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Kinetic study of decomposition of azo dyes and phenol in advanced oxidation processes: Reaction mechanisms, pathways and intermediates

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New Jersey Institute of Technology, 1993

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KINETIC STUDY OF DECOMPOSITION OF AZO DYES AND PHENOL IN ADVANCED OXIDATION PROCESSES: REACTION MECHANISMS, PATHWAYS AND INTERMEDIATES

by
Hung-Yee Shu

A Dissertation
Submitted to the Faculty of
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Department of Chemical Engineering,
Chemistry, and Environmental Science

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ABSTRACT

Kinetic Study of Decomposition of Azo Dyes and Phenol in Advanced Oxidation Processes: Reaction Mechanisms, Pathways and Intermediates

by
Hung-Yee Shu

Advanced Oxidation Processes (AOP) are an emerging technology for treatment of various hazardous organics in wastewater and groundwater. However, the kinetics and mechanisms for AOP have not been well understood. A mechanism including light intensity was studied for the decomposition of azo dyes and phenol in an AOP reactor with a 5,000 watt low pressure mercury lamp. UV light absorption is an important parameter. The effect of pH, hydrogen peroxide dosage, and dye concentration on the decomposition of azo dyes in an H_2O_2/UV reactor were also studied. Reaction pathways and intermediates of phenol oxidation by different processes were obtained using GC/MS analysis. Phenol oxidation by OH• produced some high molecular weight compounds (i.e. 2-phenoxy-phenol, 1,1'-biphenyl-2,2'-diol etc.) as well as organic acids. This phenomena has not been reported previously in other AOP studies. The results of computer modeling gave excellent agreement with experimental data for different initial conditions, and rate constants obtained from optimization method showed reasonable agreement with literature data of this type.

In this study, light intensity in the reactor and absorbance of solution were considered to improve the accuracy of modeling. To use literature data for the fundamental reactions in stead of floating fitting make the modeling results more consistent with literature. The modeling results of the proposed mechanism can fit various initial conditions to prove its effectiveness.

APPROVAL PAGE

Kinetic Study of Decomposition of Azo Dyes and Phenol in Advanced Oxidation Processes : Reaction Mechanisms, Pathways and Intermediates

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This Dissertation is dedicated to
my wife

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CHAPTER 1

INTRODUCTION

Industrial wastewater contaminated by organic compounds is a major concern. The Best Available Technologies (BATs) for treatment of organic pollutants are packed-tower aeration and granular activated carbon filtration (40 CFR). However, these processes transfer the contaminant from water media to the air or the carbon media, respectively. Other treatment processes that should degrade organic contaminants are biological and chemical oxidation. Furthermore, Advanced Oxidation Processes (AOPs) are being developed as additional BATs. For years, conventional chemical oxidation has been used in the treatment of organic contaminated water. Oxidants such as potassium permanganate, chlorine, chlorine dioxide, ozone, and hydrogen peroxide have been used for various purposes. However, the disadvantages of producing carcinogenic byproducts and difficulty in degrading refractory organics make conventional chemical oxidation less competitive to advanced oxidation processes for destroying toxic and hazardous organic compounds in water.

UV light intensity in the reactor plays an important roll for the destruction of organics in AOPs system. The transmittance is reduced by color, turbidity, and organic and inorganic compounds present in the wastewater. The light intensity in the local region decreases exponentially as the wastewater's transmittance decreases. Therefore, extremely low transmittance can make photooxidation processes very expensive or impractical. Thus, absorbance of UV light at 254 nm by wastewater is a very important parameter for the study of AOP reactors, and it is necessary to pretreat the turbidity and color prior to using UV/H_2O_2 system for treating dark turbid wastewater.

1.1 Target Compounds

Azo dyes are of concern because some azo dyes, dye precursors, and their degradation products such as aromatic amines have been shown, or are suspected to be carcinogenic. The industrial manufacturing and processing of azo dyes would generate a wastewater contaminated with azo dyes which were typically treated in a conventional wastewater treatment system. A study by EPA's Water Engineering Research Laboratory, found that 11 of the 18 dyes studied pass through the Activated Sludge Process substantially untreated, 4 were significantly adsorbed onto the Waste Activated Sludge, and 3 were apparently biodegraded (Shaul 1988). Consequently, alternative technologies which can decompose the nonbiodegradable azo dyes have to be uncovered. Approaches that combines UV radiation and hydrogen peroxide, or UV radiation and ozone may provide solutions to this problem.

From an investigation of industrial wastes, phenol was found in wastewater from various industries, for instances, dye manufacturing plant, epoxy resins plant, additives and aromatic chemical plant, solvents plant, and aromatic chemical and pharmaceutical plant, etc. (Stryker et al. 1985). These plants generated phenol from 2,200 lb/yr to 589,230 lb/yr. Besides, its high toxicity and its presence in wastes from variety of industries, phenol is a suitable substance that serves as a model for studies about the degradation of related compounds, such as chlorophenols, chlorinated pesticides, phenoxy herbicides, etc. Thus, phenol became a very interesting substance for decomposition research.

1.2 Processes

Information has been developed on the impact of carcinogens in drinking water, groundwater and surface water. This has led to a better understanding of the influences of chemicals which contaminate water and cause harmful effects to the environment and to human health. The conventional wastewater treatment processes were found not to decompose certain chemicals in industrial wastewater. These chemicals are invariably toxic substances or carcinogens. In order to decompose these chemicals to acceptable concentration levels, alternative technologies have been proposed, such as biological and chemical oxidation, packed-tower aeration, and granular activated carbon filtration. These technologies are often used to treat toxic organics in wastewater and drinking water.

It has been reported in previous studies that the combination of ultraviolet radiation and ozonation increases the rate of ozone induced organic oxidation in aqueous solution. Simultaneously, the experiments demonstrated that the O_3/UV combination oxidized organics more rapidly than ozone alone. That is because the UV induced decomposition of ozone which produced powerful oxidants such as hydroxyl radical (OH •) and hydroperoxide radical (HO_2•). The combination of hydrogen peroxide and UV radiation also induced a high decomposition rate of organics in aqueous system. For some organic decompositions, the H_2O_2/UV system was more effective than in the O_3/UV system.

1.3 Objective

The objective of this study is to determine the feasibility and the mechanism of using O_3 , O_3/UV and H_2O_2/UV for the decompositions of eight specific azo dyes, acid orange 10, acid red 1 and acid yellow 23, etc. as listed in Table 2.2 and to model the reactor system.

Furthermore, the light intensity model for an AOPs reactor is introduced for a better understanding of reaction mechanism. Phenol was chosen as a model compound to test the reaction mechanism and decomposition pathways. The intermediates were also studied by GC/MS analysis. Using a pilot size reactor, scaling up parameters such as rate constants, dosage effect and pH effect could be obtained. The determination of rate constants and mass transfer coefficients requires conducting a series of experiments of varying complexity. A reaction kinetic model which describes the contemplated experiments was developed and exercised using the Rosenbrock Hillclimb Optimization Algorithm with the LSODE ODE solver. Furthermore, the effects between different hydrogen peroxide dosages, initial concentration of azo dye and pH levels were also analyzed.

To modify the reaction model using various set of experimental results was very important for this study. A reaction mechanism of hydrogen peroxide decomposition induced by UV radiation was proposed to obtain the rate constants from which the rate constants of azo dye reacted with OH• and HO_2• could be obtained with the known rate constants from literature. This modified mechanism could be used to solve for UV/O_3 reaction rate constants. Therefore, the reaction mechanism for series of photochemical reactions was expected to be able to check the models of H_2O_2/UV and O_3/UV systems.

In order to demonstrate the treatment feasibility of the O_3/UV and H_2O_2/UV processes in wastewater, CSTR (Constant flow Stirred Tank Reactor) experiments were also conducted. By using the reaction rate constants and the mass transfer coefficients which were obtained from the batch reactor experiments, the effluent concentration for CSTR could be predicted. Comparing with the predicted and experimental data in this CSTR process, the applicability of this kinetic model and rate constants in wastewater treatment process can be confirmed.

CHAPTER 2

REVIEW OF PREVIOUS STUDIES

The literature of previous studies were divided into several sections for systematical presentations. The sections are Advanced Oxidation Processes; Photolytic Hydrogen Peroxide Oxidation; Photolytic Ozonation; Ozone combined with hydrogen peroxide oxidation; Fenton's Reagent and Hydrogen Peroxide Photooxidation; Conventional Ozonation (mechanisms); Azo Dyes in Wastewater (characteristics and problems); and Oxidation of phenol by Alternative Processes.

2.1 Advanced Oxidation Processes

EPA (Environmental Protection Agency) amended pretreatment regulations which restricted the POTWs (Publicly Owned Treatment Works) to implement testing, reporting and enforcement programs for their significant industrial dischargers in July, 1990. Effluents from receiving dischargers should be necessarily inspected by POTWs for regulated toxics (Kobylinski et al. 1992). All the significant industrial users of POTWs regulated legally binding permits governing pretreatment and discharges, similar to the NPDES (National Pollutant Discharge Elimination Standards) permits for direct discharges. The amended regulation compelled POTWs to exert tighter control upon industrial waste generators. The control appeared in the form of local ordinances which requested industries to institute their own pretreatment programs.

Industrial process plants generated a wide variety of water pollutants which can not be treated simply but expensively. For example, industries such as pharmaceuticals, organic chemicals, petroleum refining, pulp and paper, plastic and resins, produced wastewater containing organic pollutants which were forced to perform pretreatment before discharging into POTWs. Goronszy et al. (1992) introduced that the most simple and effective pretreatment method for organics was chemical oxidation which use oxidants such as chlorine, ozone, hydrogen peroxide, potassium permanganate and chlorine dioxide to destroy the odor causing sulfur compounds, control bacterial growth, and reduce COD (Chemical Oxygen Demand). The most thorough destruction of organic contaminants was achieved while combining the chemical oxidizing agent with a source of ultraviolet radiation to generate a hydroxyl radical (OH•). The process was called Advanced Oxidation Processes (AOPs) which generally apply ultraviolet (UV) radiation with ozone (O_3) or hydrogen peroxide (H_2O_2).

O_3 and H_2O_2 were utilized as oxidants in many water and wastewater treatment applications. Theoretically, O_3 and H_2O_2 should be able to oxidize inorganics to their highest stable oxidation states, to oxidize organic compounds into CO_2 and H_2O. Since the limited selectivity and lower reaction rate of O_3 and H_2O_2, the Advanced Oxidation Processes were developed to degrade the refractory organics in water. Consequently, O_3 and H_2O_2 were generally employed with UV radiation in AOPs to dynamically destroy the refractory organics.

2.2 Photolytic Hydrogen Peroxide Oxidation (Hydrogen Peroxide with UV Radiation)

The photolytic hydrogen peroxide oxidation has proved to be effective for the treatment of refractory compounds such as nitrosamines in groundwater and industrial wastewater. Total Organic Carbon in distilled water and tap water; various halogenated aliphatics; aromatic organics (benzene, toluene, chlorobenzene, phenol, chlorophenols, dimethyl phthalate and diethyl phthalate, etc.); 2,4-Dinitrotoluene (explosive from military munition facilities); groundwater contaminated with TCE (Trichloroethylene), 1,1-DCA (1,1-Dichloroethane), and 1,1,1-TCA (1,1,1-Trichloroethane); bleaching water in paper industry.

Advanced Oxidation Processes (AOP) or Enhanced Oxidation Processes has gained acceptance as a capable method to destroy toxic and hazardous organic compounds in water. Smith (1992) reported that the AOPs were successful for treating the nitrosamines in groundwater and industrial wastewater. Although wastewater showed the low absorbance of UV light, the AOPs system could even provide apparently attributable treatment.

It is important to measure the UV transmittance of the effluent at the predominant wavelength of 253.7 nm emitted by UV lamp. Transmittance was reduced by turbidity, colored organic and inorganic compounds presented in the wastewater. Therefore , transmittance was generally improved by increasing degree of pretreatment. The light intensity of lamp in the local region decreased exponentially as the wastewater's transmittance decreased. But, the extremely low transmittance could make photooxidation process very expensive or impractical (Mann et al. 1992). Usinowicz et al. (1993) concluded that for treating the dark turbid groundwater, it was required to pretreat the turbidity and color by using UV/H_2O_2 system. They also concluded the capital cost of UV/H_2O_2 system which included color and turbidity removal pretreatment was similar to Bioultrafilter's. However, its operation and maintenance costs were 4 times of bioultafiltration's.

Light intensity which affected the decomposition rate of pollutants in an AOP reactor was an important parameter in reactor modeling. However, few studies were focused on the light intensity in an AOP reactor. Suidan et al. (1986) employed annular UV disinfection reactors to compare two different light intensity in his models, infinite line source model and finite line source model. According to no significant differences between two models, the results suggested no reasons to use the more complex finite line source model in stead of infinite line source model. Radial approximation of the infinite line source model can be described as follows :

The light intensity, I, at any point p in the reactor was related to the surface flux, I_0, by a one-dimension form of Lambert's law of absorption

$$\frac{1}{r}\frac{d(rI)}{dr} = -EI$$

where E is the monochromatic absorbance of water using logarithms to the base e. Integration of the above equation using boundary condition of $I = I_0$ when $r = r_0$ gives

$$I = I_o \frac{r_o}{r} e^{-E(r-r_o)}$$

Therefore, the ratio of the average point intensity to the surface flux at the quartz tube in the reactor was defined as the intensity factor, *m*.

$$m = \frac{I}{I_o} = \frac{2r_o}{E(R^2 - r_o^2)}[1 - e^{-E(R-r_o)}]$$

Here, R denotes radius of reactor, r_0 is radius of lamp with quartz shell.

Although the O_3/UV treatment was undoubtedly effective on a wide range of refractory organic compounds, it still has some disadvantages. Firstly, ozone is an unstable gas which must be generated and used on-site immediately. Secondly, must provide an ozone contacting device which can achieve adequate O_3 mass transfer into the liquid phase. An oxidant which may oxidize as effectively as ozone but easier for storage and transportation while using in AOPs system, is hydrogen peroxide. H_2O_2 which was weak acidic, colorless and rather stable was completely miscible in water. Furthermore, it is more economical since the price has actually decreased 20% over past years (Shearman 1992). Besides, H_2O_2 was generally regarded to have one of the most favorable performance profiles because it yielded only water and oxygen while decomposing but producing no toxic byproducts. For the photosensitive characteristics of hydrogen peroxide, it has often been used to induce oxidation of compounds which were not attacked by hydrogen peroxide without UV radiation. Moreover, the other superiority of H_2O_2/UV process which formed no residual sludge or vapor emission could save another waste-disposal problems.

