THESIS

This is to certify that the

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The Photodegradation of 2-Chlorophenol in Aqueous TiO_2 Suspensions: The Effect of Hydrogen Peroxide Addition

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Major professor

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THE PHOTODEGRADATION OF 2-CHLOROPHENOL IN AQUEOUS TiO_2 SUSPENSIONS: THE EFFECT OF HYDROGEN PEROXIDE ADDITION

By

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ABSTRACT

THE PHOTODEGRADATION OF 2-CHLOROPHENOL IN AQUEOUS TiO_2 SUSPENSIONS: THE EFFECT OF HYDROGEN PEROXIDE ADDITION

By

Chih-Chang Wang

The photocatalytic degradation of 2-chlorophenol (2CP) has been investigated in aqueous suspensions of TiO_2 over the wavelength range of 300-390 nm. The optimum pH range to operate the photocatalytic degradation without hydrogen peroxide addition is between 5 and 8. With the addition of hydrogen peroxide the optimum pH range for the photocatalytic degradation of 2CP is between 3.6 and 5. Bubbling air or pure oxygen into UV/TiO_2 system does not increase the rate of degradation of 2CP to a great extent. The degradation rate of 2CP was faster when both hydrogen peroxide and oxygen were present. At 100% of light intensity (3 mW/cm^2) the effect of adding hydrogen peroxide on photocatalytic degradation rate was significant. However, at the 35% of light intensity the addition of hydrogen peroxide did not significantly increase the photocatalytic degradation rate.

DEDICATION

To My Parents

ACKNOWLEDGMENTS

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

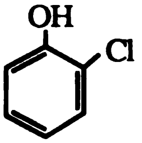
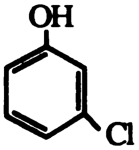
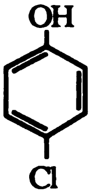
Chapter 1

Introduction

1.1 The reason for studying 2-chlorophenol

The widespread utilization of chlorinated aromatic compounds as pesticides and herbicides is attracting increased concern (1). The occurrence of highly chlorinated organic compounds, such as polychlorinated biphenyls and chlorobenzene is wide spread in the environment (2). These compounds are important from a health perspective due to their carcinogenicity or potential carcinogenicity (3,4) and their persistence in the environment (5). This has led to a better understanding of the influences of chemicals that contaminate water which endangers both the environment and human health. Chlorinated organics are abundant pollutants and some of them withstand biodegradation. Among them, monochlorophenols are moderately toxic to aquatic life. Chlorophenols induce disagreeable taste and odour in water and accordingly impair the flavor of fish even at ppb (μg·kg^{-1}) levels. Several of the important physical properties of monochlorophenols are summarized in Table 1.1 (6).

Table 1.1 Physical properties of the monochlorophenols (6)

Parameter	2-chlorophenol	3-chlorophenol	4-chlorophenol
Chemical structure			
Molecular mass	128.6	128.6	128.6
Physical state	liquid	solid	solid
Color	colorless	white	white
Melting point (°C)	9.3	33	43
Boiling point (°C)	175	214	217
Density	d_4^{25} 1.257	d_4^{25} 1.245	d_4^{25} 1.383
Vapor pressure	1 mm Hg at 12.1 °C	1 mm Hg at 44.2 °C	1 mm Hg at 49.8 °C
Water solubility (at 20 °C, g/l)	28.5	26	27.1
pK_a	8.48	9.02	9.38

There are two important techniques to synthesize chlorophenols: direct chlorination of phenol and alkaline hydrolysis of polychlorobenzenes (7). When gases chlorine is passed into molten phenol at temperatures between

50 and 150 °C, both 2-chlorophenol and 4-chlorophenol are formed. The method of production and principal uses of the chlorophenols are presented in Table 1.2.

Table 1.2 Production and use of the chlorophenols (6)

	Production	Use
2-CP	Usually synthesized through chlorination of phenol: may be synthesized from 1,2-dichlorobenzene by alkaline hydrolysis, or from diazotized o-chloroaniline.	Intermediate in the synthesis of higher chlorophenols and phenolic resin
3-CP	May be prepared by hydrolysis of 1,3-dichlorobenzene, from m-chloroaniline through the diazonium salt, or by oxidation of p-chlorobenzenic acid with copper(II) oxides as the oxidant	Chemical intermediate
4-CP	On large scale by chlorination of phenol; may be synthesized from p-chloroaniline, from p-nitrosophenol, by selective reduction of chlorobromophenols or by alkaline hydrolysis of 1,4-dichlorobenzeze.	Intermediate in production of higher chlorinated phenols, and in synthesis of dyes and drugs (denaturant for alcohol; selective solvent in refining of mineral oils.

Industrial waste discharge is the principal source of water pollution by chlorophenols. These compounds are produced as end- or by-products in chemical synthesis or may be used as starting materials as well. Consequently, that is the reason to conduct these experiments to study chlorophenols and find out efficient methods to reduce the amount of them in environment. 2-chlorophenol was chosen in this study because it is a liquid which is easier to be prepared as a reactive solution.

1.2 The process to decompose 2-chlorophenol

There are several treatment alternatives to decompose chlorophenols in wastewater. Among them, biological treatment processes are widely used methods because of their effectiveness and low cost. Biotransformation by microorganisms in water and soil is considered to be the major mechanism by which chlorophenols are degraded in the environment (6). It has been shown that the rate of biodegradation is largely dependent on the microbial populations present, and the characteristics of the environment, like pH, oxygen level, nutrient status and temperature. The most noticeable drawback of the biodegradation is that when concentration of the pollutants in wastewater is too high, the microorganism can not function properly. In many cases, the concentration of chlorophenols in wastewater is high enough to be toxic to microorganisms. Another reason for the unsuitability of the biological treatment process are that it always needs long detention time or long start-up time to acclimate the microorganisms to the waste. In the conventional wastewater treatment processes, activated carbon adsorption which is a non-destructive process is used to remove contaminants from wastewaters, but it only concentrates the contaminants rather than destroying them. Thermal destruction could be used to treat aqueous wastes. However, the cost for treatment of diluted wastes is generally high. Alternative technologies which can efficiently decompose the chlorophenols in wastewaters are needed. Advanced oxidation processes (AOP) are a possible technologies to solve this problem.

AOPs are defined as those technologies that involve the generation of highly reactive radical intermediates, particularly the hydroxyl radical (·OH), at ambient temperature (8). The typical AOP systems utilize combination of strong oxidants, such as hydrogen peroxide and ozone, to conduct the process. The combinations used include O_3/UV, O_3/H_2O_2, O_3/H_2O_2/UV, TiO_2/UV, TiO_2/H_2O_2/UV, TiO_2/UV/Fe^{2+}, and TiO_2/UV/H_2O_2/Fe^{2+}. TiO_2 combined with UV light and hydrogen peroxide was chosen as major experimental system in this study.

1.3 Outline of this study

The objective of this study is to improve the understanding of the photodegradation of chloroaromatic compounds in titanium dioxide suspensions, and also determine the feasibility of using TiO_2/UV, TiO_2/UV/H_2O_2, TiO_2/UV/Fe^{2+}, or TiO_2/UV/H_2O_2/Fe^{2+} to degrade 2-chlorophenol in a aqueous suspensions. The specific objectives are:

1. to determine an optimum condition to operate the AOP system in a effective way.

2. to study the effect of experimental parameters such as pH, concentration of H_2O_2, and light intensity on the photocatalytic degradation of 2-chlorophenol.

and

3. to study the influence of the presence of air and oxygen on the TiO_2 induced photodegradation of the target compound.

Chapter 2

Background

2.1 Properties of TiO_2

TiO_2 is an n-type semiconductor and has a band gap energy of 3.2 eV (9). At pH 7, the conduction band is located at 2.6 V vs. NHE (10), so it has the potential to oxidize a great number of organic compounds (10). TiO_2 has been favored as a photocatalyst for treating aqueous wastes because of the strong oxidizing potential of its valance band holes and because it is not photodecomposed. In an n-type semiconductor, the reactive species is the hole, cogenerated with an electron upon absorption of a photon and carrying the major part of the light quantum energy. This excess free energy is the driving force for the oxidation of the organic and inorganic molecules that react at the surface of such a particle. Other potential photocatalysts, for example, ZnO will dissolve during photochemical reactions and generate undesirable products, such as Zn^{2+}. Two further advantages of using TiO_2 as photocatalyst are (i) it is a true catalyst because it is not consumed during the experiment and (ii) it can be easily immobilized, so the treatment process can be adapted for continuous operation (11).

2.2 Photoprocesses on TiO_2 surface

The use of TiO_2 as a photocatalyst for the degradation of organic pollutants shows considerable promise. The photo-induced processes in semi-conductor suspensions have been extensively reviewed (9, 12). When a semiconductor is illuminated with light of energy greater than its bandgap energy, an electron is transferred to the conduction band leaving a vacancy ("hole") in the valance band. The electron and hole can migrate to the surface of the semiconductor. At the interface, electron transfer can occur either from the conduction band to an acceptor, A, in solution or from a donor, D, in solution to the valence band. These processes are illustrated in Figure 2.1 (13).

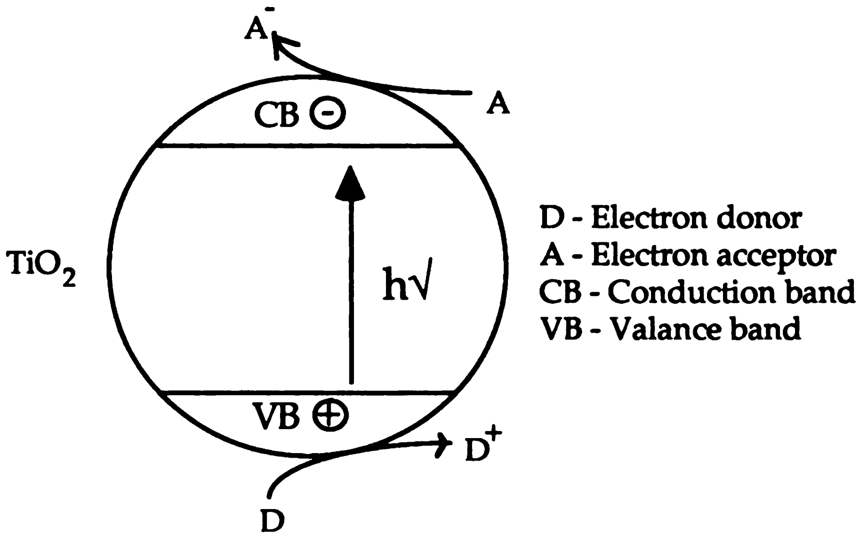


Figure 2.1 Electron transfer processes at the semiconductor-water interface.

Turchi and Ollis (1990) proposed that the hydroxyl radical, $\cdot OH$, is the primary oxidant in the photocatalytic system (14). The photocatalytic reaction scheme for the system proposed by Turchi and Ollis is given in Table 2.1.

When a semiconductor is irradiated with light of energy greater than its bandgap energy, an electron is excited into conduction band leaving a vacancy ("hole") in the valence band (reaction 1). The electron and hole can migrate to the surface of the semiconductor. If reactive species (traps) are not present at the surface of the semiconductor then the electron-hole pair will recombine (reaction 5) and the energy absorbed will be dissipated as heat. The efficient trapping of the hole and electron at the surface (reaction 6-8, 13, and 14) is a key factor in achieving efficient photochemistry. It is important that the electron acceptor and donor be adsorbed on the TiO_2 surface, since the initial reactions occur in the picosecond time domain (9). In water the solvent, itself, is a potential electron acceptor. However, since water is not easy to reduce, where oxygen is present, oxygen is the most likely electron acceptor (reaction 8a and 8b). Adsorbed oxygen is reduced to form superoxide, $\cdot O_2^-$. Superoxide is unstable and can be reduced to form hydrogen peroxide (reaction 13) and the perhydroxyl ion (reaction 14). On the TiO_2 surface, it has been suggested that the holes in the valence band appear to react with water to produce not only the hydroxyl radicals, but, possibly, another unidentified weaker oxidant (15). Holes are though to react with surface OH^- and H_2O groups to form $\cdot OH$ (reaction 6). An adsorbed organic molecule, $R_{1,\,ads}$ may be directly oxidized by a hole (reaction 7); however, this reaction is not believed to be significant, because of the lack of reactivity that is observed in organic solution (14). The oxidation of organic compounds is though to occur

Table 2.1 Photocatalystic Reaction Scheme

Excitation			
	TiO_2	$\xrightarrow{h\nu} e^- + h^+$	(1)
Adsorption			
	$O_L^{2-} + Ti^{IV} + H_2O$	$\Leftrightarrow O_LH^- + Ti^{IV} - OH^-$	(2a)
	$Ti^{IV} + H_2O$	$\Leftrightarrow Ti^{IV} - H_2O$	(2b)
	$site + R_1$	$\Leftrightarrow R_{1,ads}$	(3)
	$OH \cdot + Ti^{IV}$	$\Leftrightarrow Ti^{IV} \cdots OH \cdot$	(4)
Recombination			
	$e^- + h^+$	$\rightarrow heat$	(5)
Trapping			
	$Ti^{IV} - OH^- + h^+$	$\Leftrightarrow Ti^{IV} \cdots OH \cdot$	(6a)
	$Ti^{IV} - H_2O + h^+$	$\Leftrightarrow Ti^{IV} \cdots OH \cdot + H^+$	(6b)
	$R_{1,ads} + h^+$	$\Leftrightarrow \cdot R^+_{1,ads}$	(7)
	$Ti^{IV} + e^-$	$\Leftrightarrow Ti^{III}$	(8a)
	$Ti^{III} + O_2$	$\Leftrightarrow Ti^{IV} - \cdot O_2^-$	(8b)
Hydroxyl Attack			
Case I	$Ti^{IV} \cdots OH \cdot + R_{1,ads}$	$\rightarrow Ti^{IV} + R_{2,ads}$	(9)
Case II	$OH \cdot + R_{1,ads}$	$\rightarrow R_{2,ads}$	(10)
Case III	$Ti^{IV} \cdots OH \cdot + R_1$	$\rightarrow Ti^{IV} + R_2$	(11)
Case IV	$OH \cdot + R_1$	$\rightarrow R_2$	(12)
Reaction of other radicals			
	$e^- + Ti^{IV} - \cdot O_2^- + 2(H^+)$	$\Leftrightarrow Ti^{IV}(H_2O_2)$	(13)
	$Ti^{IV} - \cdot O_2^- + (H^+)$	$\Leftrightarrow Ti^{IV}(\cdot O_2H)$	(14)
	$(H_2O_2) + OH \cdot$	$\Leftrightarrow (\cdot O_2H) + (H_2O)$	(15)

as a result of the reaction of the molecule either with the adsorbed ·OH (reactions 9 and 11) or with ·OH that is not bonded to the surface (reactions 10 and 12). Another reaction that may occur in the system is the scavenging of ·OH by hydrogen peroxide (reaction 15).

It is proposed that the hydroxyl radical ,·OH, is the primary oxidant during the photocatalyzed degradation experiments in irradiated TiO_2 suspensions (14). The formation of ·OH radicals can be achieved by two routes: (a) via reaction of valance band holes with either adsorbed H_2O or with surface OH^- groups (reactions 1, 16, 17)

$$h^+_{VB} + H_2O(ads) \rightarrow \cdot OH + H^+ \tag{16}$$

$$h^+_{VB} + OH^-(surf) \rightarrow \cdot OH \tag{17}$$

or (b) via the H_2O_2 reaction from $\cdot O_2^-$ (16).

It is generally accepted that adsorption of oxygen inhibits the electron/hole recombination process by trapping the conduction band electron as a superoxide ion, $\cdot O_2^-$.

$$O_2 + e^-_{CB} \rightarrow \cdot O_2^- \tag{18}$$

Subsequent to reaction 18 , H_2O_2 can be formed from $\cdot O_2^-$, via reactions 19-22.

$$\cdot O_2^- + H^+ \rightarrow HO_2 \cdot \tag{19}$$

$$HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2 \tag{20}$$

$$\cdot O_2^- + HO_2\cdot \rightarrow HO_2^- + O_2 \tag{21}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \tag{22}$$

Cleavage of H_2O_2 by any of reactions 21-23 yields ·OH radicals.

$$H_2O_2 + e_{CB}^- \rightarrow \cdot OH + OH^- \tag{23}$$

$$H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + OH^- + O_2 \tag{24}$$

$$H_2O_2 \xrightarrow{h\nu} 2\cdot OH \tag{25}$$

In order for the photooxidation process to occur it is necessary to avoid accumulation of the electrons or holes in the particles. Because the accumulation would increase the recombination rate and lower the quantum yield. Thus, the electrons and holes must be removed promptly by an electron acceptor or donor at the surface. The faster this removal, the lower the concentration of electrons an holes in the particles. The lower the steady-state concentration of electrons on the particles, the lower the recombination losses (16).

2.3 Photodegradation of chloroaromatic and chloroalphatic compounds in TiO_2 suspensions

The photodegradation of chloroaromatic compounds in TiO_2 suspensions has been extensively reviewed (17). All the compounds listed in Table 2.2 could be completely mineralized.

The half-lives for the disappearance for these compounds ranged from 10 to 90 minutes.

Table 2.2 Half-lives for various Chloroaromatics

Compound	Concentration (ppm)	$t_{1/2}$ (min)
4-chlorophenol	6	14
3,4-dichlorophenol	18	45
2,4,5-trichlorophenol	20	55
Pentachlorophenol	12	20
Chlorobenzene	45	90
1,2,4-trichlorobenzene	10	24
3,3-dichlorobiphenyl	1	10

catalyst concentration 2 g/L; aerated solution; pH 3 except for chlorobenzene; pH 2.5 for chlorobenzene; suspension irradiated with light>330 nm (17).

The photocatalyzed mineralization of many chlorinated aliphatic and aromatic hydrocarbons, as well as other organic contaminants, in drinking water has been successfully demonstrated (16). The total mineralization of many of these compounds to CO_2, Cl^- and H_2O via heterogeneous photocatalysis mediated by illuminated TiO_2 has been demonstrated. Direct photolysis of these compounds by UV light generally only leads to partial degradation (16).

Al-Sayyed, D'Oliveira, and Pichat (18), have demonstrated that in the absence of a semiconductor, 4-chlorophenol is destroyed completely in 100 min (when irradiated with light of wavelength greater than 290 nm, *i.e.* within the absorption band of 4-chlorophenol). In the presence of TiO_2, a rapid degradation occurs and the concentration of pollutant is below detection limits within 60 min. The results show that the photodegradation in a TiO_2

suspension is more efficient than the direct photolysis. Al-Sayyed et al. also found that the rate of a photocatalytic reaction increased linearly with the amount of catalyst up to a level corresponding to complete adsorption of the incident light by TiO_2.

