl radical and decompose 2CP. This result proves that the contribution of direct photolysis to the photodegradation of 2CP is greater than that of titanium dioxide under the experimental conditions.

#### Effect of pH on the photodegradation of 2CP

Figure 3 illustrates the effect of pH values on the photodegradation of 2CP in the TiO<sub>2</sub>/UV system. High pH values can accelerate the decomposition rate of 2CP. The first-order rate constant of 2CP was 0.005 min<sup>-1</sup> under acidic environment (pH 2.5). A 7-fold increase in  $K_{\text{obs}}$  was obtained at pH 12.5. This may be due to the formation of hydroxyl radicals as a result of the reaction between the hydroxyl ions and holes that are formed on the surface of the photo-excited TiO<sub>2</sub> particles.



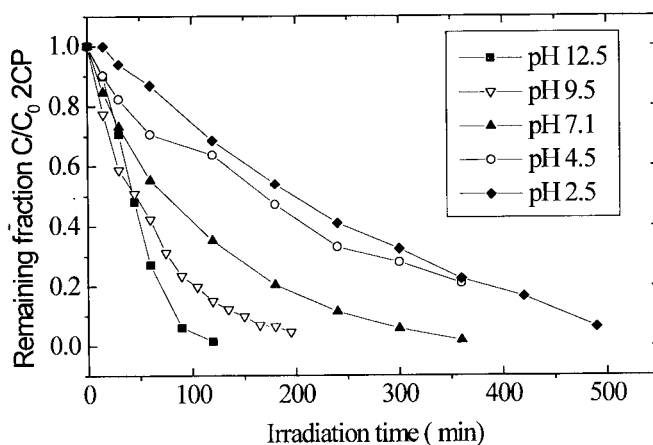
Similar 2CP degradation behaviors were observed in direct photolysis systems. As depicted in Table 1, The rate constants of 2CP in direct photolysis increased concomitant with the increasing pH values. An 8-fold difference in  $k_{\text{obs}}$  between the acidic and alkaline

**Table 1** The first-order rate constant ( $k_{\text{obs}}$ ) of 2CP with different pH values in  $\text{TiO}_2/\text{UV}$  and direct photolysis system

pH value of the solution	2.5	4.5	7.1	9.5	12.5
$k_{\text{obs}}$ ( $\text{min}^{-1}$ ) in $\text{TiO}_2$ (1.0g $\text{L}^{-1}$ )/UV	0.005	0.0042	0.0103	0.0157	0.0364
$k_{\text{obs}}$ ( $\text{min}^{-1}$ ) in direct photolysis	0.0155	0.013	0.022	0.0308	0.126

**Table 2** The first order rate constants of chlorophenol isomers under acidic and alkali conditions in  $\text{TiO}_2/\text{UV}$  system

pH value	$\text{TiO}_2$ concentration (g/L)	$k_{\text{obs}}$ ( $\text{min}^{-1}$ )		
		2CP	4CP	DCP
2.5	1.0	0.0006	0.00125	0.0008
12.5	1.0	0.00334	0.00277	0.0108

**Figure 3** Effect of pH on the degradation of 2CP in the presence of  $\text{TiO}_2/\text{UV}$  system

conditions was also demonstrated. Although there was no semiconductor in the solution, free radicals, mainly hydroxyl radicals ( $\text{OH}^\bullet$ ), were formed when water was irradiated with high energy beams (Stafford *et al.*, 1994).



This aqueous electron ( $e_{\text{aq}}$ ) can further react with oxygen in the solution and may form superoxide radicals



#### Degradation efficiency of different isomers of chlorophenol

To evaluate the competition effect of chlorophenol isomers on the photodegradation, a mixture of 2CP, 4CP and DCP was added into the  $\text{TiO}_2/\text{UV}$  system (mixture system). Table 2 illustrates the  $k_{\text{obs}}$  of chlorophenols under acidic and alkaline conditions. The sequence of efficiency for decomposition of chlorophenols is different in alkaline and acidic solutions. The rate constant for decomposition was in the order of  $4\text{CP} > 2\text{CP} > \text{DCP}$  under acidic conditions, whereas the sequence of degradation was  $\text{DCP} > 2\text{CP} > 4\text{CP}$  under alkaline