O_3/UV radiation process showed that the intermediate, hydrogen peroxide, played an distinguished action in the reaction mechanism (Peyton et al. 1987 and 1988).

Therefore, studying the photolytic oxidation of hydrogen peroxide could lead to a better understanding for the mechanism of O_3/UV photolytic oxidation.

The H_2O_2/UV reaction generated hydroxyl radicals and other reactive species by photochemical reaction of UV light on hydrogen peroxide. Ogata et al. (1981) studied the H_2O_2 with the UV which induced the photooxidation of formic, acetic, and propionic acids, and proposed the following mechanism. Hochanadel (1962) has also proposed a similar mechanism:

$$H_2O_2 \xrightarrow{h\upsilon} 2OH\bullet$$
$$H_2O_2 + OH\bullet \rightarrow HO_2\bullet + H_2O$$
$$H_2O_2 + HO_2\bullet \rightarrow OH\bullet + H_2O + O_2$$
$$2HO_2\bullet \rightarrow H_2O_2 + O_2$$

Malaiyandi et al. (1980) presented that hydrogen peroxide photolysis could reduce the TOC (Total Organic Carbon) content from distilled water about 88 % and tap water about 98 %. Under suitable operating conditions, H_2O_2/UV can provide a useful source of hydroxyl ions which promoted the chain reactions. H_2O_2 decomposed could be shown at higher pH values and base catalyzed.

Sundstorm et al. (1986) compared the reaction rates for various halogenated aliphatics with UV alone, H_2O_2 alone and H_2O_2/UV by different hydrogen peroxide dosage and different temperatures. They found the following results :

1. Compared with the other methods, H_2O_2/UV reached the highest efficiency for decomposing halogenated aliphatics.

2. The decomposition rates of halogenated aliphatics increased with increasing hydrogen peroxide concentrations and temperatures. Besides, they were degraded with highly structure dependent.
3. Unsaturated halogenated compounds were generally decomposed more rapidly.

Weir et al. (1987) studied the destruction of benzene by H_2O_2/UV process. They pointed out that :

1. Reaction rate increased with hydrogen peroxide concentration or UV light intensity.
2. At high pH level, benzene decomposed more slowly. It was probable for hydrogen peroxide decomposing itself to oxygen and water at base catalyzed condition that could not provide free radicals to oxidize the benzene.
3. Temperature effect was not significant.
4. The intermediates strongly absorbed UV light at 254 nm.

Destruction of aromatic pollutants such as benzene, toluene, chlorobenzene, phenol, chlorophenols, dimethyl phthalate, and diethyl phthalate by H_2O_2/UV process were investigated by Sundstrom et al. (1989). They found that the higher H_2O_2 to pollutant ratios, the higher decomposition rates could be happened. The intermediates formed while the aromatic pollutants degraded and caused the solution brown color which increased the absorbance at 254 nm comprehensively. The reaction rates were obtained by the order of 2,4,6-trichlorophenol > toluene > benzene > phenol > 2,4-dichlorophenol > chlorobenzene > 2-chlorophenol > diethyl phthalate > dimethyl phthalate. It apparently showed that most aromatic pollutants studied in this paper received high degradation rates for UV radiation alone. However, there were three compounds : phenol, dimethyl phthalate, and diethyl phthalate could be hardly decomposed by UV radiation alone. Nevertheless, they could be significantly improved by H_2O_2/UV process.

The application of H_2O_2/UV was also studied by Ho (1986), he reported on the decomposition of 2,4-dinitrotoluene in aqueous solution by the process. It's a treated method for explosive nitro-compounds from military munition facilities. The most effective H_2O_2/DNT ratio was approached as 26 to 52. He investigated both the reaction pathways and intermediates that the color changed form yellow to deep orange, to brown then changed into colorless finally while the pH from 6.8 to 2.8 during DNT decomposition.

H_2O_2/UV process could also be used to treat TCE (trichloroethylene), 1,1-DCA (1,1-dichloroethane), and 1,1,1-TCA (1,1,1-trichloroethane) contaminated groundwater (Lewis et al. 1990). The removal efficiencies obtained for TCE and total VOCs (Volatile Organic Compounds) as high as 99% and 90%, respectively; for 1,1-DCA, and 1,1,1-TCA about 65% and 85%, respectively. Thus could provide H_2O_2/UV process a good future in groundwater remediation.

Prat et al. (1988) investigated on bleaching water treatment in the paper industry by H_2O_2/UV process. They also reported that reaction rates decreased as pH increased.

Recently, a new technique of spin trapping with EPR (Electron Paramagnetic Resonance spectroscopy) detection of spin adducts has been applied to study the photodegradations of organic pollutants by H_2O_2 photolysis in aqueous solution. Kochany et al. (1992) obtained rate constants from the reactions of OH• radicals with benzene and its halo derivatives by EPR. However, they found that the rate constants did not make differences among the halobenzene derivatives. Usually, an average rate constant about

$5.0\times10^9 M^{-1}s^{-1}$ could be used for any of these compounds. Moreover, there's a very similar method, flash photolysis/HPLC, to study the photodegradations of phenol, and p-benzoquinone (Lipczynska-Kochany et al. 1992 a). The reaction intermediates were identified as p-benzoquinone, hydroquinone, and 2-hydroxyl-p-benzoquinone. Lipcznska-Kochany et al. (1992 b) also studied the flash photolysis/HPLC for 4-chlorophenol by direct photolysis or photolysis with hydrogen peroxide. They concluded that the major product for direct photolysis was p-benzoquinone and were 4-chlorocatechol, 1,2,4-trihydroxbenzene, and hydroquinone for photolysis with hydrogen peroxide.

In order to estimate the decomposition rates of specific chemicals which reacted with OH• and HO_2•, several reaction rate constants need to be known. The rate constants were obtained from references (Bielski, et al. 1985, Buxton, et al. 1988, Neta, etal. 1988) for the following reactions. With the rate constants in Table 2.2, a model of hydrogen peroxide reactions induced with UV radiation could be solved numerically.

Table 2.1 Rate Constants of Some Important Reactions (l/mole-sec)

Reactions	Rate Constants	Researchers
$H_2O_2 + OH\bullet \xrightarrow{K_{10f}} \rightarrow HO_2\bullet + H_2O$	$k_{10f} = 2.7 \times 10^7$	Christense (1982)
$H_2O_2 + HO_2\bullet \xrightarrow{K_{11f}} OH\bullet + H_2O + O_2$	$k_{11f} = 3.7$	Koppenol (1978)
$2OH\circ \xrightarrow{K_{14}} H_2O_2$	$k_{14} = 4.0 \times 10^9$	Thomas (1965)
$2HO_2\bullet \xrightarrow{K_{15}} H_2O_2 + O_2$	$k_{15} = 8.3 \times 10^5$	Beilski (1978)
$OH\bullet + HO_2\bullet \xrightarrow{K_{16}} H_2O + O_2$	$k_{16} = 3.7 \times 10^{10}$	Burrows (1981)
$OH\bullet + O_3 \xrightarrow{K_{8f}} O_2 + HO_2\bullet$	$k_{8f} = 1.1 \times 10^8$	Sehested (1982)

2.3 Photolytic Ozonation (Ozone with UV Radiation)

In the early 1970's, the ozonation process combined UV radiation (O_3/UV) has developed for the oxidation of refractory and toxic inorganic or organic compounds. In recent years, this combination of ozonation and UV radiation has been improved to increase ozone oxidation rates in aqueous solution, especially for those chemicals not reacting directly with ozone.

Prengle (1983) testified that UV radiation of 180 - 400 nm could provide 72 - 155 kcal/mol to decay ozone and produce oxidizing free radicals, such as OH• and HO_2•.

Although UV radiation with ozonation process has been known over 20 years as a powerful water treatment process for degrading some organics, its reaction mechanism could not be understood very well. Peyton et al. (1982), Glaze et al. (1982) and Prengle (1983) showed that the photolysis of dissolved ozone could produce hydroxyl radicals. Moreover, a series of investigations by Peyton and Glaze (1987 and 1988) have been contained two pathways : One initiated the photolytic reaction of dissolved ozone to yield hydrogen peroxide. H_2O_2 then produced hydroxyl radicals which reacted with ozone to produce hydroperoxide radicals. The other one initiated the photolysis of dissolved ozone to form the hydroxyl radicals immediately. They assumed the following initiation steps :

$$O_3 + H_2O \xrightarrow{h\upsilon} O_2 + H_2O_2 \qquad (1)$$

$$O_3 + H_2O \xrightarrow{h\upsilon} O_2 + 2OH \bullet \qquad (2)$$

An estimate of the steady state concentrations of OH• and HO_2• in solution was obtained from hydroxyl radicals as the following mechanism:

$$O_3 + H_2O \xrightarrow{h\upsilon} O_2 + H_2O_2$$
$$H_2O_2 \xrightarrow{h\upsilon} 2OH\bullet$$
$$H_2O_2 \Leftrightarrow HO_2^- + H^+$$
$$O_3 + HO_2^- \rightarrow O_3^- + HO_2\bullet$$
$$HO_2\bullet \Leftrightarrow O_2^- + H^+$$
$$O_3 + O_2^- \rightarrow O_3^- + O_2$$
$$O_3^- + H^+ \Leftrightarrow HO_3$$
$$HO_3 \rightarrow OH\bullet + O_2$$
$$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$$
$$OH\bullet + O_3 \rightarrow O_2 + HO_2\bullet$$
$$2OH\bullet \rightarrow H_2O_2$$
$$2HO_2\bullet \rightarrow H_2O_2 + O_2$$
$$H_2O + HO_2\bullet + O_2^- \rightarrow H_2O_2 + O_2 + OH^-$$

The study postulated that the initial step of photolytic ozonation was production of hydrogen peroxide. Later, H_2O_2 was degraded to strong oxidants like OH• and HO_2•.

In the earlier study, Prengle (1983) proposed an overall O_3/UV photo- oxidation mechanism of M species such as sulfur, phosphorus and halogen in an aqueous solution. The postulated oxidants were O_2*, OH• and HO_2•.

$$O_3 \xrightarrow{h\upsilon} O_2^* + O\bullet$$
$$O\bullet + H_2O \rightarrow 2OH\bullet$$
$$O_3 + OH\bullet \rightarrow HO_2\bullet + O_2$$
$$M \xrightarrow{h\upsilon} M^*$$
$$M \xrightarrow{h\upsilon} R\bullet + O_2$$
$$M + (h\upsilon, O\bullet, OH\bullet, HO_2\bullet) \rightarrow \text{Decomposition products}$$

The overall reaction was given as :

$$M, M^{*}, R\cdot, I + (h\upsilon, O\cdot, OH\cdot, O^{*}, HO_2\cdot) \rightarrow CO_2, H_2O, SO_4^{\,2-}, PO_4^{\,2-}, Cl^{-}$$

Here O_2* was activated oxygen molecule and M was a certain pollutant. Prengle took trihalomethane as M above. From the use of UV radiation, the overall oxidation rate was enhanced. Consequently, one can conclude from above studies as follows :

- UV radiation initiated a chain reaction. First of all, ozone was decomposed to an electronically excited oxygen molecule and an oxygen atom. The activated oxygen molecules reacted with water to form two hydroxyl radicals.
- Hydroxyl radicals were continually consumed in a complex free radical reaction which produced hydrogen peroxide and hydroperoxide radicals.
- The O_3/UV treatment might be related to the formation of vibrationally excited organic species which subsequently reacted with hydroxyl radicals.

A model can be developed by the following reactions for the O_3/UV photooxidation of pollutant M :

$$O_2 \xrightarrow{h\upsilon} O_2^{*}$$

$$O_3 + H_2O \xrightarrow{h\upsilon} O_2 + 2OH\cdot$$

$$OH\cdot + O_3 \rightarrow O_2 + HO_2\cdot$$

$$2OH\cdot \rightarrow H_2O_2$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + OH\cdot \rightarrow HO_2 + H_2O$$

$$H_2O_2 + HO_2\cdot \rightarrow OH\cdot + HO_2 + O_2$$

$$OH\cdot + HO_2\cdot \rightarrow H_2O + O_2$$

$$M + (h\upsilon, O_2^{*}, OH\cdot, HO_2\cdot, O_3) \rightarrow \text{Decomposition products}$$

Gurol et al. (1986) conducted photolytic ozonation of phenolic compounds to decide the effects of UV intensity and pH. Benoit-Guyod et al. (1986) obtained similar results about the effects of pH and UV light intensity while studying on the degradation of MCPA (4-Chloro-2-methylphenoxyacetic acid) induced by UV ozonation. The results can be summarized as follows :

1. Ozone was the predominant oxidant in an acidic solution.
2. Despite the absence or presence of UV radiation in neutral or basic solutions, a free radical reaction was the major oxidation pathway of phenolic compounds.
3. With or without UV radiation, the total phenol removal and total organic carbon (TOC) increased by increasing pH during ozonation. Oppositely, the removal of MCPA decreased by increasing pH.
4. For treating organic compounds, the highest removal rates for phenol, TOC, and MCPA could be reached while the O_3/UV process was employed with optimum pHs. The removal rates decreased while using the ozone only process. The UV light only approached the lowest removed rates among O_3/UV, ozone and UV light processes.

For the applications of photolytic ozonation, Glaze et al. (1984 and 1988) reported that UV/O_3 process reached very powerful effects on decomposition of THM (Tri-Halogen Methane), TCE (Tri-Chloro Ethane) and PCE (Tetra-Chloro Ethane) in groundwater. Besides, Akhlaq et al. (1990) proposed the treatment of polysaccharide alginic acid, Mc Shea et al. (1987) reported the degradation of pentachlorophenol in groundwater. Kusakabe et al. (1991, 1990) studied the destruction of 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and humic acids by UV/O_3 processes. They concluded that photooxidation rates were dependent on the UV intensity and ozone concentration in aqueous phase. Furthermore, by combining ozone pretreatment and photocatalytic oxidation, Tanaka et al. (1992) proposed more effective decomposition of dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate and asulam.