Al-Ekabi et al. in 1991 (19), showed that the degradation of both 2,4-dichlorophenol and pentachlorophenol was very efficient ,and in 12 min it was possible to degrade 95% of 2,4-dichlorophenol in an aerated aqueous TiO_2 suspension.

Photolysis in the presence of TiO_2 can detoxify PCBs. Oliver and Carey in 1985 (15), irradiated a 30 ppb Aroclor 1254 solution containing 0.5% anatase with 350 nm light for 1 hour. They found that the growth of the green algae Scenedesmus quadricauda was virtually the same in the irradiated Aroclor solution and the distilled water control. Algae growth in the unirradiated Aroclor solution was about 100 times slower than in the control.

Pruden and Ollis (20), in 1983, showed that the chloroform is degraded readily in illuminated suspensions of TiO_2 according to the following stoichiometry:

$$2CHCl_3 + 2H_2O + O_2 \xrightarrow{h\nu} 2CO_2 + 6HCl \qquad (26)$$

Their results showed that in the presence of both TiO_2 and near-UV light, $CHCl_3$ was rapidly dehalogenated, while in the presence of either UV light or TiO_2 alone, no $CHCl_3$ disappearance was observed.

2.4 pH effect

A key factor that affects the degradation rate of chemicals in TiO_2 suspensions is the pH. The results of Al-Ekabi et al. (16) show that the rate of degradation of 4-chlorophenol at pH 2.5 is 4 times less than that at pH 5.8. Hydrochloric acid appears to inhibit the degradation of 4-chlorophenol. As the addition of chloride (as KCl) does not inhibit the reaction, it is suggested that the protonation of the TiO_2 surface is responsible for the inhibition seen at low pH (16). Ollis et al. (21) has also suggested that at low pH the adsorption of H^+ may be responsible for the inhibition of TiO_2 mediated photodegradation of chlorinated hydrocarbons. The inhibition seen at low pH may be due to changes in adsorption/desorption characteristics of the reactants and/or other species with pH. A shift in surface potential of the semiconductor as result of H^+ ion sorption may also important.

Kormann et al. (22) showed that simple anions such as Cl^- and HCO_3^- decrease the photoefficiency of the catalyst at low pH where they can be absorbed to the positively charged TiO_2 particle surface (pH_{zpc}=6.25 for P25 TiO_2). However, the same anions have a negligible affect on the measured photoefficiency at high pH since their adsorption to reactive surface sites is prevented by electrostatic repulsion from the negatively charged TiO_2 particles.

D'Oliveira et al. (23) have studied the effect of pH variation on the TiO_2 induced photodegradation of 3-chlorophenol. At pH 10.8, 4.5 and 2.5 the time for 99% disappearance of 3-chlorophenol was 90, 115 and 190 minutes, respectively. The increase in the rate of photodegradation with increasing pH above can be attribute to the increased number of OH^- ions at the surface of TiO_2, since $\cdot OH$ radicals can be formed by trapping photoproduced holes. Similarly, the decrease at low pH can be explained by the lack of OH^- ions.

Al-Sayyed et al. in 1991 (18) demonstrated that the rate of photocatalytic degradation of 4-chlorophenol solutions was independent of pH in the range 3.4-6.0. Similar observations were also reported by Al-Ekabi et al. in 1989 (16).

2.5 light intensity effect

Kormann et al. (22) found that the rate of chloroform degradation is a nonlinear function of light intensity. And the quantum yield of the reaction increases with decreasing light intensity. It was found that the rate of chloroform degradation was proportional to half power of light intensity, *i.e.*,

$$-\frac{d[CHCl_3]}{dt} = kI^{1/2} \qquad (27)$$

D'Oliveira et al. (23) found that the rate of photodegradation of 3-chlorophenol was proportional to the radiant flux (or light intensity) for values smaller than ca. 20 $mWcm^{-2}$. Above this value, it is proportional to its square root, which means that the recombination of the photoproduced charges predominates and accordingly, the initial quantum yield of the degradation process decreases with increasing light intensity.

Al-Sayyed et al. (18) found that the relationship between the photodegradation rate and light intensity of 4-chlorophenol was nearly linear at low light intensity, but it was evident that a leveling off occur at higher light intensity. The rate of 4-chlorophenol disappearance became proportional to the square root of the light intensity. The results suggest that the recombination of photoproduced charges is predominant over oxidation of organic molecules at high light intensities.

2.6 O_2 effect

In many studies on photocatalysis at semiconductor surfaces it has been found that in the absence of oxygen the reaction does not occur (15, 17). The role oxygen plays is not fully understood. It is believed that adsorbed oxygen acts as an electron acceptor (17), as such the presence of oxygen tends to retard hole-electron recombination. The presence of oxygen may also enhance the formation of hydrogen peroxide (see reaction 19-22) and eventually ·OH (see reaction 23-25).

D'Oliveira et al. (23) found that oxygen (or another electrophilic species) was required for photocatalytic oxidations of 2- and 3-chlorophenol. From measurements carried out for the system O_2-UV-illuminated TiO_2 the existence of several types of negatively charged adsorbed oxygen species has been postulated: O_2^-, O_3^-, O^-, and O_2^{2-} (23). The formation of $HO_2\cdot$ radicals from O_2^- and H^+ giving rise to H_2O_2 has been proposed as another way of producing ·OH radicals. This way would be favored at low pH.

Al-Ekabi et al. (19) showed that the introduction of oxygen led to an 80% increase in the degradation rate of 2,4-dichlorophenol compared to the air saturated solution. Under nitrogen the reaction was 75% slower than in air. The data clearly indicate that oxygen plays a crucial role in the photocatalytic degradation of 2,4-dichlorophenol. They mentioned that introducing small bubbles of either air or oxygen may improve the mixing process inside the reactor and thus increase the degradation rate. However, it is not yet clear whether the role of oxygen is simply to accept the conduction band electron and thus prolong the lifetime of the photogenerated "hole" or whether it directly participates in the overall degradation process.

Gerischer et al. (24) studied the role of oxygen in the photooxidation of organic molecules on semiconductor particles, and proposed two models to explain the kinetics of the reaction between dioxygen and an electron on the semiconductor particle.

They assumed that oxygen is the only electron acceptor available initially. The primary reaction of electrons reaching the surface is:

$$e^-_{surf} + O_2 \rightarrow O_2^- \qquad (28)$$

Because the solubility of oxygen is relatively low and O_2 is not strongly adsorbed on semiconductor surfaces in contact with aqueous electrolyte, a high proportion of photoproduced electrons recombine with holes.

In case A, an electron moves freely in or on the particle and reacts anywhere on the particle surface with oxygen. The assumption, made for this process, is that the reduction can occur anywhere on the surface as long as an O_2 molecule is within the electron transfer distance δ. This requires that the electron mobility be high. This model is shown in Figure 2.2.

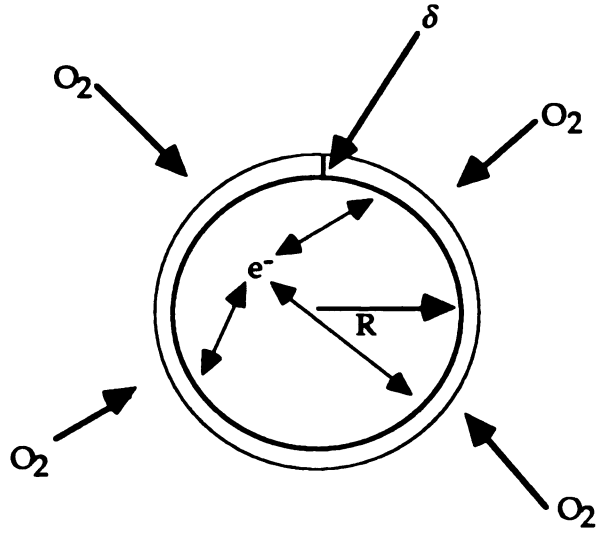


Figure 2.2 Model for reaction between O_2, diffusing from solution to particle surface, and highly mobile electrons. The reactions take place when the O_2 molecule comes within an electron-transfer distance δ from the surface.

Several assumptions in this model are unrealistic. One is the high mobility of the electrons, which guarantees that all O_2 molecules find a reaction partner during an encounter with the particle. This should be corrected by introducing a fraction of electrons on the particle that can interact. It is also postulated that electrons in a spherical shell underneath the particle surface within an interaction distance ∂ from the interface take part in the reaction. This is shown in Figure 2.3.

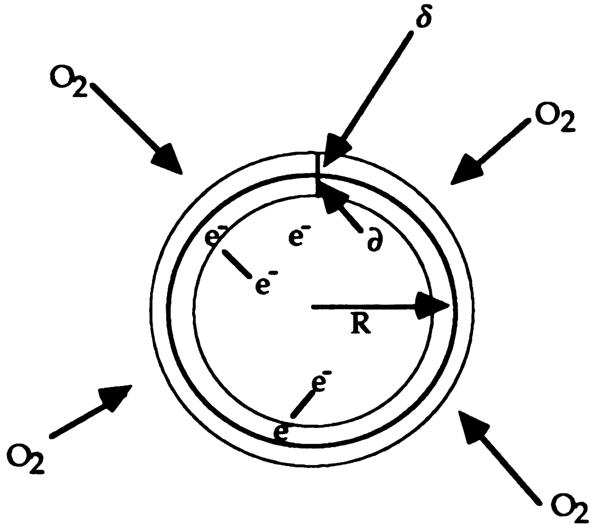


Figure 2.3 Model of Figure 2.2 modified by a limitation of the reaction with O_2 molecules to electrons at a distance ∂ from the interface.

A further correction takes into account the trapping of electrons in the bulk, which immobilizes part of them and leads to another decrease of the apparent rate constant of electron transfer.

In case B, an electron is trapped at or very close to the surface and reacts with oxygen from its trapped state (see Figure 2.4). The modified reaction is:

$$e^-_{trapped} + O_2 \rightarrow O_2^- \qquad (29)$$

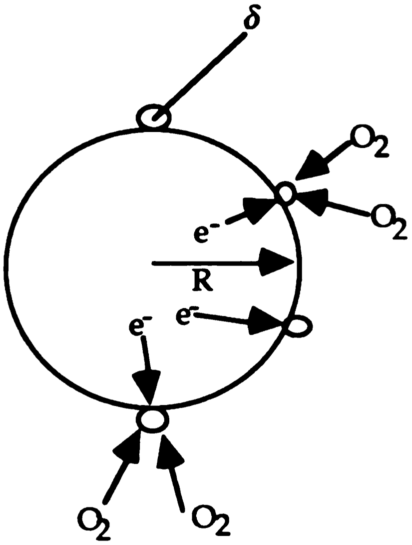


Figure 2.4 Model for reaction in which the O_2 molecules have to diffuse from solution to surface sites, where a trapped electron resides. Only oxygen molecules within a distance δ can react with trapped electrons.

After the analysis of case A and case B, their results showed that case B appears to be the most realistic.

Gerischer and Heller (24) suggest that the rate of electron transfer to oxygen (reaction 8) is the decisive factor in determining the overall efficiency of the photocatalytic process. They also suggest one means of improving the efficiency of the process is to catalyze the electron transfer to oxygen.

2.7 Fenton's Reagent and Fenton-like Chemistry

In 1876, H.J.H. Fenton published the first account of the reaction between ferrous ion and hydrogen peroxide.

Metelitsa (25) proposed the following mechanism for the reactions occurring in the Fenton's system.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\cdot \qquad (30)$$

$$Fe^{2+} + HO\cdot \rightarrow Fe^{3+} + OH^- \qquad (31)$$

$$H_2O_2 + HO\cdot \rightarrow HO_2\cdot + H_2O \qquad (32)$$

$$Fe^{2+} + HO_2\cdot \rightarrow Fe^{3+} + HO_2^- \Leftrightarrow H_2O_2 \qquad (33)$$

$$Fe^{3+} + HO_2\cdot \Leftrightarrow Fe^{2+} + H^+ + O_2 \qquad (34)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \qquad (35)$$

Metelitsa conclude the following refers to the pure system. In acid solution with an excess of hydrogen peroxide, reactions 34 and 35 can be neglected and reactions 30, 32, and 33 predominate. With an excess of ferrous ions, reactions 30 and 31 predominate. When the concentration of ferrous ions are approximately equal to the concentration of hydrogen peroxide, only reactions 30, 31, 32, and 33 are important.

Mertz and Waters (26) demonstrated that the oxidation of organic compounds by Fenton's reagent could be occurred by both chain and non-chain reaction mechanisms. The rate limiting step is the formation of hydroxyl radicals. The mechanism is the following.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\cdot$; chain initiation (36)

$R-H + HO\cdot \rightarrow R\cdot + H_2O$; chain propagation (37)

$R\cdot + H_2O_2 \rightarrow ROH + HO\cdot$; chain propagation (38)

$Fe^{2+} + HO\cdot \rightarrow Fe^{3+} + OH^-$; chain termination (39)

$R\cdot + HO\cdot \rightarrow ROH$; non-chain termination (40)

$2R\cdot \rightarrow$ Products ; non-chain termination (41)

The classical Fenton's reagent chemistry is conducted in acid solution with relatively high hydrogen peroxide to ferrous ion ratios. The purpose of this is to prevent the precipitation of the iron as iron hydroxide. In the neutral pH range, researchers have to give considerations to the autooxidation and the type of buffer utilized.

2.8 Hydrogen peroxide with UV radiation over TiO_2 suspensions

Based on the reaction scheme presented in section 2.2, the addition of hydrogen peroxide would generate ·OH radicals (see reaction 19-22). As it is widely believed that ·OH radical is responsible for the oxidation of organic compounds in illuminated TiO_2 suspensions, one would expected that the addition of hydrogen peroxide would accelerate the photodegradation of sorbed compounds in these system. Also, the addition of hydrogen peroxide would be expected to enhance the rate of oxidation of organic compounds, as its decomposition generates oxygen which also enhances the rate of degradation of organic compounds (27).

Tanaka et al. (28) studied the degradation of trichloroethylene as a function of illumination time, and the effect of added hydrogen peroxide on the degradation rate. Their results showed that addition of 4 mM hydrogen peroxide accelerated the degradation rate by 6 to 8 times. In the absence of TiO_2, only 5% was degraded after illumination for 10 minutes. When trichloroethylene alone was illuminated virtually, no degradation was observed within 1 hour.

They concluded:

- The optimal concentration of H_2O_2 was $4x10^{-3}$ to $1.2x10^{-2}$ for $3.5x10^{-4}$ M of trichloroethylene.

- The photodegradation rate in the absence of TiO_2 increased with the concentration of H_2O_2.

- The same effects of added H_2O_2 were observed when WO_3 was employed as a catalyst instead of TiO_2.

Harada et al. (29) have shown that the addition of hydrogen peroxide enhanced the photocatalytic degradation of dimethyl-2,2-dichlorovynyl phosphate (DDVP) and dimethyl-2,2,2-trichloro-1-hydroxyethyl phosphate (DEP). The effect of the hydrogen peroxide depends on its concentration. Control experiments conducted in the absence of TiO_2 or H_2O_2 showed that this effect was not merely the sum of the effect of illuminated H_2O_2 and that of illuminated catalyst. They found the addition of $1.2x10^{-2}$ M H_2O_2 increased the rate of degradation of DDVP by 10 fold.

Auguliaro et al. (30) studied the influence of hydrogen peroxide addition on the photodegradation of phenol in TiO_2 suspensions. They found that the addition of hydrogen peroxide enhanced the rate of degradation significantly. The photodegradation rate increased at H_2O_2 concentrations up to $5x10^{-3}$ M, above that concentration the rate of reaction was independent of H_2O_2 concentration. The photodegradation rate was greatest when both oxygen and hydrogen peroxide were present.

Pacheco and Holmes (31) studied the influence of H_2O_2 addition on the photocatalytic oxidation of salicylic acid in the presence of TiO_2. They found the addition of 100 ppm ($2.9x10^{-3}$ M) H_2O_2 increased the initial degradation rate by 8 fold. When 300 ppm ($8,8x10^{-3}$ M) H_2O_2 was added the salicylic acid degradation rate was 10 times greater than with no added peroxide.

2.9 Kinetics studies

The rate of the photocatalytic degeneration of chlorinated compounds depends upon various parameters including initial concentration of the compound, pH, light intensity, temperature, wavelength, mass and type of photocatalyst, and type of photoreactor.

Kormann et al. (22) showed that the degradation (oxidation) of a general chlorinated hydrocarbon, $C_xH_yCl_z$, can be described by the following stoichiometry.

$$C_xH_yCl_z + \left(x + \frac{y-z}{4}\right)O_2 \rightarrow xCO_2 + zH^+ + zCl^- + \left(\frac{y-z}{2}\right)H_2O \qquad (42)$$

The CO_2 will be present as HCO_3^- ($pK_{a1}=6.3$) and CO_3^{2-} ($pK_{a2}=10.3$). The heterogeneous rate of photodegradation of chlorinated compound can be described in terms of a second order kinetic expression.

$$-\frac{d[C_xH_yCl_z]}{dt} = k[O_2]_{surf}[C_xH_yCl_z]_{surf} \tag{43}$$

$k[O_2]_{surf}$: the concentration of oxygen adsorbed on the TiO2 surface

$[C_xH_yCl_z]_{surf}$: the concentration of chlorinated compound adsorbed on the TiO_2 surface

Harada et al. (29) found that the photodegradation reaction of DDVP and DEP follows first-order kinetics in illuminated TiO_2 suspensions. Similarly, Al-Ekabi et al. (19) found that the photocatalytic degradation of 2,4-dichlorophenol can be described by first order kinetics (up to 80% degradation).

Pruden and Ollis (20) studied the degradation of chloroform under UV-TiO_2 suspensions. They showed that the reaction rates for both chloroform degradation and chloride production followed first-order kinetics.

Al-Ekabi et al. (16) studied the photocatalytic degradation of phenol, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,5-trichlorophenol over TiO_2. The results indicate that the degradation of the four phenols in aerated aqueous solutions was a function of irradiation time, and that the reaction kinetics were approximately first-order to a high degree of degradation (>85% for phenol).

Similarly, Okamoto et al. (32) in the study of heterogeneous photocatalytic decomposition of phenol over TiO_2 powder showed that the degradation reaction followed the first-order kinetics.