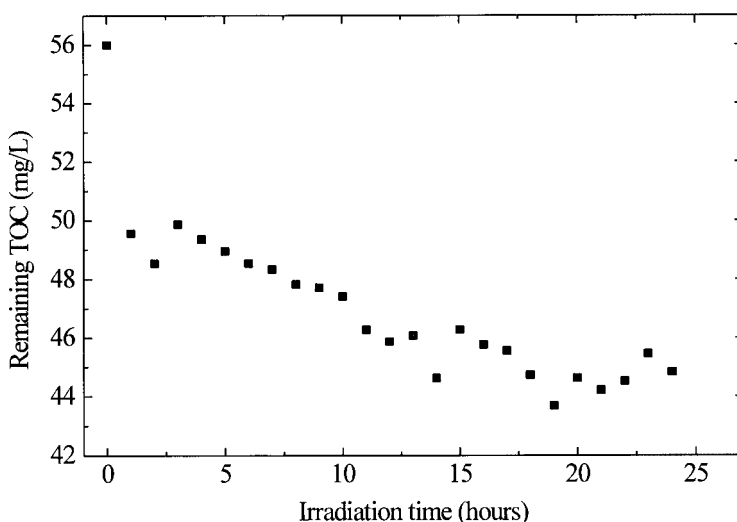
conditions. Several researchers have proposed mechanisms for the photocatalytic decomposition of chlorophenols and relevant chlorinated aromatic hydrocarbons (Oliveira *et al.*, 1990, Stafford *et al.*, 1994). It is believed that  $\text{OH}^\bullet$  can attack the ring leading to the production of a phenoxy radical. The attack on the aromatic ring by hydroxy radicals could increase the electron density in the aromatic ring, thereby creating a positive charge at the ortho and para sites. The entire charge balance may vary according to the position of  $\text{Cl}^-$  and the number of  $\text{Cl}^-$  attached to the aromatic ring. When both the chlorine atoms on DCP are in the ortho and para sites, the electron density in the aromatic ring would be lowered. This could indicate that DCP had a lower rate constant compared to 2CP and 4CP under acidic conditions. Moreover,  $k_{\text{obs}}$  of 2CP in the mixture system (Table 2) was lowered greater than that in the single system (Table 1). This means that the existence of co-occurring chlorophenols could compete for the radicals in the system, subsequently lowering the degradation rate of the target compounds.

#### Concentration of TOC in UV/TiO<sub>2</sub> system

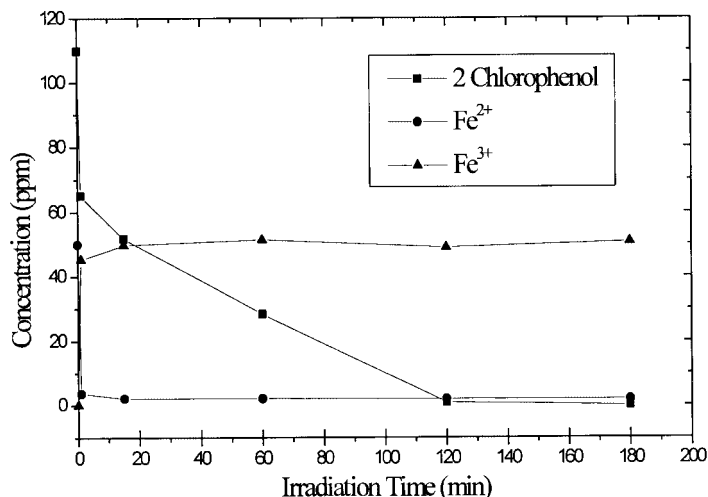
Although the concentration of 2CP can be nearly completely decomposed during 360 min in the presence of TiO<sub>2</sub> and UV light, the mineralization ratio of 2CP was low. Figure 4 illustrates the concentration profile of TOC in the liquid phase of the UV/TiO<sub>2</sub> system with the amendment of 100 mg/L 2CP. The TOC concentration slowly decreased from 56 mg/L initially to 44.2 mg/l after 19 hours of irradiation. The decrease in TOC also followed a first-order reaction rate and the rate constant was  $0.00005 \text{ min}^{-1}$ . This value is far less than that for photodegradation. Moreover, the photodegradation intermediates, such as hydroquinone, benzoquinone, phenol and chlorocatechole were identified, suggesting that the mineralization of 2CP in UV/TiO<sub>2</sub> system is very slow.