2.4 Ozone Combined with Hydrogen Peroxide Oxidation

Pallard et al. (1988) showed that the decomposition of organic compounds such as trichloroethane and oxalic acid in an ozone-hydrogen peroxide system approached a higher reaction rate than ozone alone, or hydrogen peroxide alone. They proposed a mechanism that ozone combined with hydrogen peroxide could produce free radicals such as hydroxyl radical and hydroperoxide radical to improve the reaction rate. The suggested initiation step was:

$$O_3 + HO_2^- \rightarrow O_2 \cdot^- + O_2 + OH \cdot$$

The other steps were similar to the O_3/UV system. This process improved some organic compound oxidation efficiencies of ozonation. For oxalic acid, it could be obtained by experiments or oxalic acid the optimal pH value at 7.5 and H_2O_2/O_3 ratio at 0.5. Furthermore, Glaze and Kang (1988) and Duguet et al. (1985) showed that producing hydroxyl radicals enhanced degradation. In this process, the ratio of ozone to hydrogen peroxide was a very important parameter of reaction rate. Glaze et al. concluded the best H_2O_2/O_3 ratio as 0.5 to 0.7 for treatment of TCE and PCE in groundwater. Then, a kinetic model for ozone and hydrogen peroxide in semibatch reactor were proposed by Glaze et al. (1989 a, b) for treating PCE in groundwater. The effects of OH• scavengers such as bicarbonate and carbonate were also discussed. Wolfe et al. (1989) reported the H_2O_2/O_3 ratio effect on the disinfection of microorganisms in surface water and less than

0.3 was suggested. However, this method drawback in the limited solubility of ozone, difficult to maintain the narrow pH range, and twice amount of oxidant demand to generate the same amount of OH• than UV enhanced processes. As a result, this process should be used only while the contaminants existed in relatively low concentrations (Goronszy et al. 1992).

The effective and economic evaluation of advanced oxidation processes was also investigated by some researchers. Garland (1989) evaluated advanced oxidation including O_3/UV, H_2O_2/UV and O_3/H_2O_2 while treating chlorinated hydrocarbons in groundwater with the other processes. The result showed that the advanced oxidation processes were competitive with other processes such as activated carbon adsorption, stripping, etc.

2.5 Fenton's Reagent and Hydrogen Peroxide Photooxidation

The mechanism of this process is very similar to AOP reactions. Zepp et al. (1992) reported the degradation of anisole and nitrobenzene by H_2O_2 and Fe^{2+}, oxalate, citrate, and phosphate complexes. Recently, a study of degradation of 2,4-D (2,4-Dichlorophenol) using Fe^{3+}/H_2O_2/UV reaction were investigated by Sun et al. (1993). Besides, by using aqueous TiO_2 suspension as a catalyst in H_2O_2/UV system, Ku et al. (1992) studied the treatment of 2,4-D. Glaze et al. (1993) identified the chlorinated byproducts for photodegradations of TCE (Trichloroethane) and PCE (Pentachloroethane) in water. Moreover, Augugliaro et al. (1991) found photon can be absorbed by TiO_2 suspension in a stirred photoreactor. There was the other catalyst for phenol decomposition pathways, alumine supported iron in H_2O_2/UV system, which was investigated by Al-Hayek et al. (1990). Meanwhile, catechol hydroquinone, and p-benzoquinone were identified as intermediates.

2.6 Conventional Ozonation

Conventional ozonation has been applied to disinfect, decolorize, deodorize in drinking water for a long time. Ozonation of organics could promote significantly the overall photolytic ozonation rate. For this reason, the mechanism of ozone decomposition in aqueous solution should be studied. The reaction mechanisms and kinetics of ozone decomposition in water was still uncertain although a lot of researchers studied Ozonation of various organic pollutants in aqueous solution (Gurol 1985; Sehested et al. 1973; Glaze et al. 1990; Legube et al. 1987; Gilbert et al. 1992; Galvosa et al. 1991 and Yao et al. 1991). The key point to be considered was whether ozone reacted directly with dissolved substances or it was decomposed to form secondary oxidants such as OH• and HO_2• which then reacted rapidly with the dissolved substances. Therefore, the uncertainties of different reaction pathways resulted in a more complex mechanism study.

2.6.1 Proposed Mechanism

Nadezhdin (1988) suggested a reaction mechanism that ozone decomposed in water at a given pH and was catalyzed by the hydroxyl ion (OH^-) in the initial reaction. The overall reaction mechanism which he suggested as :

$$O_3 + OH^- \rightarrow O_2 \cdot^- + HO_2 \cdot$$
$$O_3 + H_2O \rightarrow 2HO_2 \cdot$$
$$HO_2 \cdot \Leftrightarrow H^+ + O_2 \cdot^-$$
$$O_2 \cdot^- + O_3 \rightarrow O_2 + O_3 \cdot^-$$
$$O_3 \cdot^- \rightarrow O \cdot^- + H^+$$
$$OH \cdot \Leftrightarrow O \cdot^- + H^+$$
$$O_3 + OH \cdot \rightarrow O_2 + HO_2 \cdot$$

$$2HO_2\bullet \rightarrow O_3 + H_2O$$
$$HO_2\bullet + O_2\bullet^- \rightarrow HO_2^- + O_2$$
$$O_3\bullet^- + O_2\bullet^- \xrightarrow{H_2O} 2O_2 + 2OH^-$$

From above, Nadezhadin calculated ozone decomposition kinetics which were 1 to 3/2 order with respect to the O_3 concentration, and from 0.5 to 1 order with respect to OH^- concentration.

Sotelo et al. (1987) studied on ozone decomposition at pH 2.5 to 9.0 and temperature from 10°C to 40°C. They suggested the following first order reaction mechanism :

$$O_3 + H_2O \rightarrow 2OH\bullet + O_2$$
$$O_3 + OH^- \rightarrow O_2\bullet^- + HO_2\bullet$$
$$O_3 + OH\bullet \rightarrow O_2 + HO_2\bullet$$
$$O_3 + HO_2\bullet \rightarrow HO\bullet + 2O_2$$
$$2HO_2\bullet \rightarrow H_2O_2 + O_2$$

The higher pH, the important the peroxyl radical became. Besides, the rate of the hydroxide ion in initiation step could increase.

Peleg (1976), Staehelin and Hoigne (1985), Tomiyasu et al. (1985) have proposed more complex reaction mechanisms for the ozone decomposition in pure water and in the presence of organic solutes.

2.6.2 Simplified Mechanism

Based on the mechanisms above, all investigators generally agreed that the ozone decomposition in an aqueous solution could produce hydroxyl radicals and hydroperoxide radicals. Thus, an overall ozone decomposition mechanism in an aqueous solution can be built up as follows :

$$O_3 + H_2O \rightarrow 2OH\bullet + O_2$$
$$O_3 + OH\bullet \rightarrow O_2 + HO_2\bullet$$
$$O_3 + HO_2\bullet \rightarrow HO\bullet + 2O_2$$

Comparing the ozone decomposed on to hydroxyl radical without UV radiation with photolytic ozonation, it was significantly slower and the reaction rate constant very small. Consequently, the Ozonation of organics could be simplified as proportional to ozone concentration and ozone mass transfer in the present studies. The mechanism turned out as the following type :

$$O_{3g} \xrightarrow{K_{LO_3} A} O_{3l}$$
$$O_3 + M \xrightarrow{K_1} \text{Decomposition products}$$

2.7 Azo Dyes In Wastewater

Azo dyes were broadly used in the textile industry, and also widely used to color solvents, inks, paints, varnishes, paper, plastic, rubber, foods, drugs, and cosmetics. Up to now, more than two thousand azo dyes are known. Besides, over half of the commercial dyestuffs are azo dyes (Rounds 1963). The manufacturing of azo dyes and dye house work produced wastewater contaminated with azo dyes (Stryker 1985) which substantially passed through a conventional wastewater treatment plant. Unfortunately, the activated sludge process could not decompose most azo dyes which caused a potentially serious disposal problem.

Generally, azo dyes contained one to three azo linkages (-N=N-) which linked phenyl and napthyl radicals. The radicals were usually substituted by some combinations of functional groups like amino ($-NH_2-$), chloro (-Cl-), hydroxyl (-OH-), methyl ($-CH_3-$), nitro ($-NO_2-$) and sulfonic acid, sodium salt ($-SO_3Na-$).

Some azo dyes and their dye precursors have been shown or were suspected to be human carcinogens (Bethesda 1985). Therefore, studying the fate of azo dyes in the wastewater treatment processes is of utmost concern. The effectiveness of wastewater treatment of azo dyes must be known in order to estimate its safe release from specific sources.

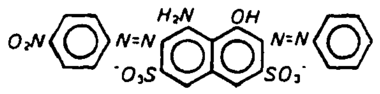
After a series of studies, Shaul and his coworker in EPA Water Engineering Research Laboratory gave a result that 11 of the 18 azo dyes were found to pass through the activated sludge process substantially untreated. Table 2.2 shows a list of azo dyes which were studied by Shaul et al. (1988).

The results proved that a substantial amount of azo dyes were not biodegraded in conventional wastewater treatment processes. However, some alternative treatment methods must be found. Hafez et al. (1989) studied ozonation of m-toluidine (azo dye) and reported that ozonation decomposed some azo dyes. Meanwhile, the advanced oxidation processes such as UV/O_3 and UV/H_2O_2 could reach effectively for degrading azo dyes. Figure 2.1 shows the chemical structures of these two azo dyes.

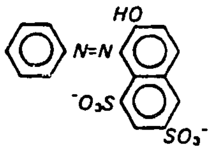
Table 2.2 Azo Dyes studied by EPA Water Research Lab

Azo dyes	Effect of ASP*
C.I. Acid Black 1	untreated
C.I. Acid Orange 10	untreated
C.I. Acid Red 1	untreated
C.I. Acid Red 14	untreated
C.I. Acid Red 18	untreated
C.I. Acid Red 337	untreated
C.I. Acid Yellow 17	untreated
C.I. Acid Yellow 23	untreated
C.I. Acid Yellow 49	untreated
C.I. Acid Yellow 151	untreated
C.I. Direct Yellow 4	untreated
C.I. Acid Blue 113	adsorbed on sludge
C.I. Acid Red 151	adsorbed on sludge
C.I. Direct Violet 9	adsorbed on sludge
C.I. Direct Yellow 28	adsorbed on sludge
C.I. Acid Orange 7	biodegraded
C.I. Acid Orange 8	biodegraded
C.I. Acid Red 88	biodegraded

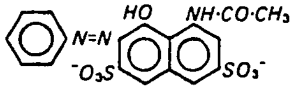
ASP* = Activated Sludge Process



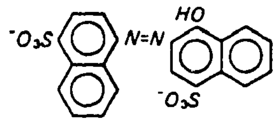
C.I. Acid Black 1



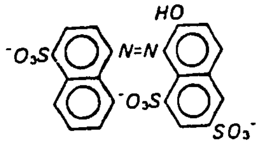
C.I. Acid Orange 10



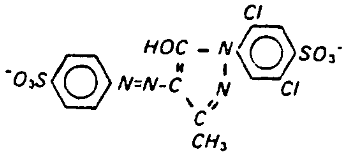
C.I. Acid Red 1



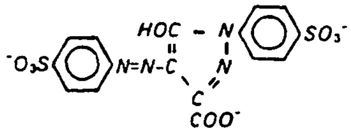
C.I. Acid Red 14



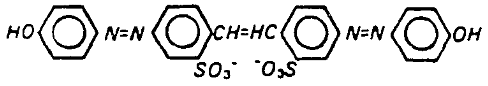
C.I. Acid Red 18



C.I. Acid Yellow 17



C.I. Acid Yellow 23



C.I. Direct Yellow 4

Figure 2.1 Chemical Structures of Azo Dyes

2.8 Oxidation of Phenol by Alternative Processes

From investigating industrial wastes, phenol was found in the wastewater of various industries, for instance, dye manufacturing plant, epoxy resins plant, additives and aromatic chemical plant, solvents plant, and aromatic chemical and pharmaceutical plant. (Stryker et al. 1985). These plants generated phenol from 2,200 lb/yr to 589,230 lb/yr. Besides, phenol was a suitable substance which could be served as a model for its high toxicity and presence in wastes from variety of industries. Especially, it could improve the understanding of the degradation of derivative compounds, such as chlorophenols, chlorinated pesticides, phenoxy herbicides, etc. Thus, phenol became a very interested substance for decomposition research by any treatment method.

The heterogeneous photocatalytic oxidation of phenol in aqueous by UV induced oxidation on TiO_2 particles was reported by Trillas et al. (1992) and Wei et al. (1991). The intermediates were detected to be hydroquinone, paraquinone, and 1,2,4-benzenetriol. They suggested the lower phenol initial concentrations, the higher degradation rates could be approached. Moreover, the maximum rate was obtained at the most optimal pH at 8. Similarly, Al-Hayek et al. (1990) treated phenol in water by hydrogen peroxide on alumine supported iron. They proposed pyrocatechol, hydroquinone, and p-benzoquinone as intermediates. Another process which was so-called, "supercritical fluid oxidation", was also applied to oxidize phenol in water by Thornton et al. (1991, 1992 a, b). They studied the pathways and reaction kinetics of phenol oxidation in supercritical water. Simultaneously, they identified some multiring compounds such as 2-and 4-phenoxyphenol, 2,2'-biphenol, and dibenzofuran as byproducts. They suggested rate equation as following :

$$\text{Rate} = k\,[\text{phenol}]^{1.0}[O_2]^{0.5}[H_2O]^{0.7}$$

The reaction rates of phenol with hydroxyl radical were reported by Field et al. (1982) as 4.5×10^9 for addition reactions and 2.1×10^9 for abtract reactions.

2.8.1 By-products of Photolytic Oxidation

It was very important for the identification of by-products which were found in the effluents. The importance was to reach the byproducts which were produced from photolytic ozonation or photolytic hydrogen peroxide oxidation. If the by-products were toxic or harmful for humans or the environment, they might cause new problems. Fortunately, some recent studies appeared that the by-products from photolytic oxidation processes looked not to be toxic. Peyton et al. (1989) investigated by-products from photolytic ozonation of organic pollutants. They suggested a mechanism that pollutants HRH (R was organic functional group) could be decomposed by hydroxyl radical as follows :

$$HRH + OH\bullet \rightarrow HR\bullet + H_2O$$

$$HR\bullet + O_2 \rightarrow HRO_2\bullet$$

$$2HRO_2\bullet \rightarrow HRO_4RH$$

The tetroxide can decompose to R, HRO, O_2, H_2O_2, etc.

$$HRO_4RH \rightarrow 2RO + H_2O_2$$

$$HRO_4RH \rightarrow 2HRO + O_2$$

Two types of mechanisms showed that the decomposition of tetroxide formed peroxyacetate and the decomposition of peroxyacetate tetroxide formed oxygen. Figure 2.2 and Figure 2.3 were the expressions of this two mechanisms.