Chapter 3

Materials and Methods

3.1 Experimental equipment

3.1.1 Photochemical reactor

The photochemical reactor used to conduct the studies described in this work is illustrated in Figure 3.1. It consists of a Supermix® reactor. The reason that this photochemical reactor was used in these studies is that mixing in the reactor is experimentally efficient. There are two chambers in the reactor which is equipped with a 85 ml recirculation loop, and has a working volume of 250 ml. A quartz immersion well housing a Double-bore® lamp was placed in the larger chamber in this reactor. A glass impeller shaft (Model 8068-08, Ace Glass, Inc., Vineland, NJ) in the smaller chamber was used to circulate the solution in the reactor. The shaft was rotated by

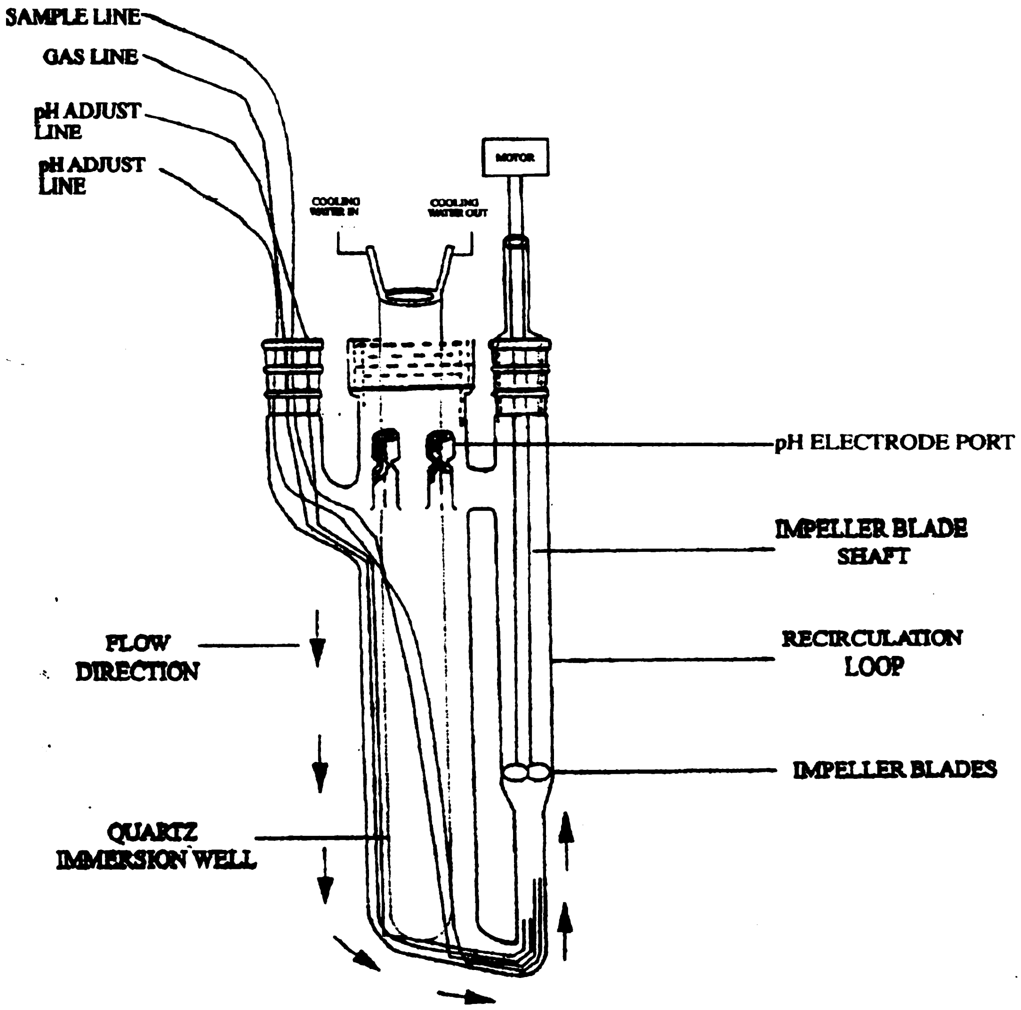


Figure 3.1 Schematic of Supermix® Photochemical Reactor (Model #7868, Ace Glass, Inc., Vineland, NJ)

using an electric motor (Model 102, Talboys Engineering Corp., Montrose, PA).

3.1.2 Ultraviolet light source

The ultraviolet light source was manufactured by the Jelight Co., Laguna Hills, CA. The lamp is a Double-bore® phosphor coated lamp (Model 84-2011-8) with a peak output wavelength of 351 nm. It is a low pressure, cold cathode phosphor coated mercury vapor lamp. The dimensions of the lamp are shown in Figure 3.2. The lamp consists of quartz tubing with a quartz partition or septum through the center. A Model PS-2000-20 power supply (Jelight Co., Laguna Hills, CA) was used.

3.1.3 Experimental scheme

A schematic diagram of the apparatus used in this experiment is shown in Figure 3.3. There are three sample ports at the top of the reactor. All the tubes connected to the reactor were made of Teflon®, except the tubings used for cooling loop.

To maintain a constant temperature in the reactor a peristaltic pump (Model 503U, Watson-Marlow, Concord, MA) was used to cycle cooling water through the cooling jacket of the reactor.

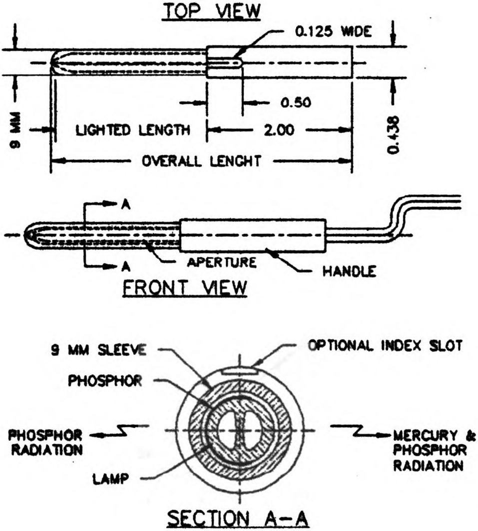


Figure 3.2 Structure of UV lamp

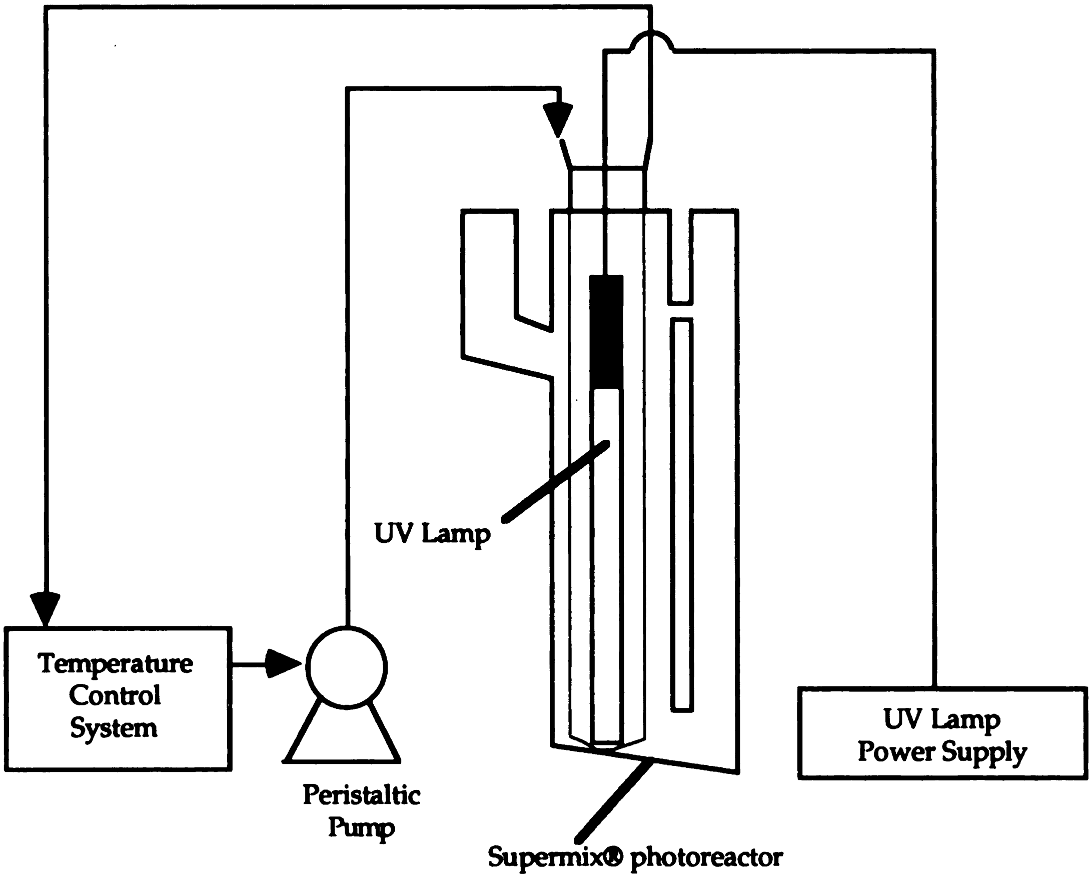


Figure 3.3 Experimental Scheme

To measure the pH in the solution in the reactor a pH electrode was located at the sampling port. To maintain the required pH in the reactor sodium hydroxide or sulfuric acid were, when necessary, introduced through tubing into the bottom of the smaller chamber of the reactor.

Air or pure oxygen were bubbled into the bottom of the smaller chamber through Teflon® tubing.

3.1.4 pH control system

A pH meter (Model 720 Laboratory Instrument, Orion Research Incorp., Boston, MA) connected to a pH probe (Model 91-16 Orion Research Incorp., Boston, MA) a semi-micro pH electrode with a length of 180 mm and body diameter of 6 mm were used to measure pH in the reactor.

3.1.5 High Performance Liquid Chromatograph

A Gilson high performance liquid chromatograph (HPLC) (Middleton, WI) equipped with two model 303 piston pumps, a 802B manometric module, 811 dynamic mixer, 116 UV detector, 231 auto-sampling injector, and 401 dilutor was used for the 2-chlorophenol analyses. A C-18 PR column (Whatman, Clifton, NJ) was used for the chromatographic separations. The C-18 column has a length of 235 mm, O.D. of 7.94 mm, I.D. of 4.70 mm, void volume of 2.38 ml, and the particle size of the packing was 5 µm. A mobile phase consisting 50% acetonitrile and 50% of 1% phosphorus acid in water was used. The flow rate was 1.5 ml/min and a sample volume of 20 µl was used. The UV detector was set at 230 nm. The retention time for the peak of 2-chlorophenol was 3.6 min.

All the samples containing titanium dioxide will be filtrated through 0.2 µm or 0.22 µm filters before analyzing by HPLC.

3.1.6 Spectrophotometer

A UV-visible recording spectrophotometer (Model UV 160, Shimadzu corp., Kyoto, Japan) was used to measure the absorbance of the filtering solution and for the actinometry. 1 cm pathlength cells (from Spectrocell corp., Oreland, PA.) were used for these determinations.

3.1.7 Sample collection

A sampling tube located at the bottom of the smaller chamber in the Supermix® reactor was used for sample collection. A 15 to 20 ml sample was collected and filtered through 0.2 µm (Scientific resources Inc., North Brunswick, NJ., and Gelman Science, Ann Arbor, MI.) or 0.22 µm pore size filter (Millipore Products Division, Bedford, MA.).

3.1.8 Nonlinear fit computer program

Systat ver. 5.2.1 for Macintosh was used as the nonlinear fit program in this study.

3.2 Experiments:

3.2.1 Materials

Acetonitrile and ferrous chloride were purchased from EM Science, Gibbstown, NJ. Ferric sulfate, hydrogen peroxide, and 2-chlorophenol were purchased from Sigma Chemical Co., St. Louis, MO. Sodium bicarbonate, sodium hydroxide, sulfuric acid, and pH 7 calibration buffer solution were obtained from J.T. Baker Inc., Phillipsburg NJ. Methanol was purchased from Baxter Healthcare Corp., Muskegon, MI. Sodium carbonate was purchased from Mallinckrodt Inc., Paris, Kentucky. 1,10-phenanthroline was purchased from Aldrich Chem. Co., Milwaukee., WI. Phosphoric acid, and potassium dichromate were obtained from Mallinckrodt Chemical Works, St. Louis, MO. pH 4 calibration buffer solution was purchased from Baxter Healthcare Corp., McGraw Park, IL. The photocatalyst Titanium Dioxide P25 was obtained from Degussa Corp., Ridgefield Park, NJ. It consists mainly of anatase. It has an average primary particle size 30 nm, surface area 50 m^2/g, and pH_{zpc} 6.3. P25 contains some impurities such as Al_2O_3 (<0.3%), SiO_2 (<0.2%), Fe_2O_3 (<0.01%), and HCl (<0.3%).

3.2.2 Chemical preparations

Chemical and solvents were of reagent grade and used without further purification. Stock solutions of 2-chlorophenol (10000 ppm), sodium bicarbonate (6.875×10^{-3} M), ferrous chloride (5.5×10^{-3} M), potassium dichromate (1×10^{-2} M), ferric sulfate (2×10^{-1} M), $K_2C_2O_4$ (1.2 M), sulfuric acid (1×10^{-1} M), and sodium hydroxide (1×10^{-2} M), were prepared and used in the same day. All solutions were prepared by dissolving the appropriate amount of chemical in deionized water.

3.2.3 Standard calibration curve

Five 2-chlorophenol standards (1 to 10 ppm) were used to prepare calibration curve for HPLC. A calibration curve was prepared for each experiment by plotting peak area vs. 2-chlorophenol concentration.

3.2.4 pH calibration

The pH meter was calibrated using two buffer solutions.

3.2.5 Batch experiments-UV/Titanium dioxide system

The experimental conditions used in the experiments were as follows:

Volume of solution	275 ml
TiO_2 concentration	1 g/L
2-chlorophenol concentration	10 ppm
Gas flow rate	175 ml/min

After the solution was placed in the reactor, recycling was started. Gas was bubbled into reactor, when required. The suspension was stored one hour in the dark before illumination to allow a sorption equilibrium between catalyst and 2-chlorophenol to be achieved.

The pH was adjusted before the photolysis was commenced. Temperature was controlled over the entire irradiation period by circulating cooling water to maintain a temperature of approximately 300±2 K.

A light intensity of 3 mW/cm^2 was used during experiments unless otherwise indicated.

3.2.6 Batch experiments-UV/Titanium dioxide/Hydrogen peroxide system

The reaction solutions were prepared as described in section 3.2.5. The desired amount of hydrogen peroxide was added to the reactor immediately before the UV light was turned on.

A series of experiments were conducted using different hydrogen peroxide concentrations (0.001, 0.050, 0.0250 M) without TiO_2 at equilibrium pH to determine the effect of H_2O_2 on 2-chlorophenol degradation.

3.2.7 Effect of pH

A series of experiments at an initial pH of 3.6, 5, 6.5, 8, or 10 were conducted using UV/Titanium dioxide system and UV/Titanium dioxide/Hydrogen peroxide system. In these experiments sulfuric acid or sodium hydroxide were added to adjust the pH to the desired value.

3.2.8 Effect of light intensity

A series of experiments at various light intensities (100%, 70%, 58%, or 35% lamp output) were conducted using UV/Titanium dioxide system and UV/Titanium dioxide/Hydrogen peroxide system. In these experiments a potassium dichromate solution containing 3% sodium carbonate was used as a filter solution to decrease the light intensity. This solution was cycled through the cooling jacket in the photoreactor.

3.2.9 Potassium ferrioxalate actinometry

The potassium ferrioxalate actinometer developed by Parker and Hatchard and Parker (33) was used to measure light intensity. Fe^{2+} was determined by the phenanthroline method (34). The net reaction is the following (35):

$$2Fe^{3+} + C_2O_4^{\,2-} \xrightarrow{h\nu} 2Fe^{2+} + 2CO_2 \tag{44}$$

The Fe^{2+} is subsequently determined via spectrophotometric determination of its phenanthroline complex at $5100\,\mathring{A}$. Fe^{3+} forms only a weak complex with phenanthroline which is transparent at $5100\,\mathring{A}$.

3.2.10 Effect of illuminated method

Two different illumination methods were used. One is referred to as the continuous method, the other is referred to as the intermittent method.

The continuous method was used unless otherwise indicated. In these experiments the UV light was switched on, and was not turned off until the end of this experiment.

For the intermittent method the UV power was turned on for 2 minutes then turned off for 3 minutes. Sample collection was during the dark period.

3.2.11 Effect of oxygen concentration

A series of experiments were conducted by bubbling air or pure oxygen into the reactor containing titanium dioxide or titanium dioxide with hydrogen peroxide. Experiments were also conducted without any bubbling.

3.2.12 Effect of Fe^{2+}

A series of experiments were conducted in 1×10^{-4} M ferrous chloride. Ferrous chloride was put into reactor at least one hour before turning on the UV light or adding hydrogen peroxide.

3.2.13 Buffer system

A series of experiments were conducted using different concentrations of sodium bicarbonate (0.5 and 2.5 mM) to find the relationship between the rate of decomposition of 2-chlorophenol and concentration of sodium bicarbonate in solution.

Chapter 4

Results and Discussion

The rate of the photocatalytic degradation of 2-chlorophenol depends upon various parameters including initial 2-chlorophenol concentration, pH, light intensity, temperature, , wavelength of incident light, mass and type of photocatalyst, and the design of photoreactor.

In this work the effect of pH, light intensity, concentration of hydrogen peroxide, oxygen, and ferrous ion on the rate of photocatalytic degradation of 2-chlorophenol was studied. The initial conditions used in the experiments conducted are summarized in Table 4.1.

Table 4.1 The initial conditions of experiments

No.	Experimental systems	Illuminated Method^a	pH Control^b	Other control parameters
1	UV/Air^c	Continuous	None^d	
2	UV/H_2O_2	Continuous	None	H_2O_2=0.001, 0.050, 0.250 M
3	UV/TiO_2^{e}	Continuous	None	
4	UV/TiO_2/Air	Continuous	None	
5	UV/TiO_2/O_2^{f}	Continuous	None	
6	UV/TiO_2/H_2O_2	Continuous	None	H_2O_2=0.001 M
7	UV/TiO_2/O_2	Intermittent	7.58	
8	UV/TiO_2/H_2O_2	Intermittent	7.19	H_2O_2=0.001 M
9	UV/TiO_2	Intermittent	3, 5, 6.5, 8, 10^g	
10	UV/ TiO_2	Continuous	8.20	$NaHCO_3$=2.5 mM
			7.51	$NaHCO_3$=0.5 mM
11	UV/TiO_2/Air	Continuous	3.6, 5, 6.5, 8, 10	$NaHCO_3$=0.5 mM
12	UV/TiO_2/Air/H_2O_2	Continuous	3.6, 5, 6.5, 8, 10	$NaHCO_3$=0.5 mM H_2O_2=0.001 M
13	UV/TiO_2/Air/Fe^{2+}^{h}	Continuous	6.87	$NaHCO_3$=0.5 mM Fe^{2+}=0.0001 M
14	UV/TiO_2/Air/Fe^{2+}/ H_2O_2	Continuous	6.93	$NaHCO_3$=0.5 mM Fe^{2+}=0.0001 M H_2O_2=0.001 M
15	UV/TiO_2/Air	Continuous Light intensity		$NaHCO_3$=0.5 mM
		100%	6.74	
		70%	6.84	
		58%	6.86	
		35%	6.92	
16	UV/TiO_2/Air/H_2O_2	Continuous Light intensity		$NaHCO_3$=0.5 mM H_2O_2=0.001 M
		100%	6.85	
		70%	6.87	
		58%	6.86	
		35%	6.96	

a: The illumination method is explained in section 3.2.11.

b: In this study pH was adjusted to desired value prior to illumination.

c: Flowrate of gas was 175 ml/min.

d: None means pH was not adjusted.

e: Concentration of TiO_2 was 1 g/l.

f: Flowrate of pure oxygen is 175 ml/min.

g: The pH was maintained at constant value in these experiments. In other experimental systems the reported value is the initial pH.

h: Initial concentration of Fe^{2+} is 0.1 mM.