#### Degradation of 2CP in Fenton system

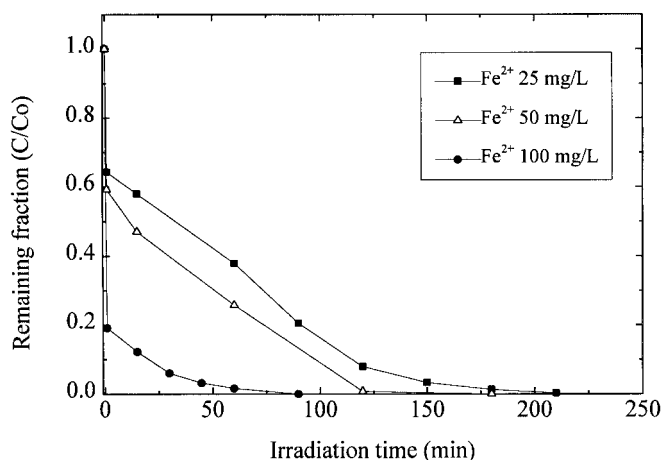
Fenton reagent is a mixture of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{+2}$  ions that can produce  $\text{OH}^\bullet$  to oxidize refractory compounds. In this study the effect of the Fenton system on the decomposition of 2CP was also evaluated. Figure 5 illustrates the concentration profiles of 2CP, ferrous and ferric irons in the Fenton system. The concentration of 2CP decreased rapidly in the first 1 min when Fenton reagent was added into the solution. Nearly complete degradation was observed within 120 min with the initial rate constant of  $0.401 \text{ mM/min}$ . Also, the



**Figure 4** The concentration profile of total organic carbon in photodegradation of 2CP in TiO<sub>2</sub>/UV system



**Figure 5** The concentration profiles of 2CP, Fe<sup>2+</sup> and Fe<sup>3+</sup> in Fenton system



**Figure 6** Effect of Fe<sup>2+</sup> concentration on the Fenton's activity on 2CP (H<sub>2</sub>O<sub>2</sub> conc.=291 ppm)

concentration of ferrous iron was rapidly decreased concomitantly with the increase in ferric ions. Pignatello and his colleagues (1992, 1995) demonstrated that ferric ion in the Fenton system can be reoxidized to form ferrous ions and hydroxyl radicals. In this study, the ferrous ions were nearly completely converted into ferric ions within 20 min and a low conversion ratio of Fe<sup>3+</sup> to Fe<sup>2+</sup> was observed. This may be due to the excess hydrogen peroxide in the system that can react with the newly forming ferrous ion. Pignatello (1995) also depicted that the Fe<sup>2+</sup> can be reoxidized into Fe<sup>3+</sup> in the presence of hydrogen peroxide, which is consistent with our results.



#### Effect of ferrous concentration

The addition of high concentrations of ferrous ion can promote the reaction with H<sub>2</sub>O<sub>2</sub> to form OH<sup>•</sup> and enhance the decomposition of 2CP. As depicted in Figure 6, nearly complete degradation of 2CP within 210 min was observed in 25 mg/l Fe<sup>2+</sup>-amended system.

Increasing the concentration of ferrous ions can shorten the reaction time and only 90 min was needed to completely decompose 2CP when 100 mg/L ferrous ion was added into the system. Also, the initial rate constants increased from 0.27 to 0.63 mM/min as the concentration of ferrous ion increased from 25 to 100 mg/l. However, no linear relationship between the rate constants and initial concentration of ferrous ion was observed. Although the addition of high concentrations of ferrous ions can generate higher amounts of hydroxyl radicals in the solution, the recombination rate of radicals was also higher.



### Conclusion

Results obtained in this study showed that homogeneous photocatalytic degradation is more efficient than a heterogeneous system for the degradation of chlorophenol. The catalytic activity of  $\text{TiO}_2$  decreased concomitantly with the increase of dosage due to the shielding effect. Direct photolysis was shown to be a more effective system for the degradation of chlorophenols. Introducing the hydroxide ions into the solution can increase the efficiency of decomposition in the  $\text{TiO}_2/\text{UV}$  system. Direct photolysis effect was also accelerated under alkaline conditions due to the formation of  $\text{OH}^\bullet$  and  $\text{O}_2^\bullet$  by the illumination of UV. Nearly complete degradation was observed within 120 min with the amendment of Fenton reagent. The addition of high concentrations of ferrous ions could enhance the generation of free radicals. However, it will also increase the recombination rate of the radical, subsequently lowering the decomposition rate constant.

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