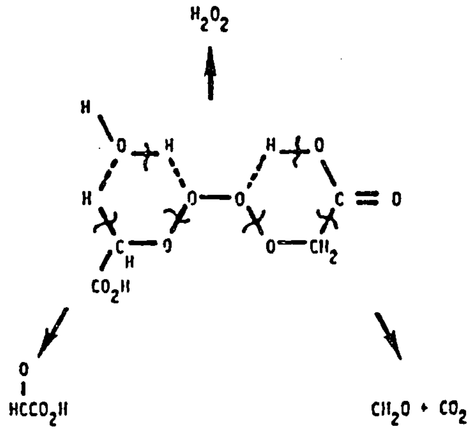


Figure 2.2 Mechanism of Tetroxide Decomposition

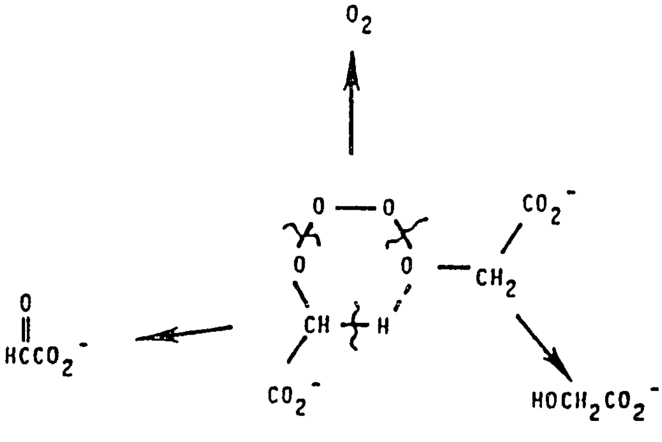


Figure 2.3 Mechanism of Peroxyacetate Tetroxide Decomposition

CHAPTER 3

REACTION MECHANISM AND KINETIC MODELS

3.1 Outline

The processes that combine hydrogen peroxide or ozone with ultraviolet radiation are widely used for treating some water contaminants. Although the processes perform with high efficiency in degrading water contaminants, the mechanisms are not well understood. In this study, a series of experiments were used to determine the rate constants for a group of reactions, then with computer simulation a kinetic model of this kind of reaction can be studied.

The reaction kinetic models for the present experiments were initially developed by Dr. C. R. Huang in 1983 and revised in 1984, 1988 and 1990. Recent modifications focused on the contribution of hydrogen peroxide, hydroxyl radical and hydroperoxide radical and light intensity model. The termination reactions of hydroxyl radical and hydroperoxide radical are very important in establishing the rate laws. Because of the high reactivity of those free radicals and oxidants, their concentration can not be easily determined by chemical analysis. The rate constants obtained from some physical chemistry studies become very important in checking the mathematical model. In order to distinguish the effects of the different processes and solve for the reaction rate constants, at least 9 experiments were run for each azo dye ; i.e. (1) bubbling with nitrogen; (2) UV radiation only; (3) nitrogen bubbling with UV radiation; (4) ozone bubbling only; (5) ozone bubbling with UV radiation; (6) hydrogen peroxide only; (7) hydrogen peroxide with UV radiation; (8) CSTR for ozone/UV reaction, and CSTR for hydrogen peroxide/UV reaction. The reaction kinetic models set up for each experiments are based upon the following three assumption :

1. The reactions in each mechanism are considered to be first order respect to both reactants.
2. The reactants and intermediates which absorb UV photons will take into account by a light intensity model by measuring absorbance at 254 nm.
3. Assume complete mixing by both bubbling and pumping circulation.

The detailed models are described in following section. Symbols and the relationship of rate constants and experiments are shown in Table 3.1 , 3.2.

Table 3.1 Rate Constants Obtained from Each Experiment

Experiments	Rate constants solved
From literature	k_{8f}, k_{10f}, k_{11f}, k_{14}, k_{15}, k_{16}
O_3 mass transfer, decomposition by UV	$K_{LO_3}A$, $k_{IO_3}I$
H_2O_2 mass transfer, decomposition by UV	$k_{IH_2O_2}I$
Ozonation only	k_1
H_2O_2/UV	k_4, k_5
O_3/UV	k_4, k_5, k_1 reconfirm
CSTR experiment	reconfirm rate constants

Table 3.2 Definition of Symbols in Kinetic Model

Symbols	Units	Definitions
$K_{LO_2}A$, $K_{LO_3}A$, $K_{LA}A$	1/sec	Area combined mass transfer coefficient
A	cm^2	Total surface area of gas bubbles in mass transfer term
M	dimentionless	Henry's law constants
O_{2l} , O_{3l}		Oxygen, ozone in liquid phase
O_{2g} , O_{3g}		Oxygen, ozone in gas phase
C_{O_2} , C_{O_3} , C_a	mole/l	Concentration of oxygen, ozone, or azo dye A
C_{O_20} , C_{O_30} , C_{a0}	mole/l	Initial concentration of oxygen, ozone or azo dye A
C_{O_2S} , C_{O_3l}	mole/l	Satuated concentration of oxygen, ozone
$k_{IA}I$, $k_{IH_2O_2}I$, $k_{IO_2}I$, $k_{IO_3}I$	1/sec	Intensity combined photo-decomposition constant
k_{IO_2b}	1/sec	Backward rate constant for oxygen photo-decomposition
A^* , O_2^*		Excited state of azo dye A and oxygen
r_a	mole/l-sec	Decomposition rate of azo dye A
V	l	Volume of reactor
Q	l/sec	Flow rate of influent in CSTR experiment
Q_g	cm^3/sec	Flow rate of gas into reactor in azo dye A mass transfer from liquid phase to gas phase
C_{ag} , C_{as}	mole/l	Azo dye A concentration in gas phase and liquid film at gas-liquid interphase
k_1 , k_4 , k_5 , k_6	l/mole-sec	Rate constants of azo dye decomposition by oxidants
k_2 , k_3	1/sec	Rate constants of excited state azo dye decaying
k_{8f} , k_{10f} , k_{11f} , k_{12f} , k_{14} , k_{15} , k_{16}	1/mole-sec	Rate constants of oxidants react to each other

3.2 Mass Transfer Of Ozone/Ozone Decomposition under UV Radiation

These experiments are used to determine the mass transfer coefficient of ozone from gas phase to liquid phase by bubbling ozone into the uncontaminated water. Since the concentration of ozone in liquid phase can be measured at different time period, the mass transfer coefficients can be found in these experiments.

$$O_{3g} \xrightarrow{K_{LO_3}A} O_{3l}$$

The material balance for oxygen and ozone can be expressed as follows :

$$\frac{dC_{O_3}}{dt} = K_{LO_3}A(C_{O_3S} - C_{O_3})$$

Initial conditions : t = 0 , $C_{O3} = C_{O3o}$

By applying UV radiation of O_3 saturated solution, O_3 decomposed by UV light to a steady state concentration then $K_{IO3}I$ could be obtained by following equation :

$$K_{LO_3}A(C_{O_3S} - C_{O_3}) = K_{IO_3}IC_{O_3}$$

3.3 Light Intensity Model

Light intensity which affected the decomposition rate of pollutants in an AOP reactor was a moderately important parameter. Radial approximation of the infinite line source model can be described as follows :

The light intensity, I, at any point p in the reactor was related to the surface flux, I_0, by a one-dimension form of Lambert's law of absorption

$$\frac{1}{r}\frac{d(rI)}{dr} = -EI$$

where E is the monochromatic absorbance of water using logarithms to the base e. Integration of the above equation using boundary condition of $I = I_0$ when $r = r_0$ gives

$$I = I_o \frac{r_o}{r} e^{-E(r-r_o)}$$

Therefore, the ratio of the average point intensity to the surface flux at the quartz tube in the reactor was defined as the intensity factor, m.

$$m = \frac{\bar{I}}{I_o} = \frac{2r_o}{E(R^2 - r_o^{\,2})}[1 - e^{-E(R-r_o)}]$$

Here, R denotes radius of reactor, r_0 is radius of lamp with quartz shell.

3.4 Hydrogen Peroxide Decomposition Under UV Radiation

These experiments are the fundamental study of AOPs (Advanced Oxidation Processes) reactor. Hydrogen peroxide in different initial concentrations are decomposed by UV light. The reactions involved are as follows :

$$H_2O_2 + hv \xrightarrow{k_{H2O2}I} 2OH\cdot$$

$$H_2O_2 + OH\bullet \xrightarrow{k_{10f}} HO_2\bullet + H_2O$$

$$H_2O_2 + HO_2\bullet \xrightarrow{k_{11f}} HO\bullet + H_2O + O_2$$

$$2OH\bullet \xrightarrow{k_{14}} H_2O_2$$

$$2HO_2\bullet \xrightarrow{k_{15}} H_2O_2 + O_2$$

$$OH\bullet + HO_2\bullet \xrightarrow{k_{16}} H_2O + O_2$$

The reaction rate for each species are as following :

$$\frac{dC_{H_2O_2}}{dt} = -k_{IH_2O_2} I C_{H_2O_2} - k_{10f} C_{H_2O_2} C_{OH\bullet} - k_{11f} C_{H_2O_2} C_{HO_2\bullet} + k_{14} C_{OH\bullet}{}^2 + k_{15} C_{HO_2\bullet}{}^2$$

$$\frac{dC_{OH\bullet}}{dt} = 2k_{IH_2O_2} I C_{H_2O_2} - 2k_{14} C_{OH\bullet}{}^2 - k_{16} C_{OH\bullet} C_{HO_2\bullet} + k_{11f} C_{H_2O_2} C_{HO_2} - k_{10f} C_{H_2O_2} C_{OH\bullet}$$

$$\frac{dC_{HO_2\bullet}}{dt} = -2k_{15} C_{HO_2\bullet}{}^2 - k_{11f} C_{H_2O_2} C_{HO_2\bullet} + k_{10f} C_{H_2O_2} C_{OH\bullet} - k_{16} C_{OH\bullet} C_{HO_2\bullet}$$

Initial condition : t=0, $C_{OH\bullet} = C_{HO\bullet} = 0$, $C_{H_2O_2} = C_{H_2O_20}$

The rate constant $k_{IH2O2}I$ can be obtained by fitting experiment data

3.5 Mass Transfer of Phenol and Studied Azo Dyes

The purpose of this experiment is to estimate the evaporation effect of the azo dyes and phenol due to nitrogen bubbling. Two film theory is used to carry out the material balances in the different phases.

No mass transfer between liquid phase and gas phase was found for eight azo dyes and phenol. The effect of stripping can be neglected.

3.6 Reaction With UV Light

The purpose of this set of experiments is to determine the effect of UV radiation on the azo dyes and phenol. There are two types of experiments, one with nitrogen and the other without nitrogen. If the pollutant easily evaporates by bubbling, nitrogen is introduced into the reactor under UV radiation; otherwise, the experiment is run without using nitrogen.

Azo dyes and phenol were found not decomposed by UV radiation. From experiment data, there were no significant degradation under UV radiation for 60 minutes.

3.7 Reaction With Hydrogen Peroxide Only

In this experiment, the azo dyes and phenol can not react with hydrogen peroxide without UV radiation.

3.8 Reaction With Ozone Alone

Ozone has the oxidation power to decompose pollutants in water. From this experiment, the effect of ozone on decomposition of the pollutants can be determined . The ozone is generated from pure oxygen by use of an ozonator and the concentration is at least 2% by weight.

From a review of the literature, ozone is found to decompose to hydroxyl radical as a initiation step. Hydroxyl radicals oxidize the pollutants in water and produces hydroperoxide radicals which also oxidize pollutants in water. The reaction rate of ozone decomposing in water and the rate of production of hydroxyl radical is too slow with respected to ozone mass transfer and ozonation of pollutants. So these steps are neglected. The mechanism of ozonation of azo dyes can be simplified to :

$$A + O_3 \xrightarrow{K_l} \text{Decomposition products}$$

Ozone mass transfer :

$$O_{3g} \xrightarrow{K_{LO_3}A} O_{3l}$$

The reaction rates for each species are as follows :

$$\frac{dCa}{dt} = -k_l C_a C_{O_3}$$

$$\frac{dC_{O_3}}{dt} = -k_1 C_a C_{O_3} + k_{LO_3} A (C_{O_3S} - C_{O_3})$$

Initial conditions : t=0, $Ca = Ca_0$, $C_{O_3} = 0$

Rate constant k_1 is determined using the same optimization method.

3.9 Reaction with Hydrogen Peroxide And UV Light

Hydrogen peroxide can serve as a source of hydroxyl radical in aqueous solution under UV radiation. This experiment is a fundamental to quantitatively understanding the UV/ozone process. Hydrogen peroxide also plays an important role in the UV/ozone process. The proposed reaction models are :

$$H_2O_2 + hv \xrightarrow{k_{IH2O2}I} 2OH\bullet$$

$$H_2O_2 + OH\bullet \xrightarrow{k_{10f}} HO_2\bullet + H_2O$$

$$H_2O_2 + HO_2\bullet \xrightarrow{k_{11f}} HO\bullet + H_2O + O_2$$

$$2OH\bullet \xrightarrow{k_{14}} H_2O_2$$

$$2HO_2\bullet \xrightarrow{k_{15}} H_2O_2 + O_2$$

$$OH\bullet + HO_2\bullet \xrightarrow{k_{16}} H_2O + O_2$$

$$A + OH\bullet \xrightarrow{k_4} \text{Decomposition products}$$

$$A + HO_2\bullet \xrightarrow{k_5} \text{Decomposition products}$$

The reaction rates for each species are as following :

$$\frac{dC_{H_2O_2}}{dt} = -k_{IH_2O_2} I C_{H_2O_2} - k_{10f} C_{H_2O_2} C_{OH\bullet} - k_{11f} C_{H_2O_2} C_{HO_2\bullet}$$
$$+ k_{14} C_{OH\bullet}{}^2 + k_{15} C_{HO_2\bullet}{}^2$$

$$\frac{dC_{OH\bullet}}{dt} = 2k_{IH_2O_2} I C_{H_2O_2} - k_4 C_a C_{OH\bullet} - 2k_{14} C_{OH\bullet}{}^2 - k_{16} C_{OH\bullet} C_{HO_2\bullet}$$
$$+ k_{11f} C_{H_2O_2} C_{HO_2} - k_{10f} C_{H_2O_2} C_{OH\bullet}$$

$$\frac{dC_{HO_2\bullet}}{dt} = -k_5 C_a C_{HO_2\bullet} - 2k_{15} C_{HO_2\bullet}{}^2 - k_{11f} C_{H_2O_2} C_{HO_2\bullet} + k_{10f} C_{H_2O_2} C_{OH\bullet}$$
$$- k_{16} C_{OH\bullet} C_{HO_2\bullet}$$

Initial condition : t=0, $C_{OH\bullet} = C_{HO\bullet} = 0$, $C_{H_2O_2} = C_{H_2O_20}$

The rate constants k_4, and k_5 are optimized to give the best fit to the experimental results from this process.