The results of the experiments are described in following sections. The experimental data are given in Appendix A.

4.1 UV combined with air, H_2O_2, or TiO_2

4.1.1 UV/Air

Because air was bubbled into system, an experiment was conducted to determine how much 2-chlorophenol was lost due to volatilization. Approximately 5.3% of 2-chlorophenol was lost only due to volatilization in a two hour experiment (including in dark period). The dissolved oxygen concentration with bubbling air in the solution was 8.88 mg/l.

In an illuminated solution, the rate of 2-chlorophenol disappearance was slow. The loss of 2-chlorophenol after 60 minutes was approximately 10% (see Table A.1). If volatilization is considered, the net disappearance of 2-chlorophenol due to direct photolysis was about 4.7%. The pseudo first order rate constant including loss due to volatilization for the disappearance of 2-chlorophenol was 0.002 1/min.

The reason for bubbling air is to more closely simulate the conditions used in photocatalytic degradation experiments.

4.1.2 UV/H_2O_2

The effect of initial concentration of hydrogen peroxide on the degradation rate is shown in Figure A.2.

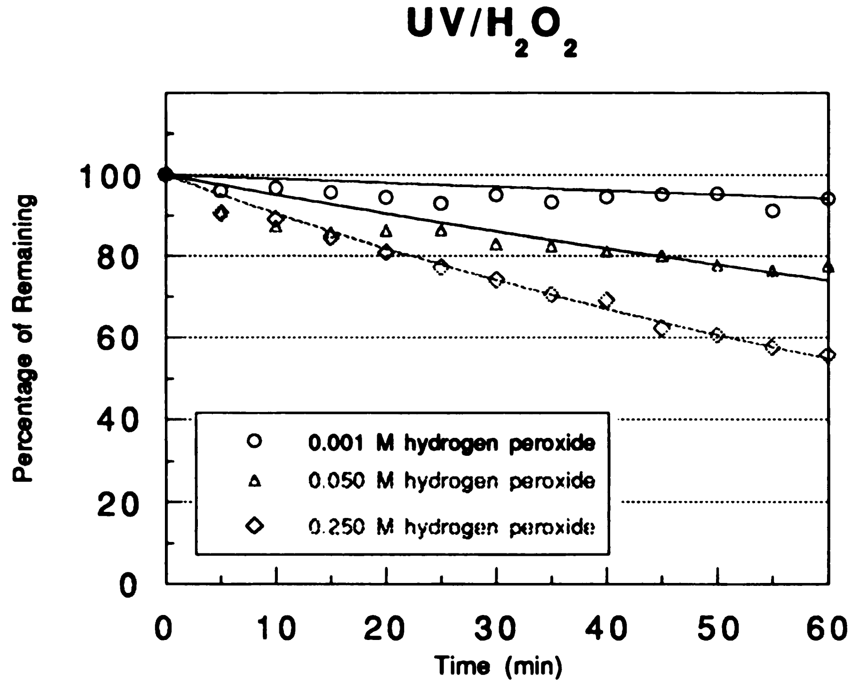


Figure A.2 2-chlorophenol decomposition in UV/H_2O_2 oxidation system

At an initial hydrogen peroxide concentration of 0.001, 0.050, and 0.250 M , 2-chlorophenol was decomposed 9%, 24%, and 45%, respectively, after 60 min illumination. The rate constant for the disappearance of 2-chlorophenol were 0.001, 0.005, and 0.010 1/min, respectively.

Because the UV produced by the lamp used in this study is not energetic enough to decompose hydrogen peroxide to ·OH radicals directly, the rate of 2-chlorophenol degradation in hydrogen peroxide solution is slow.

At 0.001 M hydrogen peroxide which was the concentration of hydrogen peroxide used in subsequent experiments, the rate of 2-chlorophenol degradation in hydrogen peroxide was not significantly different than that without hydrogen peroxide present.

4.1.3 UV/TiO_2

Figure A.3 shows the photodegradation for 2-chlorophenol in an UV/TiO_2 system. 96% of 2-chlorophenol was degraded within 60 min. and the $t_{1/2}$ for the degradation of 2-chlorophenol was 6.0 min. The first order rate constant for the degradation of 2-chlorophenol was 0.115 1/min.

As can be seen in Figure A.3 at time greater than 20 minute, the pseudo-first order kinetics does not fit the experimental data very well. This may be due to a decrease in the oxygen content of the suspension. Since if there is not enough oxygen to trap electrons excited into the conduction band then the accumulation of electrons in the TiO_2 particles will increase the recombination rate of electrons and holes and thus decrease the photodegradation rate.

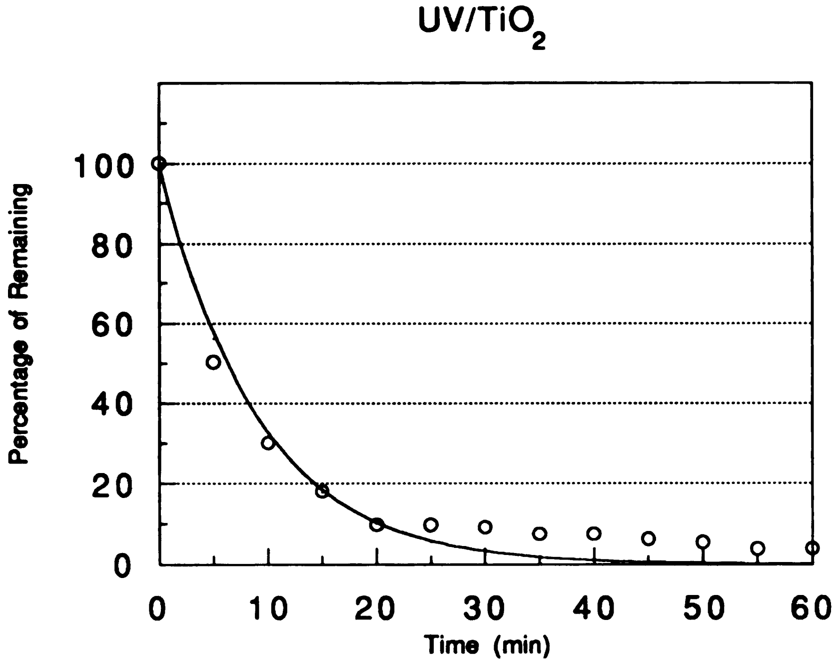


Figure A.3 Photodegradation of 2-chlorophenol in UV/TiO2 system.

The stoichiometry of the reaction is the following.

$$C_6H_4OHCl + 5.5O_2 \rightarrow 6CO_2 + 5H^+ + Cl^- \qquad (45)$$

Based on this stoichiometry one would expect in closed system 10 ppm of 2-chlorophenol would consume about 13.7 mg/l of oxygen. The initial concentration of oxygen in this study was 7.5 mg/l, so significant oxygen depletion will occur during the experiment. Thus in future experiments bubbling oxygen or air into the system was used to control the oxygen level in the suspension.

4.1.4 Comparison of UV radiation combined with air, H_2O_2, or TiO_2

From the experimental results shown in Figures A.1, A.2 and A.3, the effect of UV radiation, H_2O_2, and TiO_2 can be determined. It is concluded that

- The direct photolysis of 2-chlorophenol is very slow (see Figure A.1).
- The degradation rate increases with increasing hydrogen peroxide concentration, but the degradation rate is not proportional to the concentration of hydrogen peroxide.
- The photodegradation rate of 2-chlorophenol in the photocatalytic system is much faster (about 60 times) than that the rate of direct photolysis.
- The 2-chlorophenol degradation rates in the UV-Air and UV-0.001 M H_2O_2 are almost equal, i.e., the rate of reaction of 2-chlorophenol with H_2O_2 is not significant at low H_2O_2 concentration.

4.2 UV/TiO_2 combined with air or pure oxygen

4.2.1 UV/TiO_2/Air

In this experiment, air was bubbled into the reactor to maintain a constant oxygen concentration in UV/TiO_2 system. The result of this experiment is shown in Figure A.4.

99% of 2-chlorophenol was degraded during 35 min. and the $t_{1/2}$ was 5.5 min. The rate constant was 0.125 1/min.

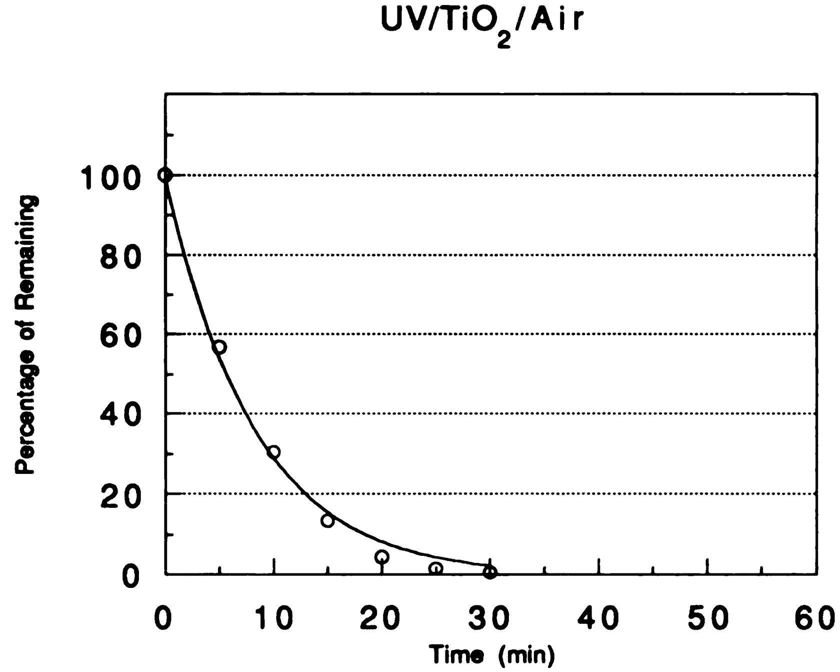


Figure A.4 Photodegradation of 2-chlorophenol in UV/TiO_2/Air system

Bubbling air into this system increased the reaction rate slightly suggesting that in the experiment described in the previous section oxygen depletion was occurring. No significant deviation from first order kinetics was observed in the later stages of this experiment.

4.2.2 UV/TiO_2/O_2

In this experiment, pure oxygen was bubbled into the UV/TiO_2 system to examine the effect of oxygen concentration on the reaction kinetics. The result of this experiment is shown in Figure A.5.

97% of 2-chlorophenol was degraded during 20 min. and the $t_{1/2}$ was 4.8 min. The rate constant was 0.145 1/min.

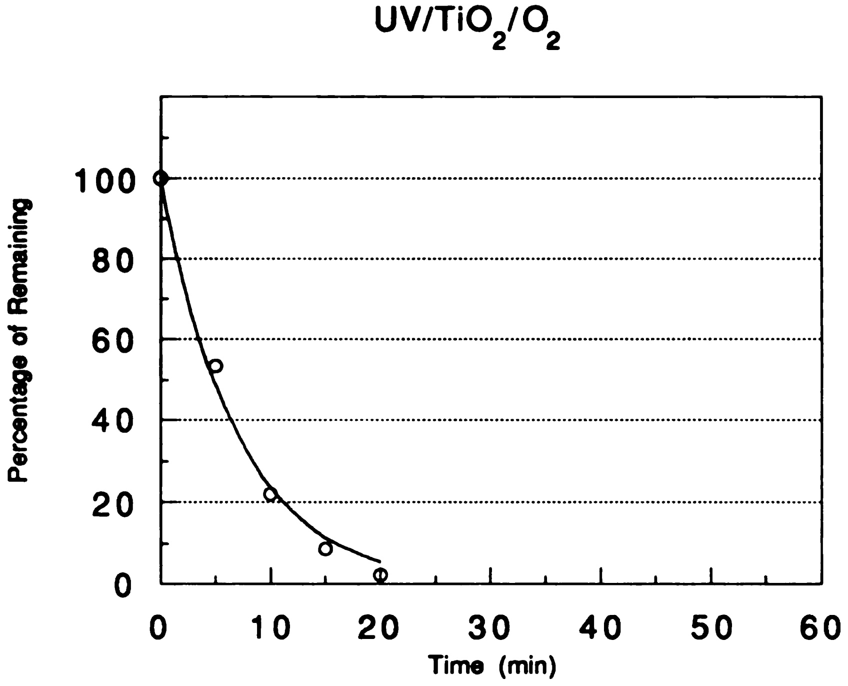


Figure A.5 Photodegradation of 2-chlorophenol in UV/TiO_2/O_2 system.

Bubbling pure oxygen into this system instead of air increased the reaction rate by 16%. The oxygen concentration in the solution with bubbling pure oxygen was 16.48 mg/l.

4.2.3 Effect of O_2 concentration on UV/TiO_2, UV/TiO_2/Air, and UV/TiO_2/O_2 system

A comparison of experimental results for the decomposition of 2-chlorophenol in UV/TiO_2, UV/TiO_2/Air, and UV/TiO_2/O_2 is presented in Figure 4.1.

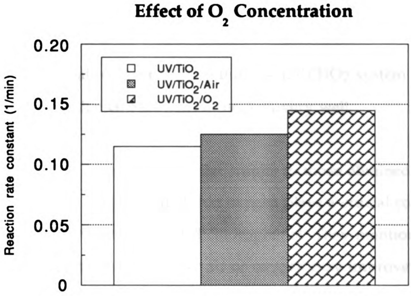


Figure 4.1 Effect of O_2 concentration on photodegradation of 2-chlorophenol in UV/TiO_2, UV/TiO_2/Air, and UV/TiO_2/O_2 system.

Our experiments show that while bubbling oxygen or air into the system does increase the rate of 2-chlorophenol degradation, but the extent of the increase is small.

From these studies on the effect of oxygen concentration of the degradation of 2-chlorophenol, the following conclusions can be made:

- Bubbling air into UV/TiO_2 system increased reaction rate by 9%.

- Bubbling pure oxygen, which increased the oxygen concentration in solution about two times compared to that when air was used, increased photocatalytic degradation rate by 26%. This shows that the reaction rate is not proportional to the concentration of oxygen in solution.

- With bubbling air or pure oxygen into the UV/TiO_2 system it was found that the first order kinetics can fit the data very well.

Al-Ekabi et al. (19) have found similar results to those obtained in our experiments. Their data indicated that oxygen plays a crucial role in the photocatalytic degradation of 2,4-dichlorophenol. They mentioned that introducing small bubbles of either air or oxygen may improve the mixing process inside the reactor and thus increase the reaction rate.

The adsorption of oxygen can be described by a simple Langmuir adsorption isotherm as follows:

$$\chi_{O_2} = \frac{K_o[O_2]}{1 + K_o[O_2]} \tag{46}$$

where χ_{O_2} is the fraction of total surface sites occupied by O_2 ($[O_2]_{surf} = \chi_{O_2}[O_2]$ and K_o is the surface binding constant for O_2 on Degussa P25 TiO_2. K_o was found to be $13 \pm 7 \times 10^4$ M^{-1} (22).

From our results, χ_{O_2} were 0.973 and 0.985 for bubbling air and pure oxygen, respectively. These indicate that the surface sites were almost occupied by oxygen.

In our experiments, we assume that conduction band electrons are scavenged by O_2 or by an alternate electron acceptor (e.g., H_2O_2) while h^+_{VB} has a slightly longer lifetime with respect to electron transfer (*i.e.*, fast recombination is no longer possible). During this longer lifetime, the holes are scavenged by the hydroxylated surface of TiO_2 to produce ·OH radicals (36).

Figure 4.2 shows the photocatalytic degradation rate of 2-chlorophenol is a nonlinear function of oxygen concentration in solution. A simple Langmuir adsorption can be used to fit the experimental data (r^2=0.995).

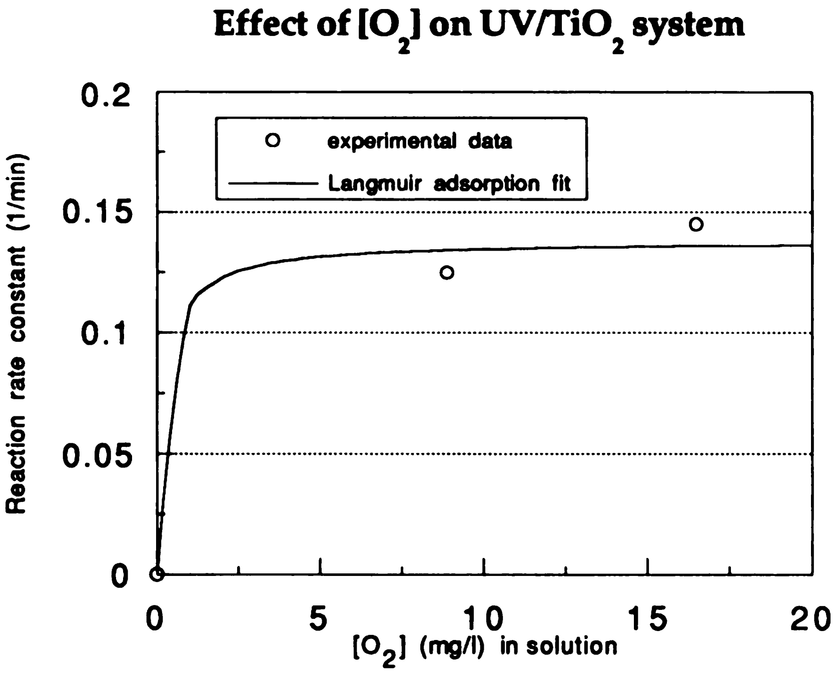


Figure 4.2 Effect of oxygen concentration on the photocatalytic degradation rate of 2-chlorophenol.

4.3 UV/TiO_2 combined with H_2O_2

4.3.1 UV/TiO_2/H_2O_2

In this experiment 0.001 M of hydrogen peroxide was added to the UV/TiO_2 system. The result of this experiment is shown in Figure A.6.

99% of 2-chlorophenol was degraded during 20 min. and the $t_{1/2}$ was 2.9 min. The rate constant was 0.235 1/min.

The reason why the reaction rate is so high is that hydrogen peroxide may trap electrons in the conduction band (see reaction 23 in section 2.2). It also produces oxygen which reacts with conduction band electrons.

Furthermore hydrogen peroxide can react with holes generated by titanium dioxide to produce $HO_2\cdot$ which can react with 2-chlorophenol and degrade it.