3.10 Reaction With Ozone And UV Light

In this experiment, the combined effect of all the radicals created by the ozone under UV radiation is determined. This reaction rate is faster and dye decomposition more effective than found in previous experiments. The mechanism is described as follows:

$$O_3 + H_2O + hv \xrightarrow{k_{IO_3}I} O_2 + 2OH\bullet$$

$$O_3 + OH\bullet \xrightarrow{k_{8f}} HO_2\bullet + O_2$$

$$O_3 + HO_2\bullet \xrightarrow{k_{12f}} OH\bullet + 2O_2$$

$$H_2O_2 + hv \xrightarrow{k_{IH2O2}I} 2OH\bullet$$

$$H_2O_2 + OH\bullet \xrightarrow{k_{10f}} HO_2\bullet + H_2O$$

$$H_2O_2 + HO_2\bullet \xrightarrow{k_{11f}} HO\bullet + H_2O + O_2$$

$$2OH\bullet \xrightarrow{k_{14}} H_2O_2$$

$$2HO_2\bullet \xrightarrow{k_{15}} H_2O_2 + O_2$$

$$OH\bullet + HO_2\bullet \xrightarrow{k_{16}} H_2O + O_2$$

$$A + O_3 \xrightarrow{k_1} \text{Decomposition products}$$

$$A + OH\bullet \xrightarrow{k_4} \text{Decomposition products}$$

$$A + HO_2\bullet \xrightarrow{k_5} \text{Decomposition products}$$

Ozone mass transfer :

$$O_{3g} \xrightarrow{K_{LO_3}A} O_{3l}$$

The reaction rates for each species are as follows :

$$\frac{dC_a}{dt} = -k_1 C_a C_{O_3} - k_4 C_a C_{OH\bullet} - k_5 C_a C_{HO_2\bullet}$$

$$\frac{dC_{O_3}}{dt} = -k_1 C_a C_{O_3} - k_{IO_3} I C_{O_3} - k_{8f} C_{O_3} C_{OH\bullet} - k_{12f} C_{O_3} C_{HO_2\bullet}$$
$$+ k_{LO_3} A (C_{O_3S} - C_{O_3})$$

$$\frac{dC_{OH\bullet}}{dt} = 2k_{IH_2O_2} I C_{H_2O_2} - k_4 C_a C_{OH\bullet} - 2k_{14} C_{OH\bullet}{}^2 - k_{16} C_{OH\bullet} C_{HO_2\bullet}$$
$$+ k_{11f} C_{H_2O_2} C_{HO_2} - k_{10f} C_{H_2O_2} C_{OH\bullet}$$

$$\frac{dC_{HO_2\bullet}}{dt} = -k_5 C_a C_{HO_2\bullet} - 2k_{15} C_{HO_2\bullet}{}^2 - k_{11f} C_{H_2O_2} C_{HO_2\bullet} + k_{10f} C_{H_2O_2} C_{OH\bullet}$$
$$- k_{16} C_{OH\bullet} C_{HO_2\bullet}$$

$$\frac{dC_{H_2O_2}}{dt} = -k_{IH_2O_2} I C_{H_2O_2} - k_{10f} C_{H_2O_2} C_{OH\bullet} - k_{11f} C_{H_2O_2} C_{HO_2\bullet}$$
$$+ k_{14} C_{OH\bullet}{}^2 + k_{15} C_{HO_2\bullet}{}^2$$

Initial condition : t=0, $C_{OH\bullet} = C_{HO2\bullet} = 0$, $C_{H_2O_2} = C_{H_2O_20}$

The computed output concentration is compared to the experimental data to evaluated the proposed reaction kinetic models and the reaction rate constants.

CHAPTER 4

EQUIPMENT AND EXPERIMENTS

4.1 Materials and Chemicals

Hydrogen peroxide was obtained from Fluka Chemie AG, in 35% content. Ozone was generated from Welbach T-816 ozone generator in 5% (w/w). Phenol was from Sigma Chemical Co., with 0.15% H_3PO_2 as inhibitor. Azo dyes were from Aldrich Chemical Co., Inc., and no further purification before using in experiments. Table 4.1 shows the formula and physical properties of azo dyes.

Table 4.1 The Characteristics of Azo Dyes

Azo dyes	Formula	λ_{max}	MW	Dye contents
Acid Black 1	$C_{22}H_{14}N_6Na_2O_9S_2$	618 nm	616.50	85%
Acid Orange 10	$C_{16}H_{10}N_2Na_2O_7S_2$	452 nm	452.38	95%
Acid Red 1	$C_{18}H_{13}N_3Na_2O_8S_2$	532 nm	509.43	60%
Acid Red 14	$C_{20}H_{12}N_2Na_2O_7S_2$	515 nm	502.44	50%
Acid Red 18	$C_{20}H_{11}N_2Na_3O_{10}S_3$	506 nm	604.48	75%
Acid Yellow 17	$C_{20}H_{10}Cl_2N_4Na_2O_7S_2$	400 nm	551.30	60%
Acid Yellow 23	$C_{16}H_9N_4Na_3O_9S_2$	425 nm	534.37	60%
Direct Yellow 4	$C_{26}H_{18}N_4Na_2O_8S_2$	497 nm	624.56	70%

Supelclean LC-18 SPE tubes (6 ml, 1g) were used for extracting and concentrating sample solutions for GC/MS (Gas Chromatography with Mass Spectroscopy Detector) analysis.

4.2 Analytical Methods

4.2.1 Hydrogen Peroxide Concentration Analysis

The hydrogen peroxide concentration determination methods have been proposed by different investigators (Bader et al. 1988; Kieber et al. 1986; Miller et al. 1988; Matsubara et al. 1985 and Masschelein et al. 1977). For examples, Bader et al. proposed a photometric method by using N, N, diethyl -p-phenylenediamine and measuring the absorbance at 551 nm; Matsubara, et al. suggested to use Titanium-4-(2'-pyridylazo) resorcinol and to measure absorbance at 508 nm; Miller et al. proposed a fluorometric method; Kieber et al. compared iodometric and fluorometric method; and Masschelein et al. proposed using Cobalt-bicarbonate and measuring absorbance at 260 nm. Reviewed and chose one of the method which was the most suitable for azo dyes and phenol samples. Since all azo dyes could appear very strong absorption between 300 nm to 600 nm, the methods proposed by Bader et al. and Matsubara et al., may lead some serious interferences. The fluorometric methods were limited by the equipment. Therefore, the method of Masschelein et al. was used to determine hydrogen peroxide concentrations in dye samples and phenol samples.

The spectrophotometric method proposed by Masschelein et al. described as follows :

1. Placed 80 ml sample solution in an 100 ml volumetric flask, added 1 ml of the Co^{++} reagent (19 g $CoSO_4 \cdot 7H_2O$ in 1 liter distilled water) and 1 ml of the sodium hexametaphosphate solution (10 g/l), then made up to 100 ml with saturated bicarbonate solution.
2. The absorbance was measured at 260 nm by comparing with a blank-reagent solution.

3. Calibration curve was made by standard hydrogen peroxide solution in different concentrations.

4.2.2 Ozone Concentration Analysis

Similarly, Ozone concentrations also can be determined by photometric methods using indigo (Bader et al. 1981 and Takeuchi et al., 1989) and measuring absorbance at 600 nm. These methods cause large interference to the absorbance for azo dyes. The iodometric methods were studied by Shechter (1972) and Gordon et al. (1989) for determining ozone concentrations in water.

The procedure for measuring ozone concentration was based on the method which Shechter proposed.

1. Add 5 ml of sample solution in a sample vial containing 5 ml of 2% neutral potassium solution. After 30 minutes, measured the intensity of absorbance at 352 nm by spectrophotometer.
2. 2% neutral potassium solution was prepared by dissolving 13.61 g potassium dihydrogen-phosphate, 14.2 g anhydrous disodium hydrogen phosphate and 20.0 g potassium iodide in 1000 ml distilled water.
3. Calibration curve was prepared by measuring absorbance of fresh iodine standard solutions at 352 nm.

4.2.3 Azo Dyes Concentration Analysis

According to the reports from Bruins et al. (1987) and Voyksner (1985). Azo dye concentrations were measured by HPLC (High Performance Liquid Chromatograph) and photospectrometer. The detailed descriptions of equipment and operation conditions would be in section 4.3.7 and 4.3.8. Phenol concentrations were determined by HPLC. Its operating conditions are described in 4.3.7.

4.2.4 Intermediates Identification

Intermediates were collected from each oxidation processes. Extracting and concentrating by using SPE (Solid Phase Extraction) tubes, then injected into GC/MS for identification. GC/MS is described in 4.3.9.. SPE tubes were preconditioned by 2 ml methanol and 2 ml water. A 400 ml of water sample was passed through SPE tube by applying vacuum, then by using 2 ml water to wash SPE tube. Finally, use 2 ml methanol to elute the organics, collect the methanol solution and analyze the extract using GC/MS.

4.3 Experimental Equipment

4.3.1 Laboratory Size Photochemical Reactor

Screening and parametric studies are generally conducted in laboratory sized reactors, because data can be generated rapidly and the cost of feed materials is minimal when compared with pilot studies. The laboratory size reactor was used in this study in order to determine reasonable decomposition rate of azo dyes. A New England Photochemical Co. Model RPR-100 photochemical reactor was used in the experiments. There are 16 high pressure mercury arc UV lamps (wavelength 253.7 nm, 35 watts/lamp) arranged on the inner wall of reactor. Therefore, a total energy of 560 watts can be used in a 500 ml quartz stirred vessel.

4.3.2 Pilot Plant Reactor

A schematic diagram of the apparatus used in the scale-up experiments is shown in Figure 4.1 The descriptions are as follows:

The vertical cylindrical type reactor is made of stainless steel type 304. The outside diameter is 13 inches and the length is 55 inches that it is approximate 100 liters of hold-up volume. There are nine vertical sample ports evenly spaced in three rows. All the tubes connected to the reactor are made of stainless steel type 304. The reactor with annular space about 3.5 inches between the reactor and the lamp wall which provided the ultraviolet light source.

A submerged pH electrode in the reactor was connected to a pH monitor/controller which controlled pH by pumping acid or basic solution into the reactor by a pH controlling pump.

There were two pumps for this reactor : One pump with 1/2 horse power was used to recycle the solution and to achieve maximum mixing. Another pump was used for feeding the solution containing the pollutants to the reactor from a reservoir tank during CSTR (Constant Stirred Tank Reactor) operation. The flow rate into the reactor was measured by a flowmeter.

Nitrogen, oxygen or ozone were introduced into the bottom of the reactor through a four-head sparger of medium porosity. The exhaust gas was vented from the top of the reactor passing through a pair of absorption bottles then vented into a laboratory hood. Complete mixing of the solution was achieved by recycling the solution and bubbling nitrogen gas into the reactor.

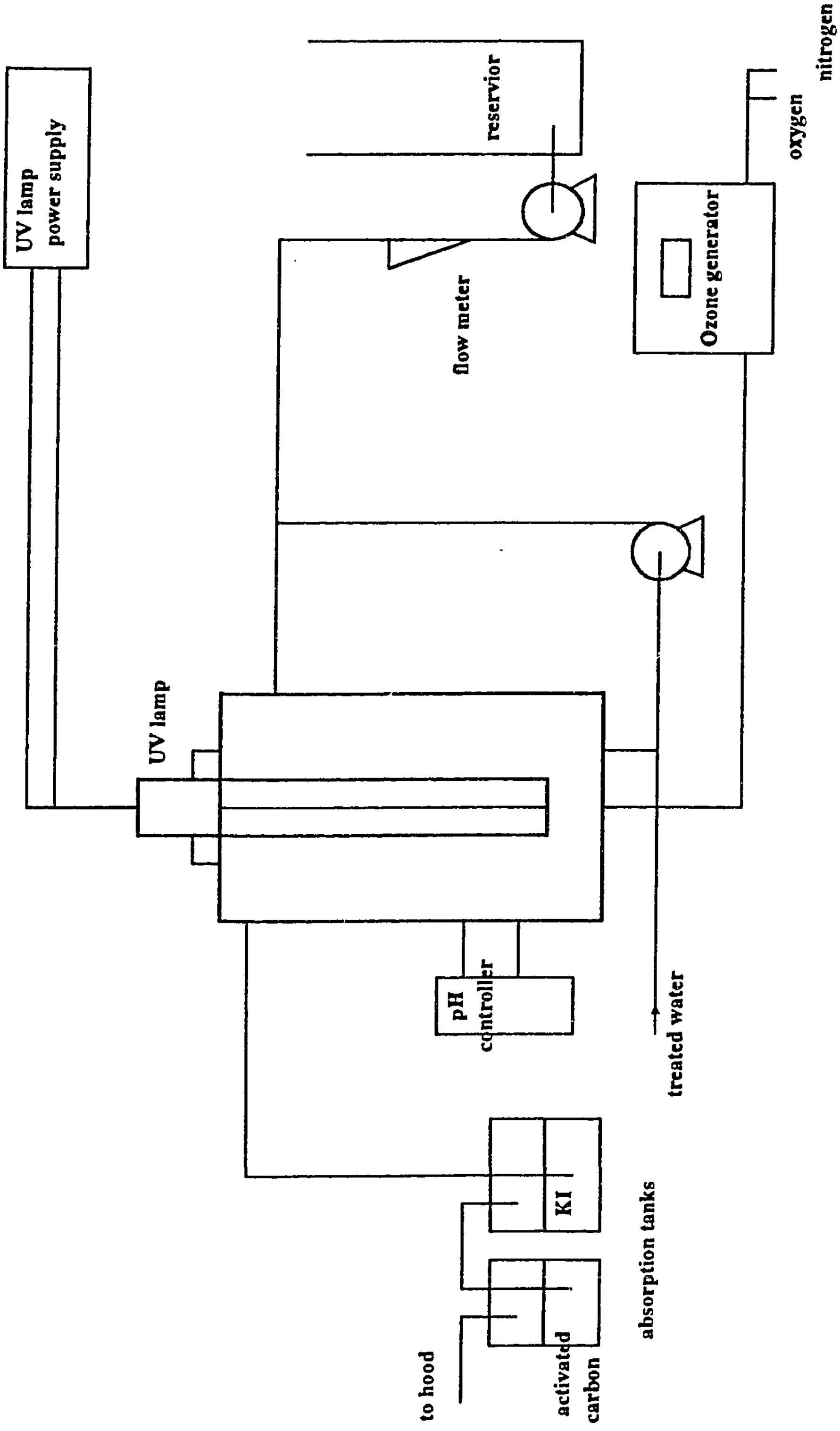


Figure 4.1 The Schematic Diagram of Experimental Equipment

4.3.3 Ozone Generator

Ozone was produced by a Welsbach T-816 ozone generator, which was manufactured by the Welsbach Ozone System Corporation, Philadelphia, PA. This generator can produce at least 16 grams of pure, dry ozone per hour. It was a corona discharge type ozone generator and was cooled by water. Ozone output flow rate was adjustable by a ball valve from 4.5 to 9.0 l/min. 99.6 % pure dry oxygen set at 110 Watts, and 105 Volts, was used for ozone generation in this experiment.