The results of this experiment are in agreement with those of Auguliaro et al. (30) which showed that the rate of photocatalytic degradation of phenol was increased in the presence of hydrogen peroxide. Tanaka et al. (28) have also shown that the addition of hydrogen peroxide to a TiO_2 suspension resulted in an increase in the rate of photocatalytic degradation of TCE.

4.3.2 Comparison of UV/H_2O_2 and UV/TiO_2/H_2O_2 system

From Figure A.2 and Figure A.6 the reaction rate in UV/TiO_2/H_2O_2 system is about 200 times faster than that in UV/H_2O_2 system. It can be concluded that the addition of hydrogen peroxide to a TiO_2 suspension can improve the efficiency of the photocatalytic degradation of pollutants.

4.4 Photocatalytic systems under intermittent illumination method

4.4.1 UV/TiO_2/O_2 system under intermittent method

The use of utilizing intermittent illumination was investigated as the reaction time of continuous method in UV/TiO_2/Air, UV/TiO_2/O_2, or UV/TiO_2/H_2O_2 system was too short to allow time to collect and process samples. By using the intermittent method it was possible to collect samples during the period when the sample was not illuminated. The results of an experiment conducted using intermittent illumination are present in Figure A.7.

81% of 2-chlorophenol was degraded during 26 minutes of illumination time and the $t_{1/2}$ was 12.4 min. The rate constant for the degradation of 2-chlorophenol was 0.056 1/min which is 160% less than that obtained using the continuous method of illumination (see Figure 4.3).

Furthermore, there was considerable scatter in the experimental data (see Figure A.7).

4.4.2 UV/TiO_2/H_2O_2 under intermittent method

In this experiment the effect of hydrogen peroxide in UV/TiO_2 system under intermittent method was studied. Figure A.8 shows the degradation of 2-chlorophenol during this experiment.

After 26 minutes of illumination, 85% of 2-chlorophenol was degraded, and the $t_{1/2}$ for the disappearance of 2-chlorophenol was 8.1 min. The rate constant for the degradation of 2-chlorophenol was 0.086 1/min.

The results indicate that the rate constant is 170% smaller than that in the same system using continuous method (see Figure 4.3). Also there was considerable scatter in the experimental data (see Figure A.8).

4.4.3 Effect of intermittent method on UV/TiO_2/O_2 and UV/TiO_2/H_2O_2 system

The results of the photodegradation of 2-chlorophenol in UV/TiO_2/O_2 and UV/TiO_2/H_2O_2 system under intermittent method show that

- The reaction rate is slower under intermittent illumination than that under continuous illumination. This suggests that the UV lamp needs time to reach full power after it is turned on.

- Under intermittent illumination the photodegradation is not well described as first order kinetics. This is consistent with the fact that the light intensity varies during the time which UV lamp is turned on.

A comparison of the photocatalytic degradation of 2-chlorophenol in $UV/TiO_2/H_2O_2$ and $UV/TiO_2/O_2$ system under different illumination method is shown in Figure 4.3.

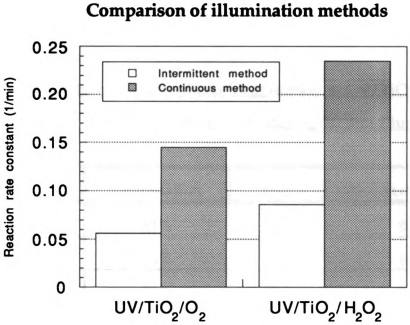


Figure 4.3 Comparison of different illumination methods in same oxidation system.

These experiments indicate that intermittent illumination is unsuitable as a method to slow down the reaction rate.

4.5 UV/TiO_2 under intermittent method and pH control

The other purpose of utilizing intermittent method is that it is easier than continuous method to control pH at certain level during photocatalytic degradation. When the UV lamp was off acidic and basic solution were added to maintain certain pH value in solution.

In this experiment pH 3, 5, 6.5, 8, and 10 were controlled to perform this photooxidation reaction. The results of these experiments are shown in Figure A.9, A.10, A.11, A.12, and A.13. The results are present in Table 4.2.

Table 4.2 The results of 2-chlorophenol degradation in UV/TiO_2 system under intermittent method at different pH during 26 min illumination

pH	degradation	$t_{1/2}$	rate constant (1/min)
3	84%	6.4	0.109
5	90%	8.5	0.082
6.5	86%	10.3	0.067
8	86%	10.8	0.064
10	52%	26.7	0.026

The fitting results were not good due to intermittent illumination, but constant pH was maintained during the experiment. Because intermittent illumination is not a good method to use, for other experiments pH was not held at a constant value.

4.6 UV/TiO_2 under buffer system

Since intermittent illumination method cannot be used to slow down the degradation rate, an alternative method to slow down the reaction is to use a bicarbonate buffer.

To determine the effect of bicarbonate ion concentration on the reaction kinetics experiments, a number of experiments were conducted in 2.5 and 0.5 mM sodium bicarbonate solution.

As seen in Figure A.14 and A.15, 74% and 92% of 2-chlorophenol was degraded during 60 min in 2.5 mM and 0.5 mM $NaHCO_3$ solution, respectively. The $t_{1/2}$ for the disappearance of 2-chlorophenol was 28.9 and 11.4 min, and the rate constant for the degradation of 2-chlorophenol was 0.024, and 0.061 1/min, respectively.

These experiments indicate that

- The higher the concentration of sodium bicarbonate the lower the reaction rate. HCO_3^- is a ·OH radical scavenger, and the rate constant for the reaction between HCO_3^- and ·OH is $8.5\times10^6\ M^{-1}s^{-1}$ (37). The addition of bicarbonate could slow down the reaction as ·OH radicals generated are scavenged by HCO_3^-.

- All subsequent experiments were conducted with 0.5 mM $NaHCO_3$ buffer solutions as this concentration is sufficient to slow down the reaction to the desired degree.

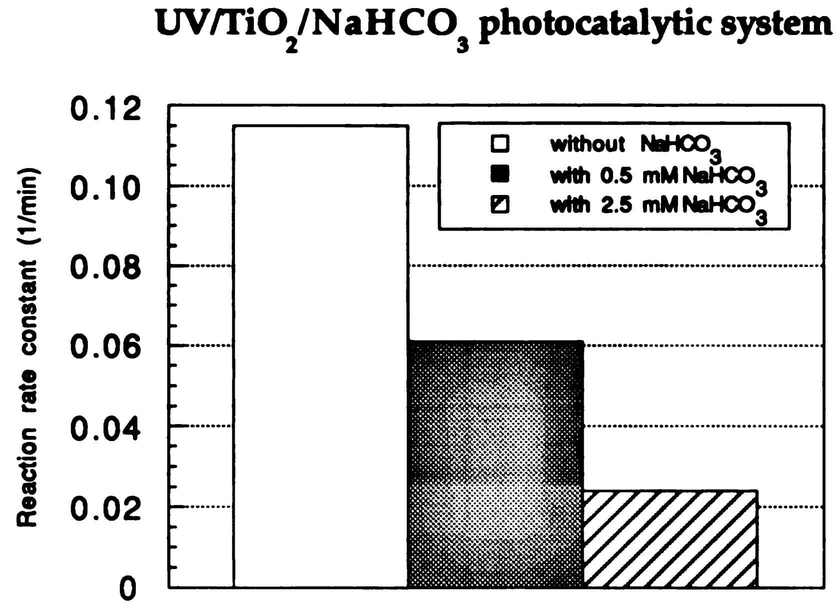


Figure 4.4 The effect of HCO_3^- on the photocatalytic degradation rate of 2-chlorophenol.

4.7 Effect of pH on photocatalytic systems

4.7.1 UV/TiO_2/Air/$NaHCO_3$ with and without H_2O_2 under pH control

In these experiments the initial pH was adjusted to 3.6, 5, 6.5, 8, and 10. The results at different initial pH value with and without hydrogen peroxide are shown in Figure A.16, A.17, A.18, A.19, and A.20. The results are summarized in Table 4.3. The effect of initial pH on rate constants is shown in Figure 4.5.

Table 4.3 The results of 2-chlorophenol degradation in $UV/TiO_2/Air/NaHCO_3$ with and without H_2O_2 at different initial pH

$UV/TiO_2/Air/NaHCO_3$ with H_2O_2			
Initial pH	degradation	$t_{1/2}$	rate constant (1/min)
3.6	98%	6.5	0.106
5	99%	6.4	0.108
6.5	93%	8.2	0.085
8	96%	8.9	0.078
10	73%	19.3	0.036

$UV/TiO_2/Air/NaHCO_3$ without H_2O_2			
Initial pH	degradation	$t_{1/2}$	rate constant (1/min)
3.6	88%	14.7	0.047
5	97%	10.5	0.066
6.5	99%	9.9	0.070
8	94%	11.4	0.061
10	69%	3.1	0.030

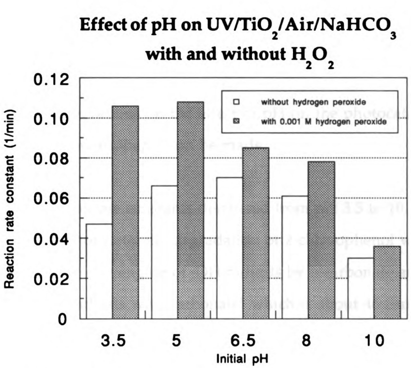


Figure 4.5 Effect of initial pH on UV/TiO2/Air/NaHCO3 system with and without H2O2.

The results show that without hydrogen peroxide the highest reaction rate was observed when the initial pH was 6.5.

Similarly, the result also shows that when hydrogen peroxide was added the highest reaction rate was observed in the experiment when the initial pH was 5.

4.7.2 Effect of pH on UV/TiO2/Air/NaHCO3 with and without H2O2

Before discussing the effect of pH on the photocatalytic degradation rate of 2-chlorophenol, some information needs to be reviewed. The pKa1 and pKa2 of H_2CO_3 at 25 °C are 6.3 and 10.3, respectively. The rate constants from Buxton et al. for the reaction of ·OH and HCO_3^-, and for the reaction of ·OH and CO_3^{2-} are 8.5×10^6 $M^{-1}s^{-1}$ and 3.9×10^8 $M^{-1}s^{-1}$, respectively (37).

The following observations on the effect of pH on the photocatalytic degradation of 2-chlorophenol can be made:

- The difference of rate constants decreased from pH 3.5 to 10. The decrease in the rate of photocatalytic degradation of 2-chlorophenol with pH can be attributed to the scavenging of ·OH radicals by bicarbonate and the rate of reaction (·OH radicals with carbonate) which is about 46 times higher than that with bicarbonate. At high pH the photocatalytic degradation rate is much slower.

- At lower pH such as pH 3.5 the photodegradation was slow without hydrogen peroxide. The decrease in the rate seen at low pH can be attributed to low concentration of OH^- ions, because OH^- ions react with holes to generate ·OH radicals. D'Oliveira et al. found the similar decrease in the rate of photocatalytic degradation of 2- and 3-chlorophenol in TiO_2 aqueous suspensions (23).

- From Figure 4.5 at an initial pH in the range 5-8, no significant change of photocatalytic degradation rate of 2-chlorophenol was observed.

4.8 Effect of Fe^{2+} on photocatalytic systems

4.8.1 UV/TiO_2/Air/$NaHCO_3$/Fe^{2+} with and without H_2O_2

In this experiment the effect of the addition of ferrous chloride on UV/TiO_2 system was studied. The results of this experiment at equilibrium pH (6.9) with and without hydrogen peroxide are shown in Figure A.21.

Without hydrogen peroxide addition 87% of 2-chlorophenol was degraded in 35 min., the $t_{1/2}$ for the disappearance of 2-chlorophenol was 15.8 min. , and the rate constant was 0.044 1/min. With 0.001 M hydrogen peroxide addition, 91% of 2-chlorophenol was degraded, the $t_{1/2}$ for the disappearance of 2-chlorophenol was 10.8 min. , and the rate constant for the degradation of 2-chlorophenol was 0.064 1/min.

The reason to add ferrous ion to the system is that in this experiment ·OH radicals could be generated from photooxidation, and produced through chain reactions by Fenton or Fenton-like reactions. Hydrogen peroxide in this system could be generated as result of the photocatalytic process (see reactions in chapter 2).

4.8.2 Effect of adding ferrous chloride

The comparison of the rate constants for the photocatalytic degradation of 2-chlorophenol with and without ferrous chloride addition is shown in Figure 4.6. The following observations can be made:

- The reaction rate constants in UV/TiO2/Air/NaHCO3/Fe^{2+} system are smaller than those in UV/TiO2/Air/NaHCO3 system.

- The addition of hydrogen peroxide enhances the photocatalytic degradation rate.

- The addition of ferrous chloride did not increase the degradation rate.

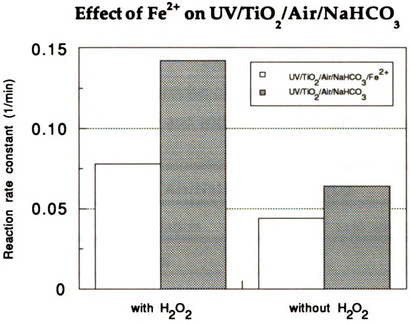


Figure 4.6 Effect of Fe^{2+} on UV/TiO_2/Air/$NaHCO_3$ with and without H_2O_2.

4.9 Effect of light intensity on photocatalytic systems

4.9.1 UV/TiO_2/Air/$NaHCO_3$ with and without H_2O_2 under different light intensity

To study the effect of light intensity on the reaction kinetics a number of experiments were conducted under different light conditions. The results of these experiments are shown in Figure A.22, A.23, A.24, and A.25. These results are summarized in Table 4.4, and Figure 4.7.

Table 4.4 The results of 2-chlorophenol degradation in UV/TiO_2/Air/$NaHCO_3$ with and without H_2O_2 at different light intensity

UV/TiO_2/Air/$NaHCO_3$ with H_2O_2			
light intensity	degradation	$t_{1/2}$	rate constant (1/min)
100%	99%	4.9	0.142
70%	96%	7.5	0.093
58%	92%	9.0	0.077
35%	73%	14.4	0.048
UV/TiO_2/Air/$NaHCO_3$ without H_2O_2			
light intensity	degradation	$t_{1/2}$	rate constant (1/min)
100%	97%	8.9	0.078
70%	93%	11.2	0.062
58%	92%	12.4	0.056
35%	81%	15.1	0.046

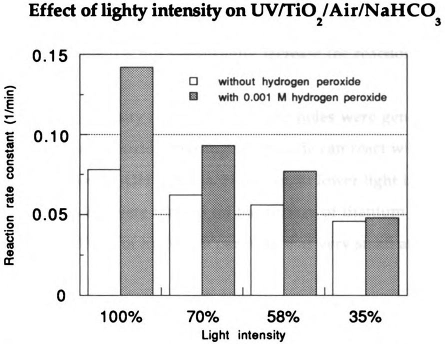


Figure 4.7 Effect of light intensity on UV/TiO_2/Air/$NaHCO_3$ system with and without H_2O_2.

4.9.2 Effect of light intensity

The following observations can be made of the influence of light intensity on the reaction kinetics.

- The higher the light intensity the higher the reaction rate.
- The difference between the system with and without adding hydrogen peroxide of rate constants decreased as light intensity decreased.

- At 100% of light intensity the effect of adding hydrogen peroxide was significant. However, at the 35% of light intensity the addition of hydrogen peroxide did not significantly increase the reaction rate.

- At higher light intensity more electrons and holes were generated on the surface of titanium dioxide. Hydrogen peroxide can react with those electrons to generate ·OH radicals. However, at lower light intensity, fewer electrons and holes were formed on the surface of titanium dioxide. The effect of the addition of hydrogen peroxide was very small at 35% of light intensity.

Figure 4.8 shows without the addition of hydrogen peroxide the rate of 2-chlorophenol photodegradation is a nonlinear function of light intensity. However, when hydrogen peroxide was added the photocatalytic degradation rate is a linear function of light intensity (r^2=0.997). A square root function can be used to fit the data from the experiments without hydrogen peroxide addition (r^2=0.999).

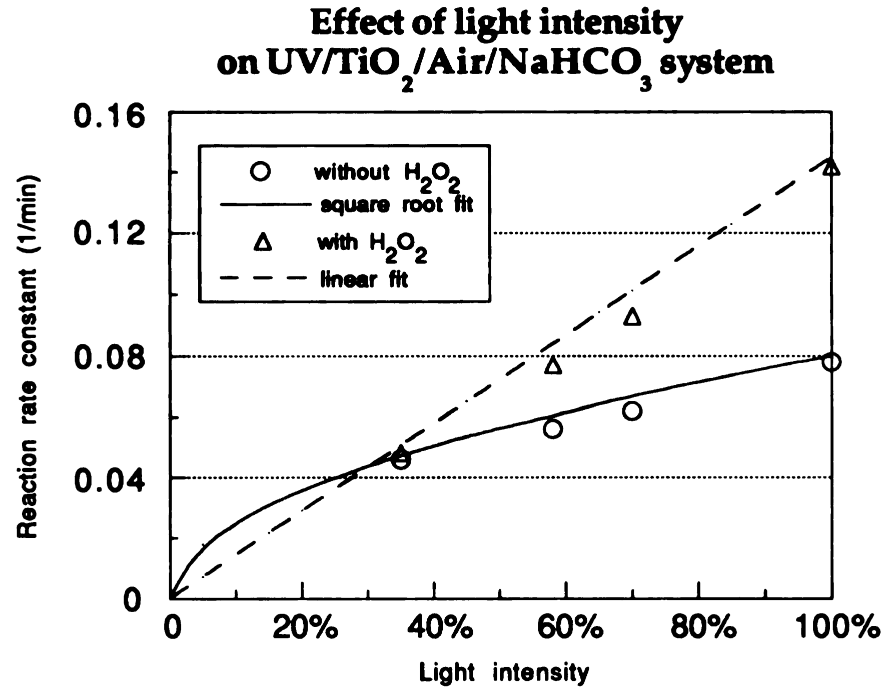


Figure 4.8 Effect of light intensity on the rate of photocatalytic degradation of 2-chlorophenol with and without adding hydrogen peroxide addition (where 100%=3 mW/cm^2).

Al-Sayyed et at. (18) and D'Oliveira et al. (23) have observed a similar dependence of light intensity for the photocatalytic degradation of 4-chlorophenol, and 2- and 3-chlorophenol, respectively.

The initial quantum yield for the photocatalytic degradation of 2-chlorophenol without hydrogen peroxide addition at different light intensity is shown in Table 4.5. These calculations assume a reflectivity of 0.15 (23). The calculations shown are lower limits for the quantum yield, since no allowance was made for scattering by the solid particles.