4.3.4 Ultraviolet Light Source

The ultraviolet light source was made by the Canard-Hanovia Inc., Newark, NJ. It was a low pressure mercury vapor lamp with a 25-inch arc length of and 5,000-watt power. The lamp filled with precise amount of mercury and argon, an inert gas, was a clear fused quartz tube with tungsten electrodes at both ends. It is encased in two concentric wells made of quartz glass. The inner well which houses the mercury lamp, was connected to a nitrogen gas feed line. The line acted as a blanket to avoid an explosive hazard. Nitrogen was fed with a flow rate of under 100 cm^3/min. The outer well was used to circulate cooling water. Cooling water flow rate was kept about 4-8 gallons/min. The supplied power of the lamp can be set at 300, 200 or 125 watts/inch levels. Experiments were conducted for the UV lamp at 200 watts/inch power level and 254 nm wavelength.

4.3.5 Absorption Bottle and Adsorption Bottle

A pair of absorption and adsorption bottles were used for off gas treatment. The first absorption bottle filled with 10 % KI (Potassium Indoine) solution was used to absorb the residual ozone in the off gas. The second bottle filled with activated carbon was used to collect organics evaporating out of the reactor. With these two bottles, the experimental set up was considered safe. No harmful gas escaped from the reactor.

4.3.6 pH Control System

A Cole Parmer Co. pH controller (pH 5654-12), pH electrode and basic pump were used in the experiment to indicate and control pH in the reactor.

4.3.7 High Performance Liquid Chromatograph

A Waters 600E system controller with Waters 715 Ultra Wisp Sample Processor and Waters 994 programmable photodiode array detector coupled with Chromatography server data acquiring system was used to determine phenol concentrations and its decomposition intermediates. The stationary phase was Nova-Pak 3.9 mm×150 mm, C_{18} column and the mobil phase was 70% of 1% acetic acid in water and 30% of 1% acetic acid in acetonitrile

A LDC/Milton Roy Co. made HPLC which includes Spectro Monitor III , Constra Metric III & I and Gradient Master, was used to determine the calibration curves and calculate the concentrations for three azo dyes, Acid Orange 10 (AO10), Acid Red 14 (AR14), and Acid Yellow 17 (AY17). Results of HPLC and UV/VIS Spectrophotometer were compared to confirm that the concentration readings from spectrophotometer were in a reasonable error range (less than 3%).

Analysis the concentrations of AO10, AR14, and AY17 were conducted using a Supelcosil LC-18, 7.5 cm x 4.6 mm, 3μm particle size column with mobile phase gradient from 50% methanol in water to 90% methanol in water at 1.0 ml/min. The absorption wavelength of the UV detector was set at 475 nm for AO 10, 515 nm for AR14, and 400 nm for AY17. This method was slightly modified from the method proposed by Voyksner (1985).

4.3.8 Spectrophotometer

A Varian DMS 200 UV-Vis spectrophotometer was used to scan dye samples from 200 nm to 600 nm. Besides, it may aid the determination of azo dye concentration in the solution. Hydrogen peroxide and ozone concentrations in water samples were also determined by iodometric method which measured absorbance by using spectrophotometer at 260 nm and 352 nm, respectively.

4.3.9 Gas Chromatograph with Mass Spectrometry Detector (GC/MS)

A HP 5890 series II gas chromatograph with HP 5988A mass spectrometry detector and Pascal Chem Station data system was used to identify the reaction intermediates from oxidation.

The column used in these experiments was a 25m×0.25 mm ID, methyl silicon cross link capillary column, Temperature was programmed from $60^{o}C$ for 1 min to $200^{o}C$ for 5 minutes with increasing rate of $8^{o}C/min$.

4.3.10 Sample Collection

One sampling port located in the reactor center was used for sample collecting. In order to eliminate the dead volume collection from the sample port, each sample jar was rinsed twice by the effluent solution from the reactor before sample collecting. A 20 ml sample was collected and analyzed several times to improve the precision.

4.4 Experiments

4.4.1 Standard Calibration Curve

The azo dyes were prepared in 1.0 to 20.0 ppm to develop calibration curves for the HPLC and Spectrophotometer. By plotting the absorption intensity or HPLC peak area versus dye concentration, two straight line calibration curves were obtained for each azo dye.

4.4.2 Laboratory Size Reactor Experiment

Before the pilot plan reactor experiments, a laboratory size reactor was used to determine the decomposition of azo dyes.

4.4.3 Kinetic Model Study of Hydrogen Peroxide Decomposition under UV Radiation

From literature review, fundamental reaction rate constants were obtained. A series of hydrogen peroxide decomposition reaction by UV light were done for different initial hydrogen peroxide concentrations. Photochemical reaction models were run for determining one of the best results which could be consistent with the experimental data.

4.4.4 Batch Experiments

The first step towards the batch experiment comprised of pumping the uniform pollutant solution into the reactor. Then recycling was followed with introducing nitrogen 10 l/min into the reactor. The UV light source, if necessary, was activated. Before switching the UV light power on, started the cooling water and nitrogen flow for the UV lamp at a safe level. Setting the power rate at 125 watts/inch first, after 30 seconds later, turn the power rate to 200 watts/inch. About 20 second later, began the experiment. The N_2 alone and the

N_2/UV processes were above mode batch experiments. The other batch mode experiments were the H_2O_2 and the H_2O_2/N_2/UV processes.

Sample solutions were prepared as the batch experiments. However, before turning the UV light power on, known amount of H_2O_2 was added to the reactor and 1 minute for complete mixing. The rest of the procedure was implemented for N_2, or for N_2/UV.

4.4.5 Semi Batch Experiments

Two experiments which were O_3 alone and O_3/UV were conducted in the semi batch mode. In the semi batch reaction, one reactant (azo dye) was initially added batchwise. The experiment was then conducted with a constant flow of the second reactant.

For experiments involving ozone bubbling, cooling water and oxygen flow to the ozone generator were started before the power was turned on. Oxygen flow rate was regulated at 8 psig for a flowrate of about 6 l/min.

4.4.6 CSTR Experiments

The O_3/UV and H_2O_2/UV experiments were introduced in the CSTR experiments. The sample solution was dissolved in a reservoir tank before feeding to the reactor. In the O_3/UV experiment, the feed, UV light and O_3 flow were turned on simultaneously. In the H_2O_2/UV process, hydrogen peroxide was dissolved in the reservoir tank. When the reaction started, the feed and UV light was turned on at the same time. The experiment was terminated when the feed solution was exhausted.

4.4.7 Effect of Hydrogen Peroxide Dosage

In order to find the relationship between the decomposition rate and hydrogen peroxide dosage, a series of experiments with different hydrogen peroxide dosage were set up. The dosage of H_2O_2 was 20 ml, 40 ml, 60 ml, 80 ml (the mole - fraction of H_2O_2 per azo dye are 240, 480, 720, 960) in H_2O_2/UV reaction experiments at pH 6.8 and 25°C. In this series of experiments, an optimum hydrogen peroxide dosage could be found.

4.4.8 Effect of pH

A series of experiments with different pH value in H_2O_2/UV reaction experiments were conducted to find the relationship between the decomposition rate and pH. In this series of experiments, an optimum pH value could be found.

4.4.9 Effect of Transmittance of Water

A series of experiments with different initial dye concentrations in H_2O_2/UV reaction experiments were conducted to find the relationship between the decomposition rate and light transmittance. In this series of experiments, effect of light absorbed by azo dye could be found.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Decomposition of Hydrogen Peroxide under UV Radiation

Hydrogen peroxide decomposition under UV radiation was the fundamental experiment to comprehend the AOPs reaction mechanisms. By adding 60, 40 and 20 ml of 35% hydrogen peroxide solution into 100 liter deionized water in AOPs reactor, the concentrations of hydrogen peroxide were prepared as 7.081, 4.736, and 2.572 mg-mole/l. Then, get sampling at different time interval while UV light was turned on. The model which was approached by experiments was modified twice. The rate constants from literature have been discussed in Chapter 2. Except hydrogen peroxide reacted with hydroxyl radical and hydroperoxyl radical, the inter-reactions of free radicals were studied for model mechanism. The photodecomposition rate constants of hydrogen peroxide were approached by fitting the experimental data into model which was modified several times. The model conditions were as follows :

1. Assuming no absorption of UV light by hydrogen peroxide solution, and neglecting volume of gas bubbles : Three different photodecomposition rate constants were obtained from three different initial concentrations of H_2O_2 as above mentioned. It could be concluded the model was not satisfied for experiment data.
2. Considering UV light absorption by hydrogen peroxide solution but neglecting volume of gas bubbles : Still got three different decomposition rate constants as first conclusion.
3. Considering both UV light absorption by hydrogen peroxide solution and volume of gas bubbles. : it could be allowed to fit one decomposition rate for three tests. Besides, the consistent agreement between experimental data and model predictions could be observed. Therefore, it was denoted that the model

better expresses the mechanism of hydrogen peroxide photooxidation. Figure 5.1 shows the experimental data and model fitting of hydrogen peroxide phtodecompostion at three different initial concentrations. Figure 5.2 gives the concentrations of H_2O_2, $HO_2\bullet$, $OH\bullet$ under the UV radiation.

Table 5.1 shows photodecomposition rate constants ($k_{IH2O2}I$) of hydrogen peroxide in three steps of modifications.

A sensitivity analysis was introduced for this experiment. The results showed that changing $k_{IH2O2}I$ and absorbance of H_2O_2 solution could affect the hydrogen peroxide decomposition more sensitively. For the rest of rate constants (k_{10f}, k_{11f}, k_{14}, k_{15} and k_{16}) , even adjusting the upper or lower by one order did not make significant differences for the ultimate concentration of hydrogen peroxide. The sensitivity analysis of this experiment are given in Table 5.2 and Figure 5.3.

Table 5.1 Photodecomposition Rate Constants ($k_{IH2O2}I$) of Hydrogen Peroxide in Three Steps of Modification

H_2O_2 concentration	7.081 mg-mole/l	4.736 mg-mole/l	2.572 mg-mole/l
Original model	0.521×10^{-3}	0.669×10^{-3}	0.778×10^{-3}
1st modification	0.943×10^{-3}	0.864×10^{-3}	0.780×10^{-3}
2nd modification	1.091×10^{-3}	1.080×10^{-3}	1.080×10^{-3}

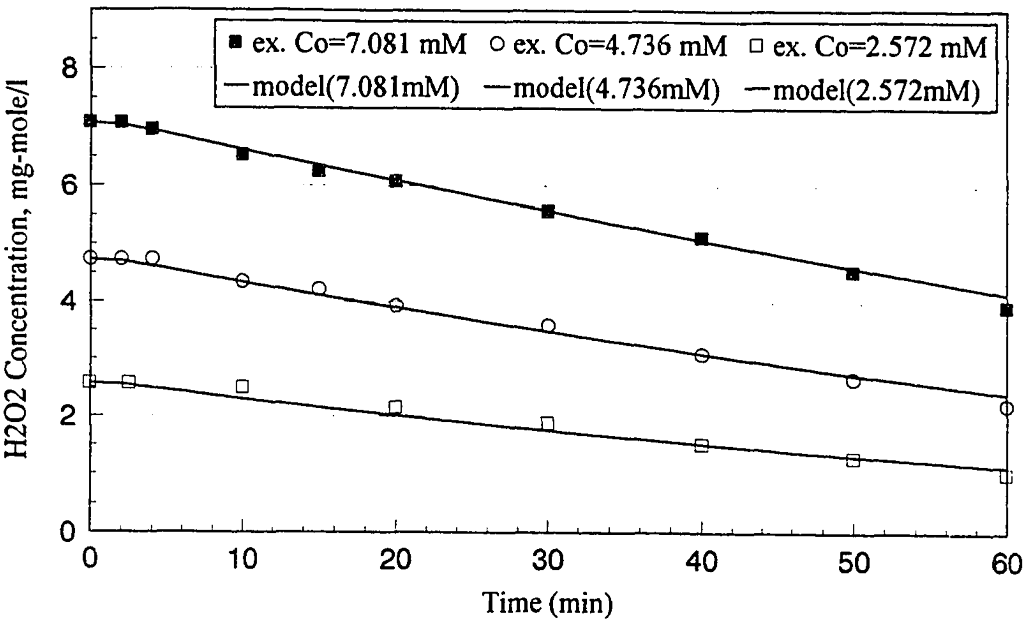


Figure 5.1 Photodecomposition of Hydrogen Peroxide

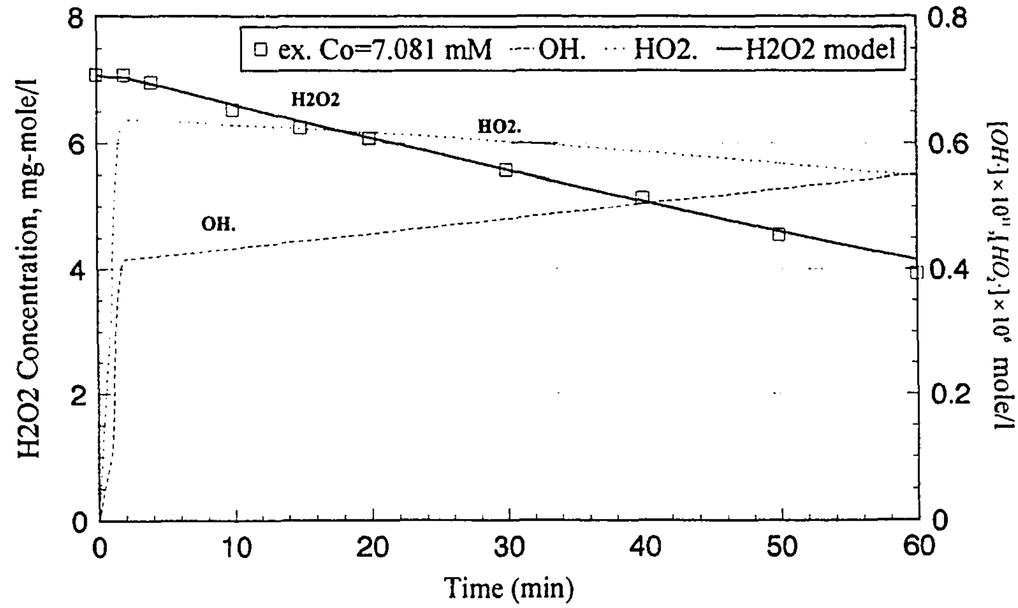


Figure 5.2 Concentrations of H_2O_2, HO_2, OH in the Reaction of Photodecomposition of H_2O_2 by UV Radiation