Table 4.5 Initial quantum yield of 2-chlorophenol

Light intensity	Initial quantum yield
100%	2.6×10^{-3}
70%	2.9×10^{-3}
58%	3.1×10^{-3}
35%	4.3×10^{-3}

Al-Sayyed et al. (18) have present a initial quantum yield of 2-chlorophenol was 0.013 and 0.009 at the 2 and 50 mW/cm^2 light intensity, respectively.

D'Oliveira et al. (23) have shown a initial quantum yield of 2-chlorophenol was 6.9×10^{-3} at a radiant flux of 50 mW/cm^2 absorbed by TiO_2.

4.10 Summary of reaction rate constants

A summary of the experimental rate constants obtained in this study is presented in Table A.25.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

From the results of this study, the following conclusions can be made:

1. The reaction rate for photocatalytic degradation of 2-chlorophenol is fast.

2. The addition of hydrogen peroxide can enhance the photocatalytic degradation rate of 2-chlorophenol significantly under appropriate conditions. The enhancement in the rate in the presence of hydrogen peroxide is greatest at low pH and under intense illumination.

3. Bubbling air or pure oxygen into UV/TiO_2 system does not increase the rate of degradation of 2-chlorophenol to a great extent.

4. The intermittent illumination method is not a good method to study the photocatalytic reaction.

5. Bicarbonate and carbonate inhibit the rate of photocatalytic degradation of 2-chlorophenol.

6. The addition of ferrous chloride inhibits the photocatalytic degradation rate of 2-chlorophenol.

7. The optimum pH range to operate the photocatalytic degradation without adding hydrogen peroxide is between 5 and 8. With the addition of hydrogen peroxide the optimum pH range for the photocatalytic degradation of 2-chlorophenol is between 3.6 and 5.

5.2 Recommendations

In order to understand more detail about the mechanism, more experiments should be considered in the further studies:

1. The effect of process parameters such as concentration of 2-chlorophenol, concentration of Fe^{2+}, concentration of reaction released products like chloride, concentration of TiO_2, other wavelength of source light and other effects such as oxygen concentration on the reaction kinetics should be studied.

2. The reaction pathway and intermediate products, by-products, and products should be studied.

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APPENDIX A

Experimental data

Table A.1 Data of Figure A.1 from experimental system No. 1

Time (min)	Percentage of Remaining	Fitting value
0	100.00	100.00
5	97.80	99.00
10	95.22	98.02
15	98.67	97.04
20	97.84	96.08
25	91.50	95.12
30	91.68	94.18
35	95.13	93.24
40	88.89	92.31
45	91.90	91.39
50	93.38	90.48
55	95.41	89.58
60	91.54	88.69

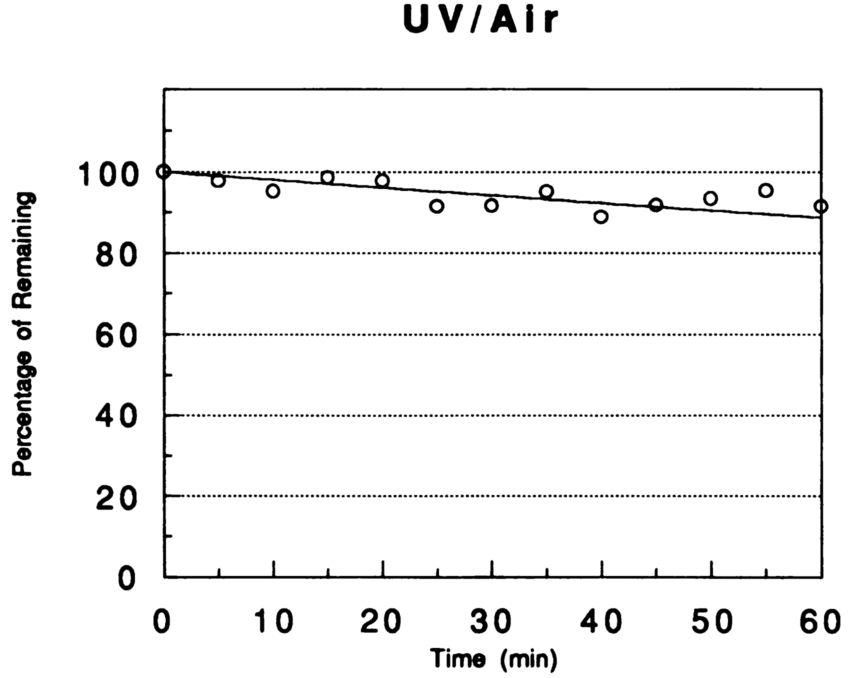

Figure A.1 Photodegradation of 2-chlorophenol under UV light

Table A.2 Data of Figure A.2 from experimental system No. 2

	0.001 M H_2O_2		0.050 M H_2O_2		0.250 M H_2O_2	
Time (min)	Percentage of Remaining	Fitting value	Percentage of Remaining	Fitting value	Percentage of Remaining	Fitting value
0	100.00	100.00	100.00	100.00	100.00	100.00
5	96.01	99.50	90.95	97.53	90.59	95.12
10	96.73	99.00	87.47	95.12	89.14	90.48
15	95.67	98.51	85.82	92.77	84.62	86.07
20	94.40	98.02	86.27	90.48	80.90	81.87
25	92.91	97.53	86.34	88.25	77.22	77.88
30	95.02	97.04	82.91	86.07	74.07	74.08
35	93.25	96.56	82.46	83.95	70.57	70.47
40	94.45	96.08	81.03	81.87	69.06	67.03
45	95.18	95.60	80.04	79.85	62.33	63.76
50	95.34	95.12	77.66	77.88	60.64	60.65
55	91.17	94.65	76.40	75.96	57.61	57.69
60	94.16	94.18	77.52	74.08	55.71	54.88

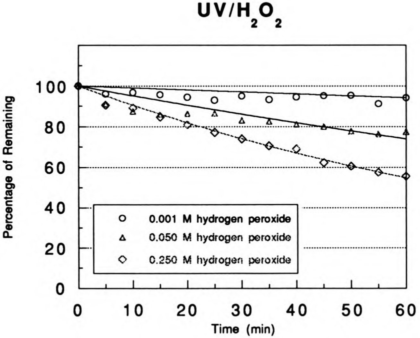

Figure A.2 2-chlorophenol decomposition in UV/H_2O_2 oxidation system

Table A.3 Data of Figure A.3 from experimental system No. 3

Time (min)	Percentage of Remaining	Fitting value
0	100.00	100.00
5	50.38	56.27
10	30.16	31.66
15	18.11	17.82
20	9.81	10.03
25	9.77	5.64
30	9.18	3.17
35	7.52	1.79
40	7.53	1.01
45	6.25	0.57
50	5.48	0.32
55	3.80	0.18
60	3.93	0.10

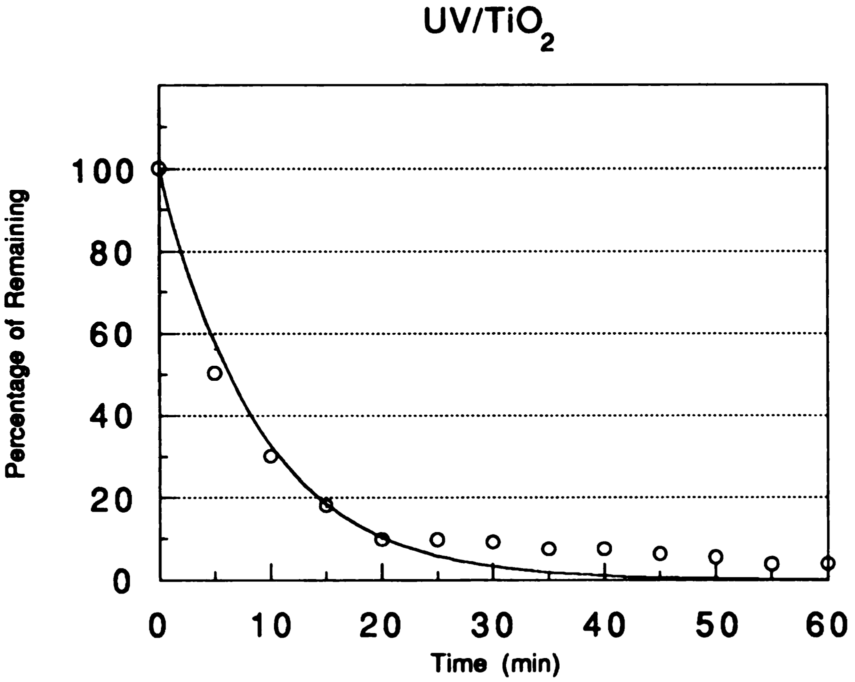

Figure A.3 Photodegradation of 2-chlorophenol in UV/TiO2 system.

Table A.4 Data of Figure A.4 from experimental system No. 4

Time (min)	Percentage of Remaining	Fitting value
0	100.00	100.00
5	56.82	53.53
10	30.45	28.65
15	13.48	15.34
20	4.51	8.21
25	1.60	4.39
30	0.63	2.35

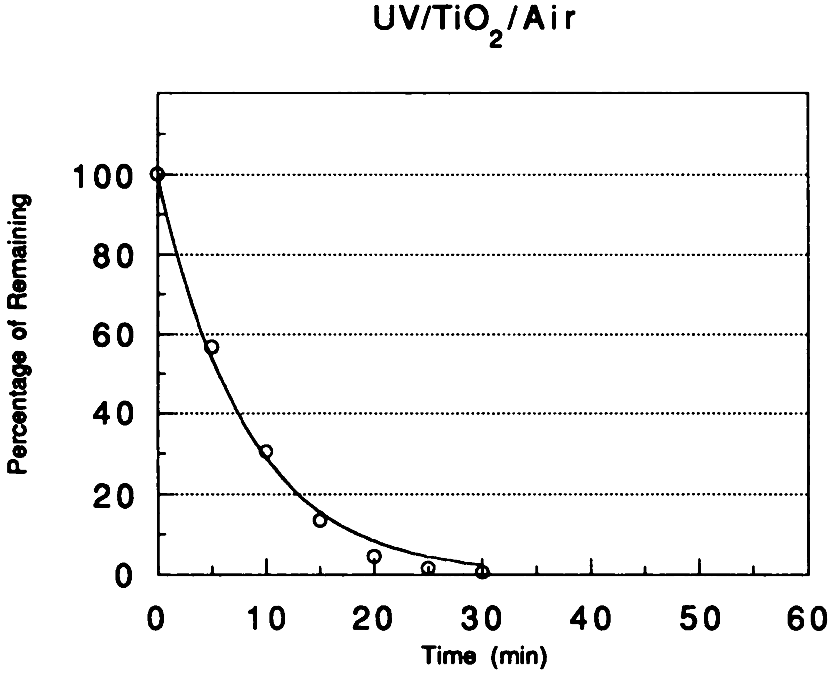

Figure A.4 Photodegradation of 2-chlorophenol in UV/TiO_2/Air system

Table A.5 Data of Figure A.5 from experimental system No. 5

Time (min)	Percentage of Remaining	Fitting value
0	100.00	100.00
5	53.41	48.43
10	22.03	23.46
15	8.75	11.36
20	2.24	5.5

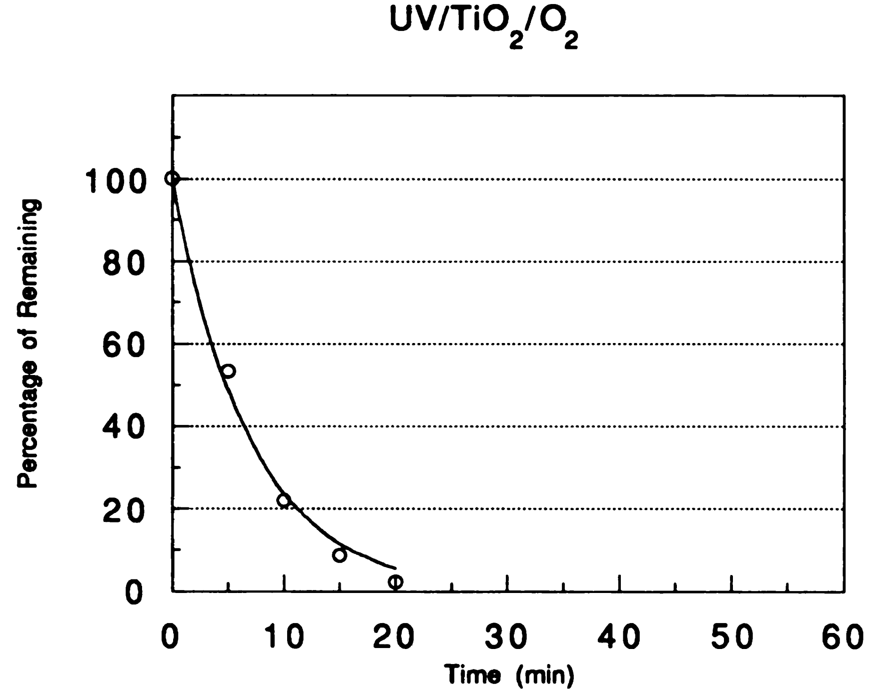

Figure A.5 Photodegradation of 2-chlorophenol in UV/TiO2/O2 system.

Table A.6 Data of Figure A.6 from experimental system No. 6

Time (min)	Percentage of Remaining	Fitting value
0	100.00	100.00
5	31.57	30.88
10	8.59	9.54
15	2.77	2.95
20	0.73	0.91

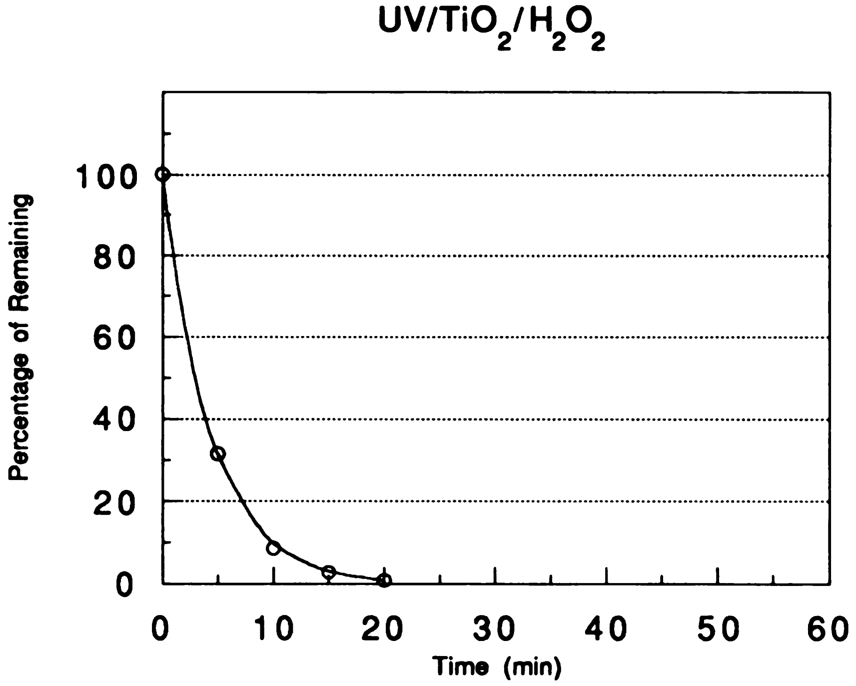

Figure A.6 Photodegradation of 2-chlorophenol in $UV/TiO_2/H_2O_2$ system

Table A.7 Data of Figure A.7 from experimental system No. 7

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	7.58
2	95.10	89.40	7.49
4	90.72	79.93	7.23
6	87.40	71.46	6.91
8	54.63	63.89	6.63
10	53.39	57.12	6.44
12	58.38	51.07	6.32
14	40.96	45.66	6.25
16	41.30	40.82	6.18
18	38.67	36.49	6.10
20	32.64	32.63	6.04
22	27.75	29.17	6.00
24	23.15	26.08	5.97
26	18.66	23.32	5.94

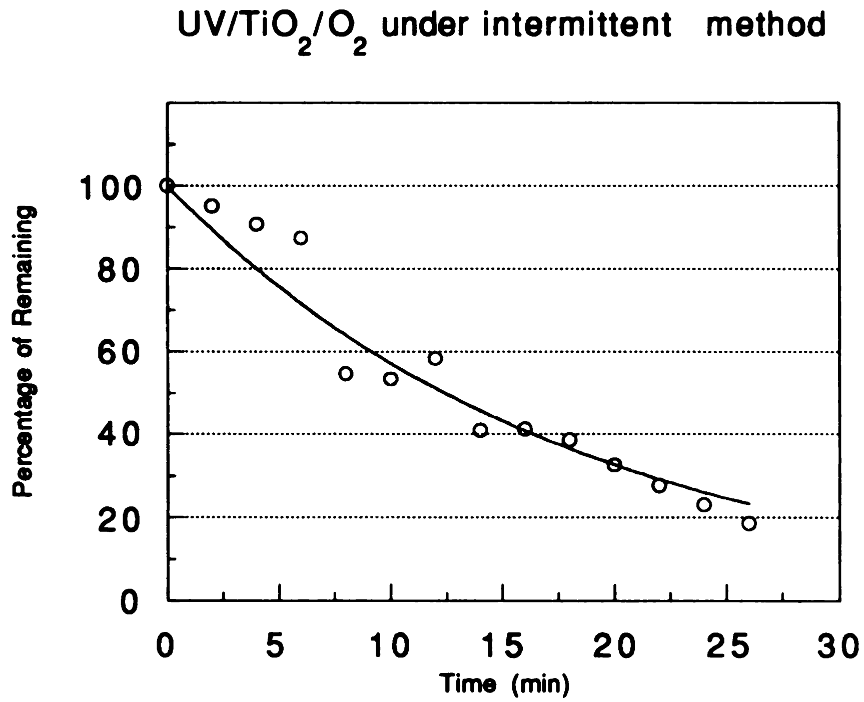

Figure A.7 Photodegradation of 2-chlorophenol in UV/TiO$_2$/O$_2$ system under intermittent method

Table A.8 Data of Figure A.8 from experimental system No. 8

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.0	7.19
4	78.15	70.89	6.61
6	55.95	59.69	6.40
8	41.27	50.26	6.19
10	38.17	42.32	6.03
12	33.56	35.63	5.90
14	32.80	30.00	5.80
16	23.31	25.26	5.71
18	23.61	21.27	5.64
20	23.28	17.91	5.59
22	15.66	15.08	5.55
24	18.05	12.69	5.51
26	14.51	10.69	5.48

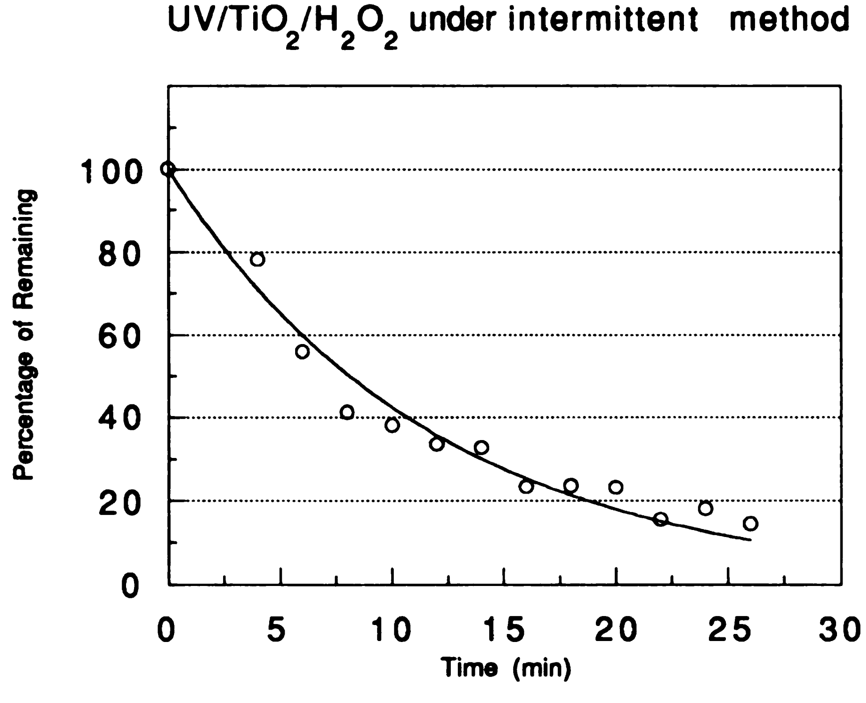

Figure A.8 Photodegradation of 2-chlorophenol in UV/TiO_2/H_2O_2 system under intermittent method

Table A.9 Data of Figure A.9 from experimental system No. 9

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	3.03
2	56.06	80.41	3.02
4	47.10	64.66	3.02
6	54.20	52.00	3.02
8	37.48	41.81	3.01
10	28.51	33.62	3.00
12	32.97	27.04	3.00
14	24.48	21.74	3.00
16	19.87	17.48	2.99
18	17.81	14.06	2.99
20	15.68	11.30	2.99
22	20.24	9.09	2.98
24	16.57	7.31	3.01
26	16.16	5.88	3.00

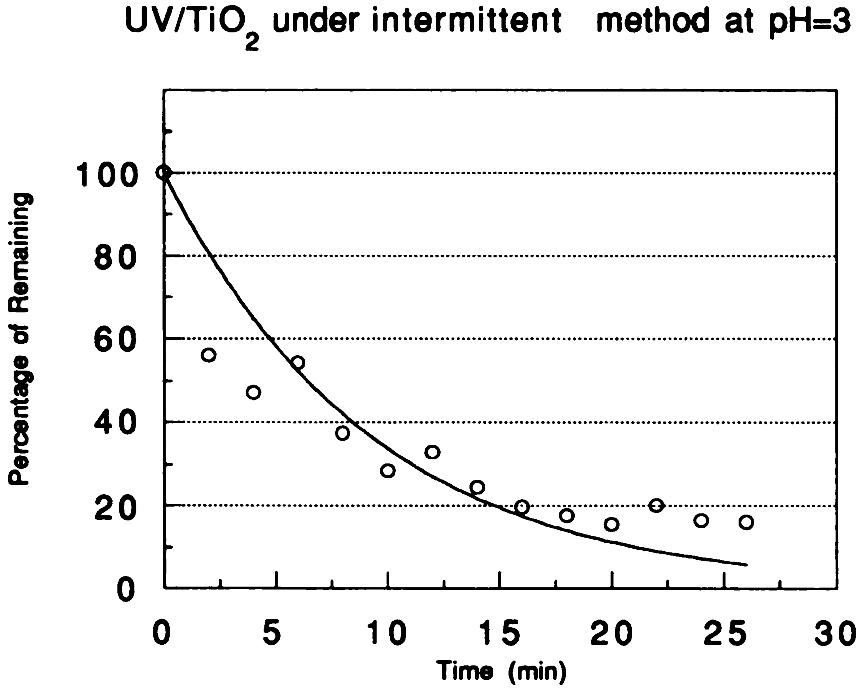

Figure A.9 Photodegradation of 2-chlorophenol in UV/TiO2 system under intermittent method at pH=3

Table A.10 Data of Figure A.10 from experimental system No. 9

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	5.05
2	86.74	84.87	5.06
4	73.14	72.04	4.99
6	66.30	61.14	5.02
8	53.78	51.89	4.98
10	40.90	44.04	5.02
12	42.42	37.38	4.99
14	37.23	31.73	4.98
16	20.99	26.93	5.00
18	20.08	22.86	5.01
20	16.40	19.40	4.99
22	15.31	16.46	4.99
24	11.71	13.97	5.00
26	9.80	11.86	5.02

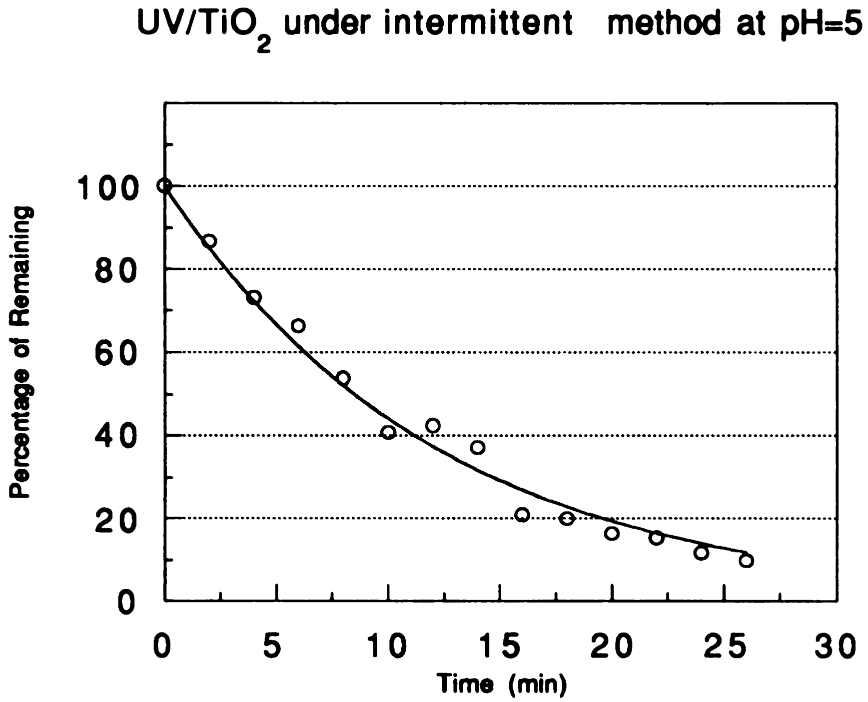

Figure A.10 Photodegradation of 2-chlorophenol in UV/TiO_2 system under intermittent method at pH=5

Table A.11 Data of Figure A.11 from experimental system No. 9

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	6.54
2	91.78	87.46	6.55
4	79.20	76.49	6.54
6	71.92	66.90	6.49
8	66.49	58.51	6.51
10	56.16	51.17	6.47
12	42.45	44.75	6.49
14	36.86	39.14	6.49
16	41.12	34.23	6.37
18	22.53	29.94	6.52
20	26.64	26.18	6.48
22	18.35	22.90	6.51
24	12.65	20.03	6.52
26	13.89	17.52	6.50

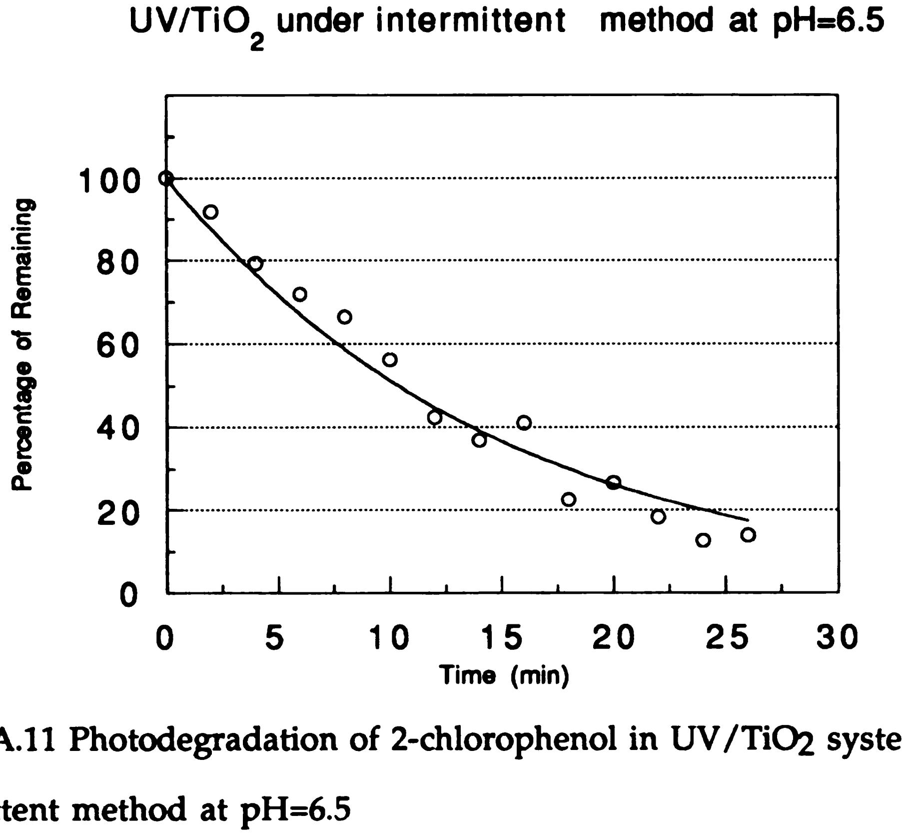

Figure A.11 Photodegradation of 2-chlorophenol in UV/TiO$_2$ system under intermittent method at pH=6.5

Table A.12 Data of Figure A.12 from experimental system No. 9

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	8.02
2	98.36	87.99	8.04
4	96.60	77.41	8.02
6	83.77	68.11	7.99
8	73.53	59.93	7.95
10	45.87	52.73	7.98
12	50.38	46.39	7.99
14	35.64	40.82	7.98
16	31.82	35.92	8.01
18	23.53	31.60	7.96
20	24.44	27.80	7.97
22	16.79	24.46	8.02
24	17.62	21.52	7.99
26	12.99	18.94	8.00

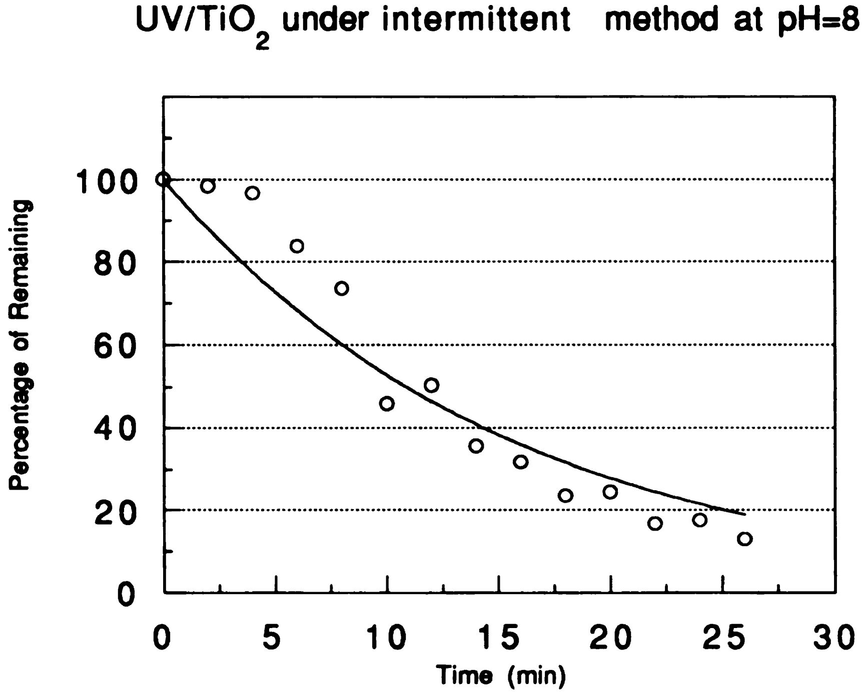

Figure A.12 Photodegradation of 2-chlorophenol in UV/TiO$_2$ system under intermittent method at pH=8

Table A.13 Data of Figure A.13 from experimental system No. 9

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	10.10
2	99.52	94.93	10.10
4	94.46	90.12	10.20
6	91.72	85.56	10.10
8	85.76	81.22	10.10
10	81.13	77.11	10.10
12	75.23	73.20	10.10
14	70.89	69.49	9.99
16	64.89	65.97	10.10
18	59.92	62.63	9.94
20	56.15	59.45	9.97
24	47.52	53.58	10.00

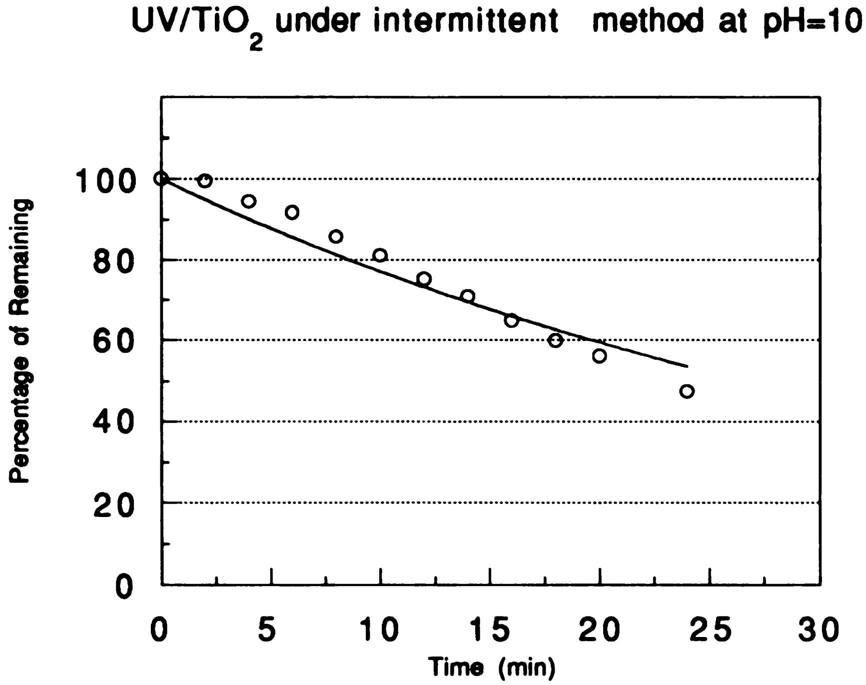

Figure A.13 Photodegradation of 2-chlorophenol in UV/TiO_2 system under intermittent method at pH=10

Table A.14 Data of Figure A.14 from experimental system No. 10

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	8.20
5	79.15	88.69	8.10
7	56.09	84.54	8.02
12	49.20	74.98	7.84
15	47.75	69.77	7.75
20	38.37	61.88	7.63
25	32.66	54.88	7.56
30	42.06	48.68	7.54
35	26.69	43.17	7.52
40	37.80	38.29	7.50
45	29.86	33.96	7.49
50	33.77	30.12	7.48
55	33.90	26.71	7.46
60	25.57	23.69	7.45

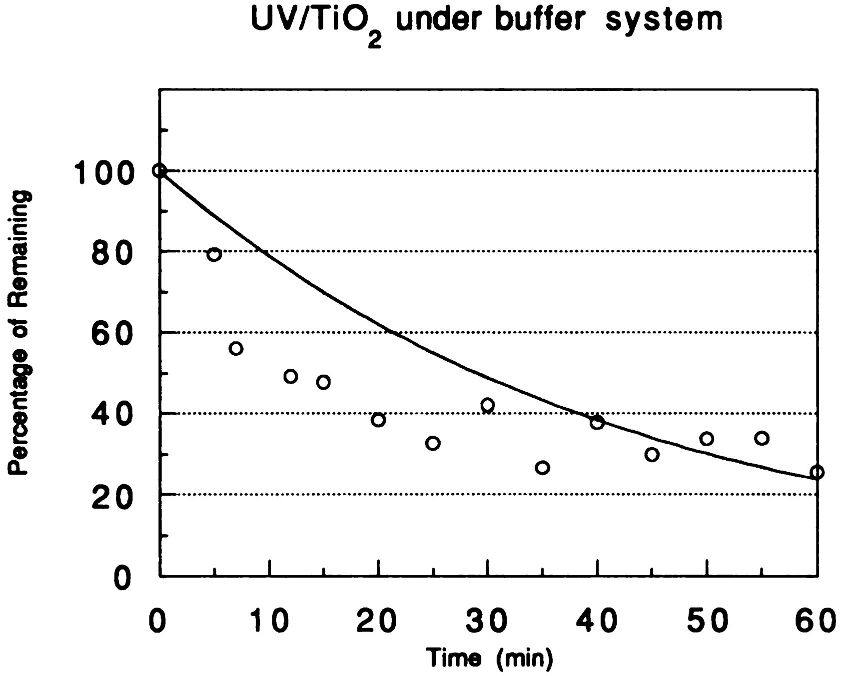

Figure A.14 Photodegradation of 2-chlorophenol in UV/TiO$_2$ system under buffer system with 2.5 mM NaHCO$_3$

Table A.15 Data of Figure A.15 from experimental system No. 10

Time (min)	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	7.51
5	80.96	73.71	7.27
7	50.16	65.25	7.13
10	41.03	54.34	6.95
12	38.01	48.09	6.86
20	28.88	29.52	6.60
25	29.21	21.76	6.49
30	22.99	16.04	6.40
35	20.15	11.82	6.34
45	13.49	6.42	6.28
50	12.43	4.74	6.28
55	12.33	3.49	6.27
60	8.91	2.57	6.27

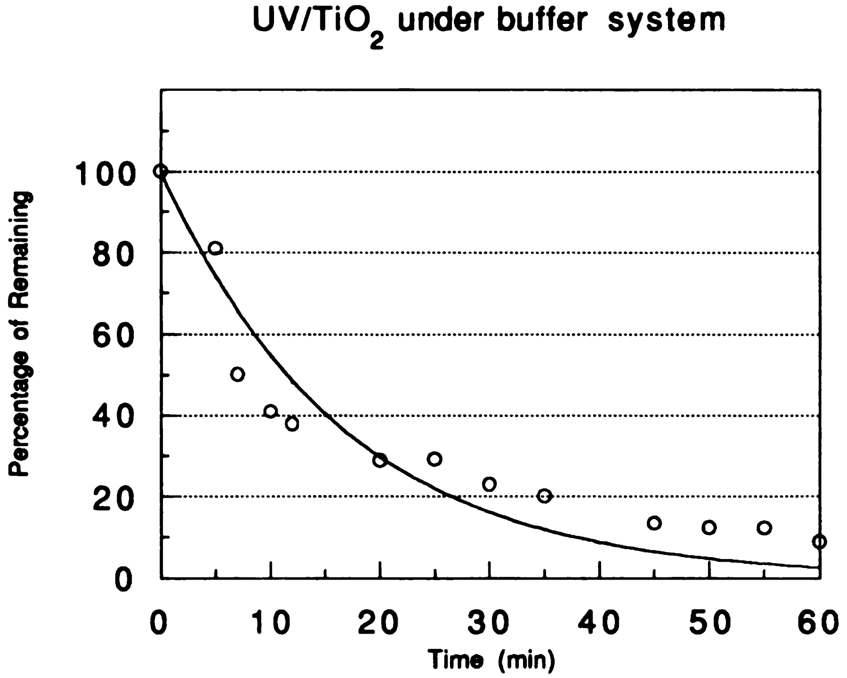
UV/TiO_2 under buffer system

Figure A.15 Photodegradation of 2-chlorophenol in UV/TiO_2 system under buffer system with 0.5 mM $NaHCO_3$