Table 5.2 Sensitivity Analysis of Rate Constants in Photodecomposition of Hydrogen Peroxide

Ratio	$K_{IH_2O_2}I$	Abs.	k_{10f} ($\times10^{-4}$)	k_{11f} ($\times10^{-2}$)	k_{14} ($\times10^{-7}$)	k_{15} ($\times10^{-4}$)	k_{16} ($\times10^{-4}$)
0.2	0.481	0.209	0.738	0.043	7.887	6.347	0.133
0.4	0.262	0.081	0.161	0.024	0.094	1.456	0.065
0.6	0.112	0.019	0.017	0.009	7.810	0.424	0.021
0.8	0.270	0.009	0.010	0.002	0.076	0.101	0.024
1.0	0.0	0.0	0.0	0.0	0.075	0.0	0.0
2.0	0.507	0.164	0.073	0.072	0.692	0.373	0.130
4.0	2.463	0.393	0.187	0.582	0.091	1.256	0.502
6.0	3.835	0.504	0.189	1.495	0.080	1.760	0.966
8.0	4.661	0.565	0.265	2.840	7.347	2.163	1.216
10.0	5.196	0.604	0.290	4.508	0.077	3.004	1.750

(Based on Hydrogen Peroxide Initial Concentration 7.081 mg-mole/l)

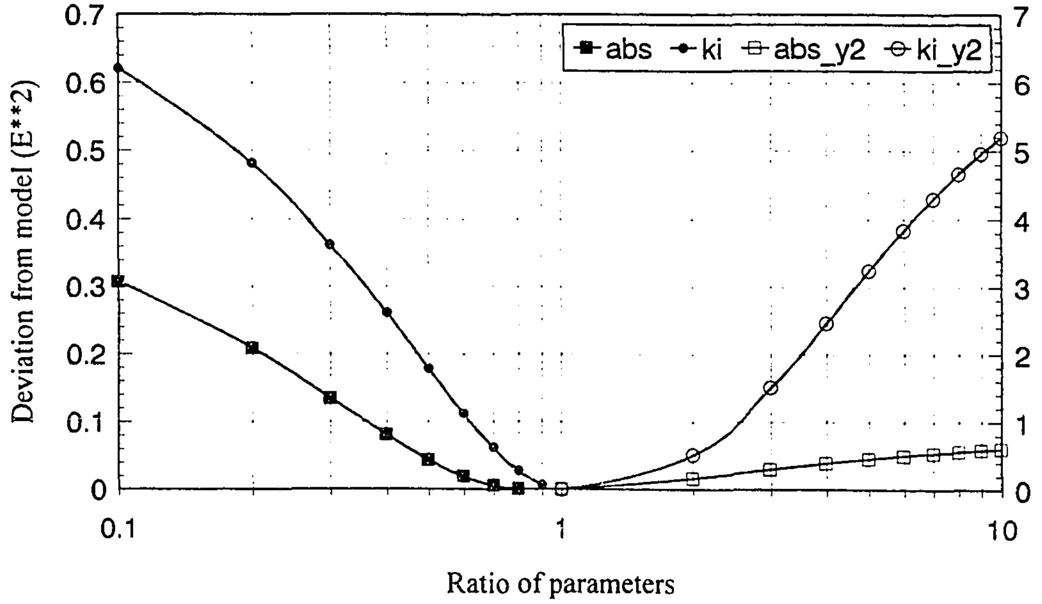


Figure 5.3 Sensitivity Analysis of Hydrogen Peroxide Photodecomposition

From Pervious study of Li (1992), the reaction could be modeled by optimization of rate constants, and the results gave a good fitting of experimental data. But the rate constants from free fitting are three order of magnitude difference from the literature data. Table 5.3 shows the differences between previous work by optimizing fitting and rate constants which were used for this study from literature. Although, Li's model could fit experimental data very well, the rate constants for fundamental reactions were doubted by other investigators. In this study the reaction rate constants for known reactions were picked from literature as mentioned in Chapter 2 to avoid rate constants running too far from the reference data.

Table 5.3 Rate Constants Used in this Model Compared to Previous Study

Reactions	Rate Constants	Previous work
$H_2O_2 + OH\cdot \xrightarrow{K_{10f}} HO_2\cdot + H_2O$	$k_{10f} = 2.7 \times 10^7$	0.522×10^5
$H_2O_2 + HO_2\cdot \xrightarrow{K_{11f}} OH\cdot + H_2O + O_2$	$k_{11f} = 3.7$	0.846×10^4
$2OH\cdot \xrightarrow{K_{14}} H_2O_2$	$k_{14} = 4.0 \times 10^9$	0.580×10^5
$2HO_2\cdot \xrightarrow{K_{15}} H_2O_2 + O_2$	$k_{15} = 8.3 \times 10^5$	not considered
$OH\cdot + HO_2\cdot \xrightarrow{K_{16}} H_2O + O_2$	$k_{16} = 3.7 \times 10^{10}$	0.468×10^4

5.2 Mass Transfer and Photodecomposition of Ozone in Aqueous Phase

Ozone generator was tested by different flow rates of oxygen and air to produce different concentrations in gas phase. The saturation curves of ozone are given in Figure 5.4. The curves are for ozone dissolved into water by different conditions (flow rate of O_2 and air) and ozone decomposed by UV radiation. Table 5.4 shows the mass transfer coefficient and saturated concentration of ozone in each experiment.

Table 5.4 Mass Transfer Coefficient, Saturated Concentration and Photodecomposition Rate Constant for Ozone

	$K_{LO3}A$ (1/sec)	Cs (mg-mole/l)	$K_{IO3}I$ (1/sec)
Oxygen 9.0 l/min	5.080×10^{-3}	0.0508	0.1449
Oxygen 7.5 l/min	3.702×10^{-3}	0.0628	0.1449
Oxygen 6.0 l/min	3.387×10^{-3}	0.0720	0.1449
Air 6.0 l/min	2.775×10^{-3}	0.0279	0.1449

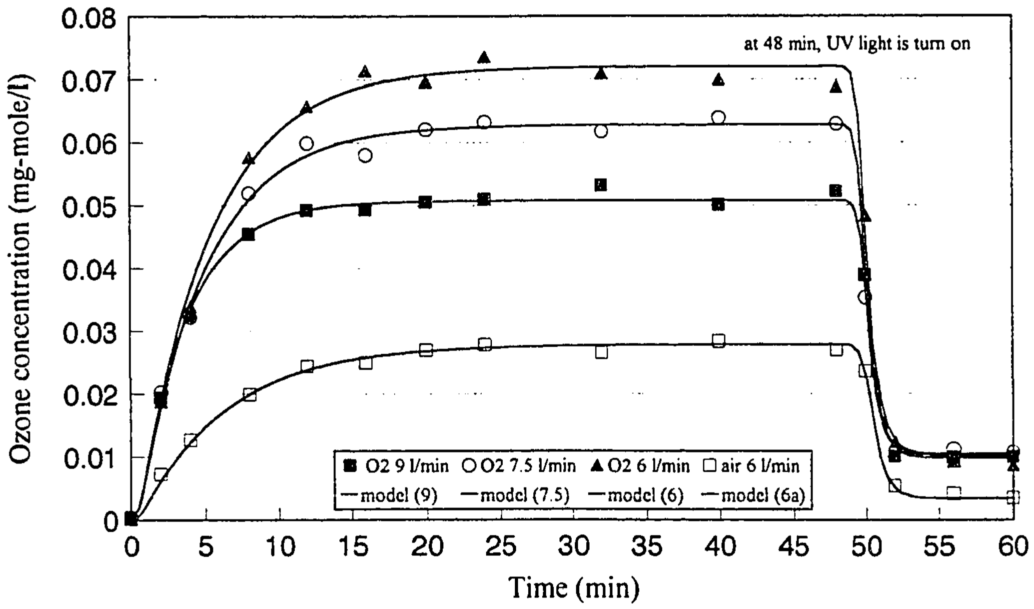


Figure 5.4 The Saturation Curves of Ozone Dissolved into Water and Decomposition by UV Radiation

5.3 Azo Dye Decomposition by Different Processes

Six sets of experiments were run. The initial conditions of these experiments are summarized in Table 5.5. The results of the experiments will be discussed in the following sections.

Table 5.5 The Initial Conditions of Experiments

Experiments	Oxidants	Initial conc.	pH
N_2 bubbling	none	20 ppm	5.5
N_2/UV	none	20 ppm	5.5
O_3 alone	O_3	20 ppm	5.5
O_3/UV	O_3,OH•,HO_2•	20 ppm	5.5
H_2O_2/UV	OH•,HO_2•	20 ppm	2.4, 5.3, 7.9, 9.7
CSTRs	OH•,HO_2•,(O_3)	20 ppm	5.5

5.3.1 N_2 Bubbling

It could be observed that the mass transfer coefficients of eight azo dyes and phenol from liquid phase to gas phase were determined in this experiment. The results showed that nearly significant concentration changes between the initial and after 60-minute bubbling. Consequently, the mass transfer coefficients ($K_{LA}A$ and M) of azo dyes and phenol could be neglected as zero.

5.3.2 N_2 Bubbling with UV Radiation

In this experiment, the effect of UV radiation could be determined. Azo dyes were undergone least decomposition under UV radiation. The effect was observed less than 1% disappearance after 60 minutes. In N_2/UV system, no oxidants existed in aqueous solution and the decomposition of azo dyes were caused by UV radiation only. Moreover, the decomposition rates were proportional to the UV light intensity. For azo dyes and phenol, the photodecomposition was neglected.

5.3.3 Ozonation of Azo Dyes

In this experiment, ozone was introduced to the reactor by bubbling. The ozonation reaction rate constants of azo dyes could be obtained from this experiment. The mass transfer was important for the reaction because that ozone reacted with each azo dyes very rapidly. Therefore, it was necessary for running a ozone mass transfer experiment to determine the ozone mass transfer coefficient ($K_{LO3}A$). Figure 5.4 shows the different ozone concentrations during ozone bubbling into pure water at different oxygen and air flow rates. For solving the rate constant k_1 of ozonation, plugged in $K_{LO3}A$ by computer simulation. Figure 5.5 shows the decomposition curves of acid orange 10 by reacting with ozone in aqueous solution for a initial dye concentration of 20 ppm, and oxygen flow rate of 6 l/min. Figure 5.6 shows the modeling of acid orange 10 decomposition by ozonation in different initial dye concentration. The ozonation of the other 7 azo dyes are given in appendix, Figure A.1 to Figure A.7. In the modeling work of this set of experiments, a intermediate B_1 was introduced into computer model as follows :

$$A + O_3 \xrightarrow{k_1} B_1$$

$$B_1 + O_3 \xrightarrow{k_2} \text{Final Products}$$

Since ozonation of Acid Orange 10 can produce more than one intermediate, the value of k_2 deviated from $0.1800\text{x}10^3$ to $0.295\text{x}10^3$ as dye concentration changes from 10 ppm to 80 ppm, but k_1 fits good for a value of $0.1481\text{x}10^3$.