Table A.16 Data of Figure A.16 experimental system No. 11 and No. 12

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	3.58	100.00	100.00	3.63
5	82.69	79.06	3.61	62.50	58.86	3.59
7	74.99	71.96	3.59	48.73	47.62	3.54
10	65.12	62.50	3.57	34.10	34.65	3.50
12	58.39	56.89	3.55	26.95	28.03	3.48
15	50.82	49.41	3.54	19.14	20.39	3.46
17	45.17	44.98	3.53	15.58	16.50	3.44
20	40.81	39.06	3.51	11.45	12.00	3.43
25	31.45	30.88	3.50	6.53	7.07	3.41
30	21.96	24.41	3.49	3.75	4.16	3.40
35	16.18	19.30	3.49	2.03	2.45	3.39
40	12.21	15.26	3.47	1.49	1.44	3.39
45	7.95	12.06	3.45	0.97	0.85	3.39
50	5.22	9.54	3.45	0.72	0.50	3.39

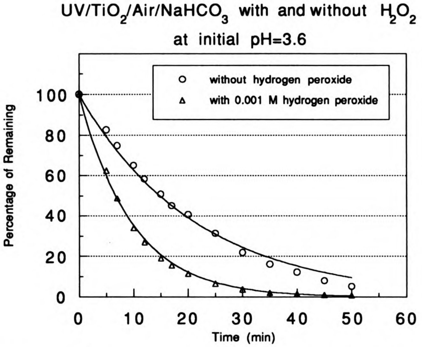
$UV/TiO_2/Air/NaHCO_3$ with and without H_2O_2 at initial pH=3.6

Figure A.16 Photodegradation of 2-chlorophenol in $UV/TiO_2/Air/NaHCO_3$ system at initial pH=3.6

Table A.17 Data of Figure A.17 experimental system No. 11 and No. 12

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	5.12	100.00	100.00	4.92
5	79.36	71.89	4.95	66.36	58.27	4.39
7	69.47	63.00	4.80	48.98	46.95	4.17
10	55.25	51.69	4.65	31.32	33.96	4.01
12	48.58	45.29	4.58	25.06	27.36	3.95
15	37.73	37.16	4.48	17.11	19.79	3.90
20	24.85	26.71	4.38	10.09	11.53	3.85
25	15.5	19.20	4.32			
30	7.92	13.81	4.29			
35	4.90	9.93	4.27			
40	2.94	7.14	4.27			
45	1.78	5.13	4.29			
50	1.02	3.69	4.31			
60	0.22	1.91	4.35			

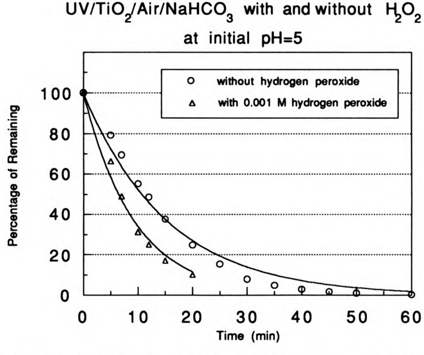

Figure A.17 Photodegradation of 2-chlorophenol in UV/TiO_2/Air/$NaHCO_3$ system at initial pH=5

Table A.18 Data of Figure A.18 experimental system No. 11 and No. 12

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	6.50	100.00	100.00	6.57
5	82.58	70.47	6.01	65.96	65.38	6.34
7	65.35	61.26	5.83	51.47	55.16	6.27
10	55.01	49.66	5.62	39.66	42.74	6.18
12	45.33	43.17	5.48	31.90	36.06	6.13
15	34.27	34.99	5.31	27.07	27.94	6.09
20	21.27	24.66	5.13	21.05	18.27	6.04
25	11.99	17.38	5.00	16.18	11.94	6.02
30	5.86	12.25	4.93	12.36	7.81	6.01
35	3.01	8.63	4.90	8.82	5.10	6.02
40	1.34	6.08	4.87	6.65	3.34	6.03

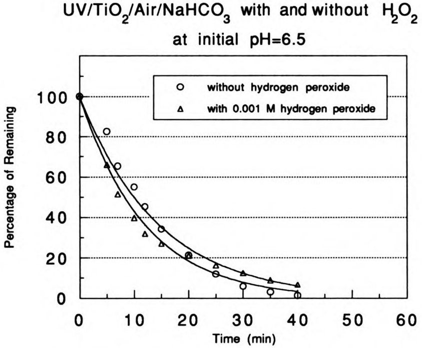
UV/TiO_2/Air/$NaHCO_3$ with and without H_2O_2 at initial pH=6.5

Figure A.18 Photodegradation of 2-chlorophenol in UV/TiO_2/Air/$NaHCO_3$ system at initial pH=6.5

Table A.19 Data of Figure A.19 experimental system No. 11 and No. 12

Time (min)	Without H_2O_2			With H_2O_2		
	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	8.05	100.00	100.00	8.11
5	82.11	73.71	7.79	67.53	67.71	7.72
7	65.15	65.25	7.59	55.54	57.93	7.57
10	56.09	54.34	7.30	44.10	45.84	7.20
12	50.68	48.09	7.16	38.63	39.22	6.94
15	40.93	40.05	6.99	32.41	31.04	6.69
20	28.70	29.52	6.82	22.86	21.01	6.50
25	20.33	21.76	6.73	15.54	14.23	6.40
30	13.71	16.04	6.67	10.15	9.63	6.38
35	9.29	11.82	6.64	6.54	6.52	6.38
40	5.85	8.72	6.65	4.25	4.42	6.37
45	3.49	6.42	6.65	2.40	2.99	6.40
50	2.08	4.74	6.64	1.44	2.02	6.44

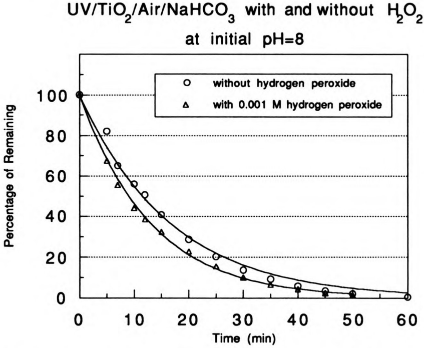

Figure A.19 Photodegradation of 2-chlorophenol in UV/TiO_2/Air/$NaHCO_3$ system at initial pH=8

Table A20 Data of Figure A.20 experimental system No. 11 and No. 12

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	10.00	100.00	100.00	10.00
5	93.18	86.07	9.95	82.74	83.53	9.92
7	88.70	81.06	9.91	69.79	77.72	9.94
10	82.77	74.08	9.86	64.05	69.77	9.90
12	78.48	69.77	9.82	60.28	64.92	9.89
15	70.49	63.76	9.76	55.43	58.27	9.84
20	64.11	54.88	9.65	48.49	48.68	9.77
25	54.84	47.24	9.52	42.80	40.66	9.73
30	46.81	40.66	9.37	36.83	33.96	9.63
35	38.46	34.99	9.18	31.71	28.37	9.54
40	31.03	30.12	8.92	27.01	23.69	9.35
45	23.01	25.92	8.51	22.69	19.79	9.37
50	14.68	22.31	7.85	17.91	16.53	9.27
55	8.98	19.20	7.36			
60	5.81	16.53	7.21			

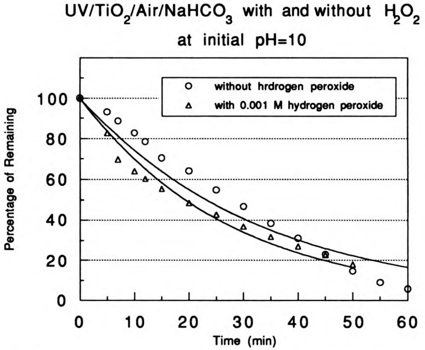

Figure A.20 Photodegradation of 2-chlorophenol in UV/TiO_2/Air/$NaHCO_3$ system at initial pH=10

Table A.21 Data of Figure A.21 from experimental system No. 13 and No. 14

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	6.87	100.00	100.00	6.93
5	88.84	80.25	6.73	66.05	70.12	6.59
7	81.53	73.49	6.61	53.57	60.84	6.49
10	71.81	64.40	6.46	45.39	49.16	6.31
15	56.61	51.69	6.26	38.10	34.47	6.11
17	52.45	47.33	6.19	32.15	29.91	6.07
20	42.68	41.48	6.13	29.97	24.17	6.00
25	30.66	33.29	6.04	18.80	16.95	5.91
35	13.44	21.44	5.96	9.15	8.33	5.93
40	2.62	17.20	5.97	5.51	5.84	5.98

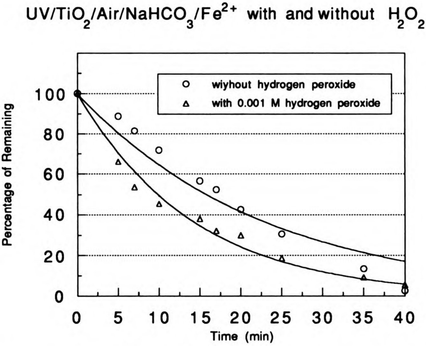

Figure A.21 Photodegradation of 2-chlorophenol in $UV/TiO_2/Air/Fe^{2+}$ under buffer system

Table A.22 Data of Figure A.22 from experimental system No. 15 and No. 16

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	6.74	100.00	100.00	6.85
2	87.36	85.56	6.62	77.08	75.43	6.49
5	67.46	67.71	6.33	41.64	49.41	6.31
7	58.58	57.93	6.17	32.02	37.27	6.21
10	45.59	45.84	6.04	25.09	24.41	6.03
12	38.11	39.22	5.98	20.92	18.42	6.00
15	32.53	31.04	5.90	16.14	12.06	5.39
17	26.75	26.55	5.89	13.59	9.10	5.93
20	21.51	21.01	5.84	10.39	5.96	5.91
25	13.93	14.23	5.84	6.19	2.95	5.90
30	8.59	9.63	5.83	3.47	1.46	5.91
35	4.80	6.52	5.84	1.85	0.72	5.94
40	3.02	4.42	5.86	0.90	0.36	5.99
45				0.46	0.18	6.02

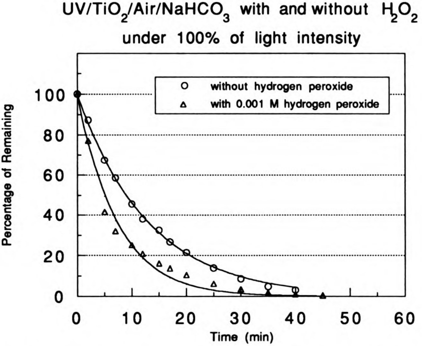

Figure A.22 Photodegradation of 2-chlorophenol in UV/TiO_2/Air/$NaHCO_3$ under 100% of light intensity

Table A.23 Data of Figure A.23 from experimental system No. 15 and No. 16

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	6.84	100.00	100.00	6.87
2	86.07	88.34	6.76	86.28	83.03	6.63
5	72.72	73.34	6.57	55.45	62.81	6.46
7	64.28	64.79	6.43	43.08	52.15	6.36
10	55.41	53.79	6.27	36.32	39.46	6.26
12	47.97	47.52	6.22	32.00	32.76	6.18
15	40.94	39.46	6.16	26.79	24.78	6.12
17	35.09	34.85	6.11	24.10	20.58	6.09
20	29.91	28.94	6.08	20.54	15.57	6.07
25	21.85	21.22	6.06	14.94	9.780	6.03
30	15.38	15.57	6.04	10.56	6.14	6.01
35	10.58	11.42	6.02	6.47	3.86	6.02
40	6.91	8.37	6.02	4.45	2.42	6.03
45	3.88	6.14	6.03	2.88	1.52	6.03
50	2.69	4.50	6.04	1.46	0.96	6.05
60	0.48	2.42	6.07	0.40	0.38	6.10

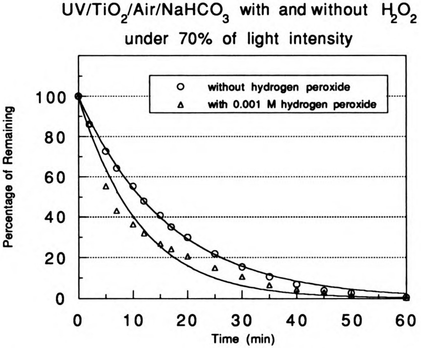

Figure A.23 Photodegradation of 2-chlorophenol in $UV/TiO_2/Air/NaHCO_3$ under 70% of light intensity

Table A.24 Data of Figure A.24 from experimental system No. 15 and No. 16

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	6.86	100.00	100.00	6.86
2	95.35	89.40	6.61	89.43	85.73	6.36
5	79.01	75.58	6.48	61.41	68.05	6.48
7	69.32	67.57	6.42	50.69	58.33	6.42
10	56.36	57.12	6.38	40.11	46.30	6.38
12	51.99	51.07	6.31	36.57	39.69	6.31
15	44.01	43.17	6.22	31.55	31.51	6.22
17	40.17	38.60	6.20	29.25	27.01	6.20
20	33.50	32.63	6.16	25.79	21.44	6.16
25	24.44	24.66	6.12	20.05	14.59	6.12
30	17.31	18.64	6.11	14.97	9.93	6.11
35	12.98	14.09	6.09	10.57	6.75	6.09
40	8.04	10.65	6.10	7.70	4.60	6.10
45	5.60	8.05	6.11	5.53	3.13	6.11
50	3.40	6.08	6.11	3.25	2.13	6.11
60	1.23	3.47	6.14	1.40	0.99	6.14

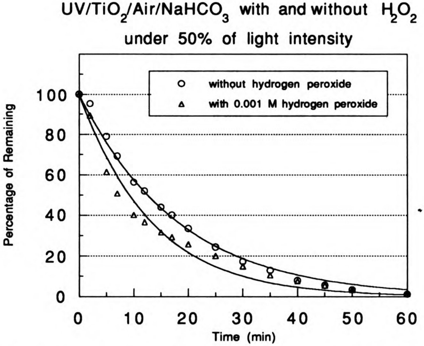
UV/TiO_2/Air/$NaHCO_3$ with and without H_2O_2 under 50% of light intensity

Figure A.24 Photodegradation of 2-chlorophenol in UV/TiO_2/Air/$NaHCO_3$ under 58% of light intensity

Table A.25 Data of Figure A.25 from experimental system No. 15 and No. 16

	Without H_2O_2			With H_2O_2		
Time (min)	Percentage of Remaining	Fitting value	pH	Percentage of Remaining	Fitting value	pH
0	100.00	100.00	6.92	100.00	100.00	6.96
2	79.91	91.21	6.87	95.87	90.85	6.77
5	78.70	79.45	6.74	72.19	78.66	6.68
10	56.23	63.13	6.49	54.67	61.88	6.54
12	59.67	57.58	6.42	50.72	56.21	6.51
15	39.97	50.16	6.35	40.98	48.68	6.49
17	42.76	45.75	6.28	40.29	44.22	6.45
20	43.73	39.85	6.20	39.54	38.29	6.34
25	34.47	31.66	6.12	31.62	30.12	6.26
30	26.41	25.16	6.06	29.51	23.69	6.20
35	20.38	19.99	6.02	22.29	18.64	6.15
40	19.28	15.88	6.00	21.04	14.66	6.10
45	17.01	12.62	5.99	19.61	11.53	6.06
50	12.59	10.03	5.96	19.90	9.07	6.02
60	8.94	6.33	5.96	12.52	5.61	5.91

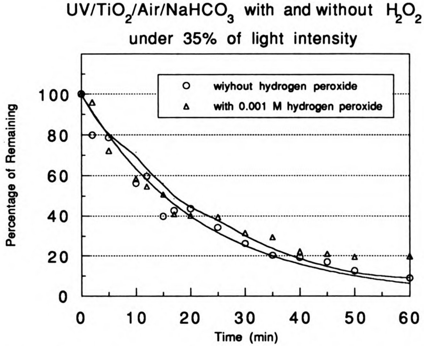

Figure A.25 Photodegradation of 2-chlorophenol in UV/TiO_2/Air/$NaHCO_3$ under 35% of light intensity

Table A.26 Rate constants of 2-chlorophenol solved by computer

Experimental systems	Illuminated Method	pH control	Rate constants (1/min)
UV/TiO_2	Continuous	None	0.115
UV/TiO_2/Air	Continuous	None	0.125
UV/TiO_2/O_2	Continuous	None	0.145
UV/TiO_2/H_2O_2[a]	Continuous	None	0.235
UV/TiO_2/O_2	Intermittent	7.58	0.056
UV/TiO_2/H_2O_2	Intermittent	7.19	0.086
UV/TiO_2	Intermittent	3	0.109
		5	0.082
		6.5	0.067
		8	0.064
		10	0.026
UV/TiO_2/$NaHCO_3$[b]	Continuous	7.51	0.061
UV/TiO_2/Air/$NaHCO_3$	Continuous	3.6	0.047
		5	0.066
		6.5	0.070
		8	0.061
		10	0.030
UV/TiO_2/Air/$NaHCO_3$/H_2O_2	Continuous	3.6	0.106
		5	0.108
		6.5	0.085
		8	0.078
		10	0.036
UV/TiO_2/Air/$NaHCO_3$/Fe^{2+}	Continuous	6.87	0.044
UV/TiO_2/Air/$NaHCO_3$/Fe^{2+}/H_2O_2	Continuous	6.93	0.064
UV/TiO_2/Air/$NaHCO_3$	Continuous Light intensity		
	100%	6.74	0.078
	70%	6.84	0.062
	58%	6.86	0.056
	35%	6.92	0.046
UV/TiO_2/Air/$NaHCO_3$/H_2O_2	Continuous Light intensity		
	100%	6.85	0.142
	70%	6.87	0.093
	58%	6.86	0.077
	35%	6.96	0.048

a: Concentration of hydrogen peroxide in this Table is 0.001 M.