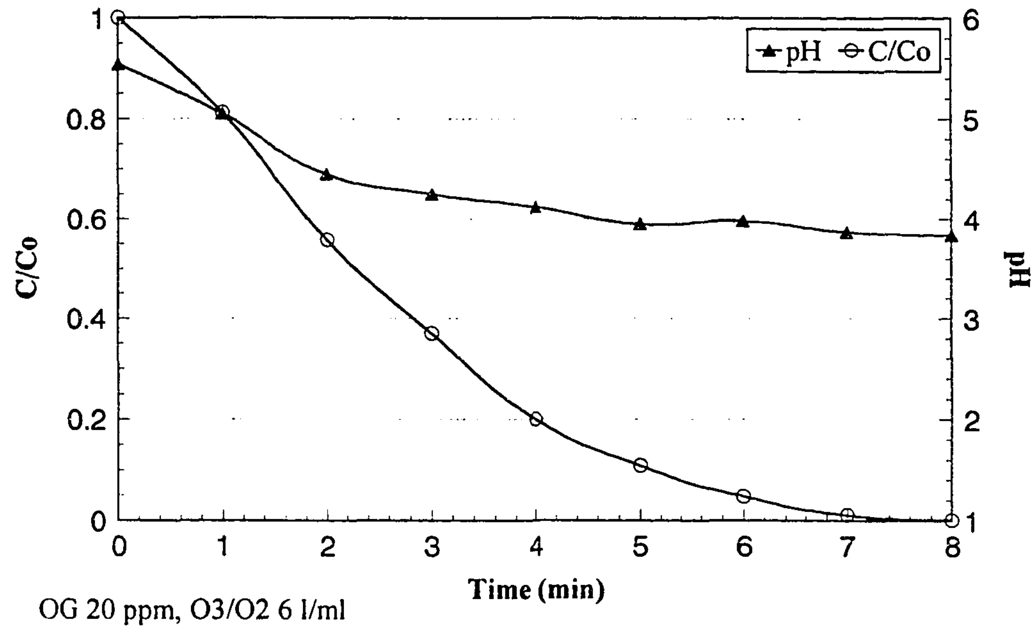


Figure 5.5 Acid Orange 10 Decomposition Curve by Reacting with Ozone

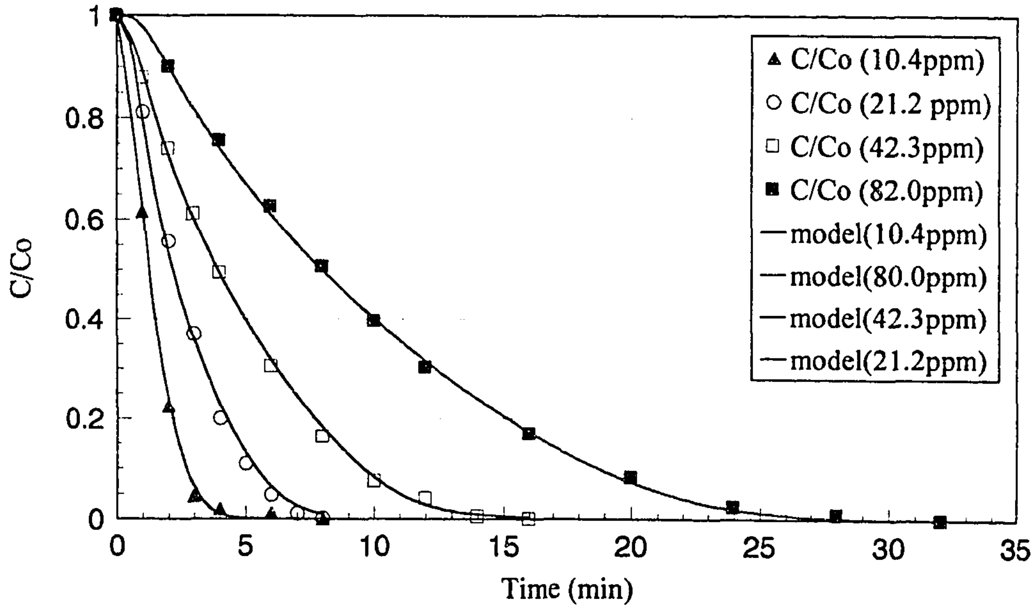


Figure 5.6 Acid Orange 10 Decomposition by Ozonation for Different Initial Dye Concentration

5.3.4 Photolytic Hydrogen Peroxide Oxidation

From literature review, it could be ascertained that hydrogen peroxide played a very important role in photolytic ozonations. In photolytic hydrogen peroxide oxidation system, hydrogen peroxide was decomposed by UV light to form OH• and HO_2• radicals. Hereby, the azo dyes were oxidized by OH• and HO_2•. Figure 5.7 shows the photolytic hydrogen peroxide oxidation of acid orange 10 at initial dye concentration of 20 ppm, hydrogen peroxide concentration of 7.081m-mole/l. For the decomposition of the other 7 azo dyes by photolytic hydrogen peroxide oxidation, the results are given in Figure A.1 to Figure A.7 in Appendix A.

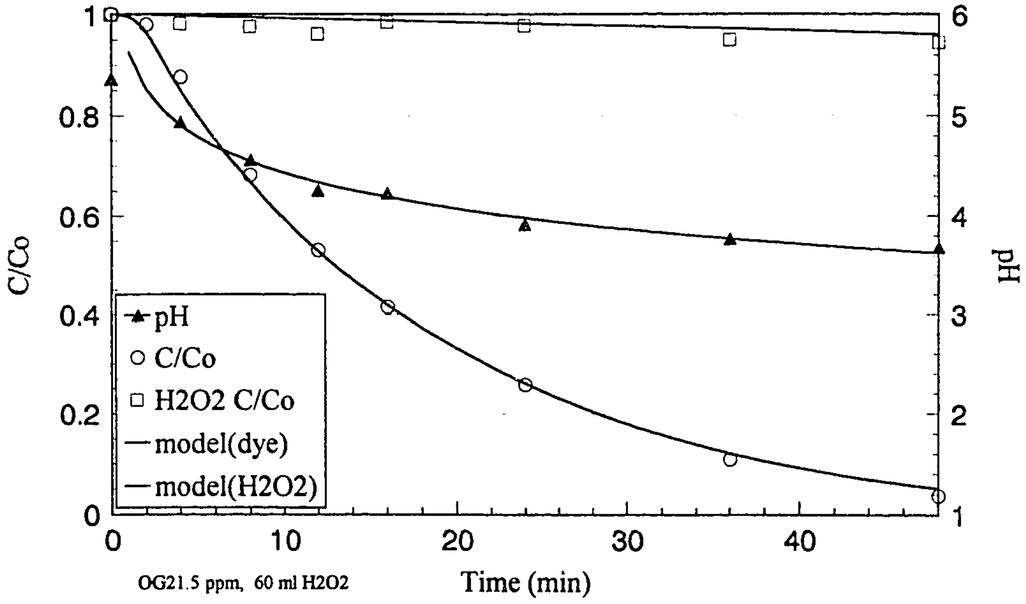


Figure 5.7 The Photolytic Hydrogen Peroxide Oxidation for Acid Orange 10

The photolytic hydrogen peroxide oxidation experiments were tested to adjust the pH values and initial concentrations of hydrogen peroxide. At different pH, the results are shown as Figure 5.8 for Acid Orange 10. Comparing azo dye decomposition at different pH in photolytic hydrogen peroxide oxidation, it seems that the reaction rates decreased by increasing pH values. It appeared that the hydrogen peroxide could be decomposed at higher pH value before the reaction started (UV light started).

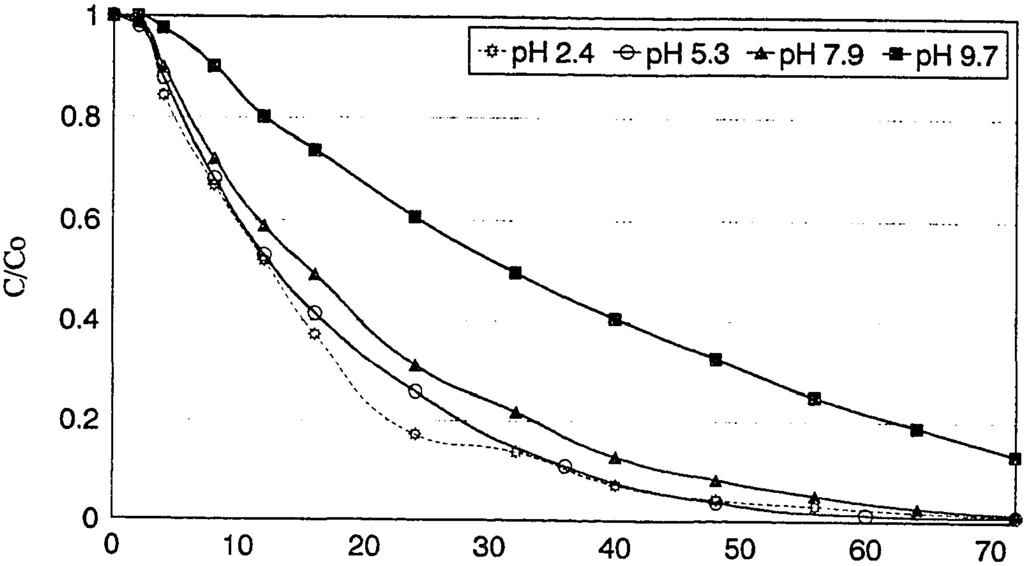


Figure 5.8 The Effect of pH on Acid Orange 10 Decomposition by Photolytic Hydrogen Peroxide Oxidation.

Figure 5.9 gives the effect of different hydrogen peroxide initial concentrations on the Acid Orange 10. It could be observed that the higher initial H_2O_2 concentrations, the higher decomposition rates could be approached. However, the decomposition rates maintained similar maximum values despite of the H_2O_2 concentration over $9x10^{-3}M$. This meant that higher initial concentration of hydrogen peroxide could improve the decomposition rate of azo dyes, yet there was a optimum initial concentration for approaching the maximum reaction rates. The effect of initial dye concentration is also very important for this reaction. The different initial dye concentration can change the absorbance of UV light and also consume different amount of oxidants. Figure 5.10 gives the effect of initial dye concentration on photolytic hydrogen peroxide oxidation of acid orange 10.

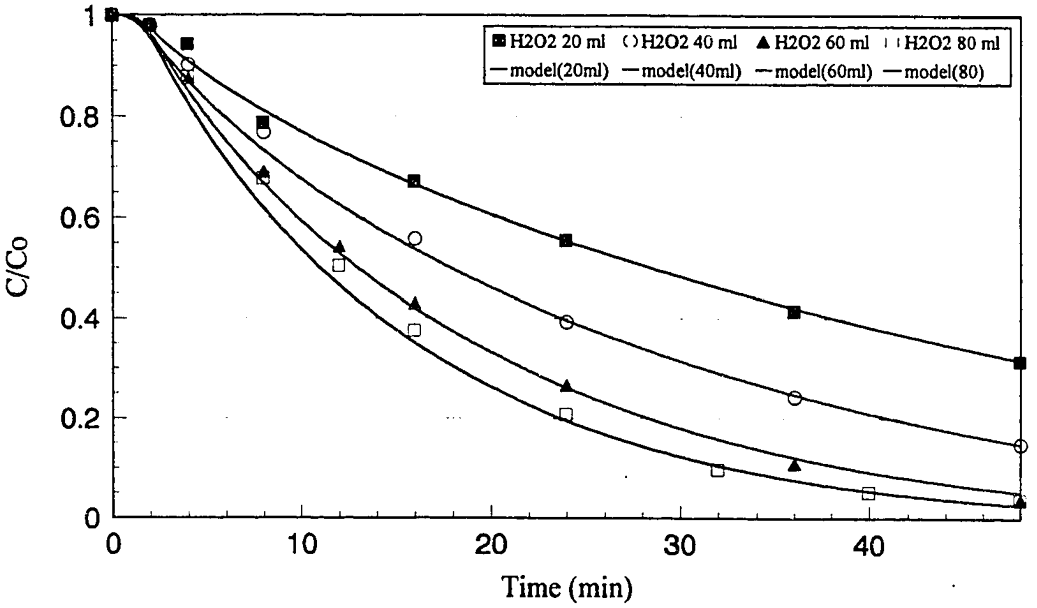


Figure 5.9 The Effect of Different Hydrogen Peroxide Initial Concentrations on Acid Orange 10 Decomposition

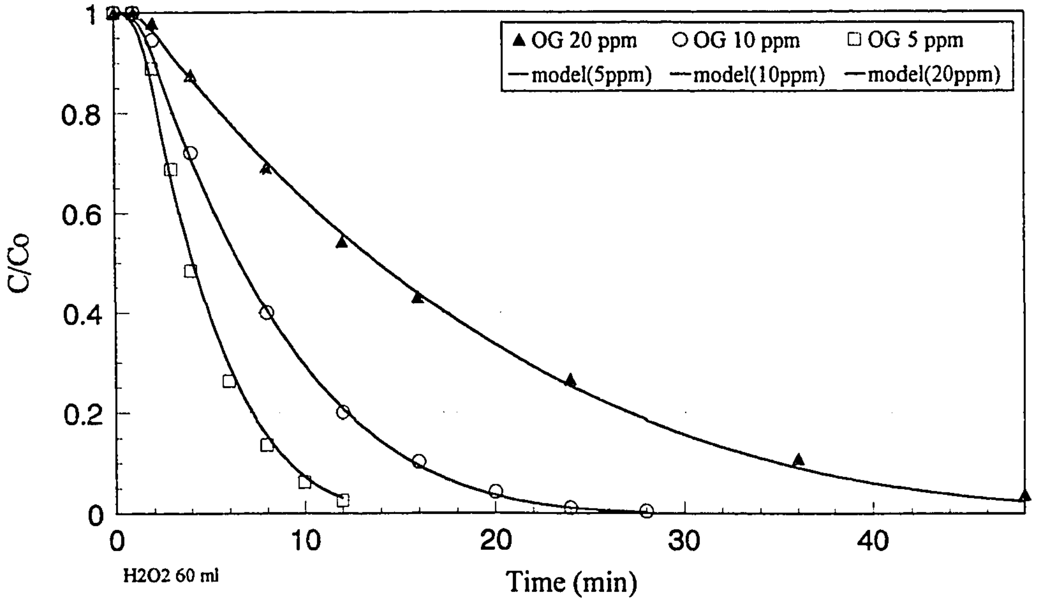


Figure 5.10 The Effect of Different Initial Dye Concentrations on Acid Orange 10 Decomposition

From the literature data of free radical reactions presented in Table 2.2, the reaction rate constants (k_4 and k_5) and hydrogen peroxide photodecomposition constant ($k_{IH2O2}I$) could be solved. The constants then were modified by fitting experimental data from hydrogen peroxide decomposition under UV radiation. Also a sensitivity analysis for photolytic hydrogen peroxide oxidation was studied. Figure A.8 gives the sensitivity of each rate constant for this experiment.

5.3.5 Photolytic Ozonation

It was easier for solving the rate constants in photolytic ozonation after getting the reaction kinetic model of photolytic hydrogen peroxide oxidation. In this experiment, the azo dyes were decomposed by ozone combined with UV radiation. The reaction rate was faster than H_2O_2/UV system and ozonation alone. Reaction rates between photolytic ozonation and ozonation alone were observed little differences.

Figure 5.11 shows the difference between photolytic ozonation and ozonation of Acid Orange 10. The photolytic ozonation of the other 7 azo dyes could be checked in appendix. The rate constants (k_4 and k_5) could be reconfirmed here again and the ozone photodecomposition rate constant ($k_{IO3}I$) was solved here by computer simulation.

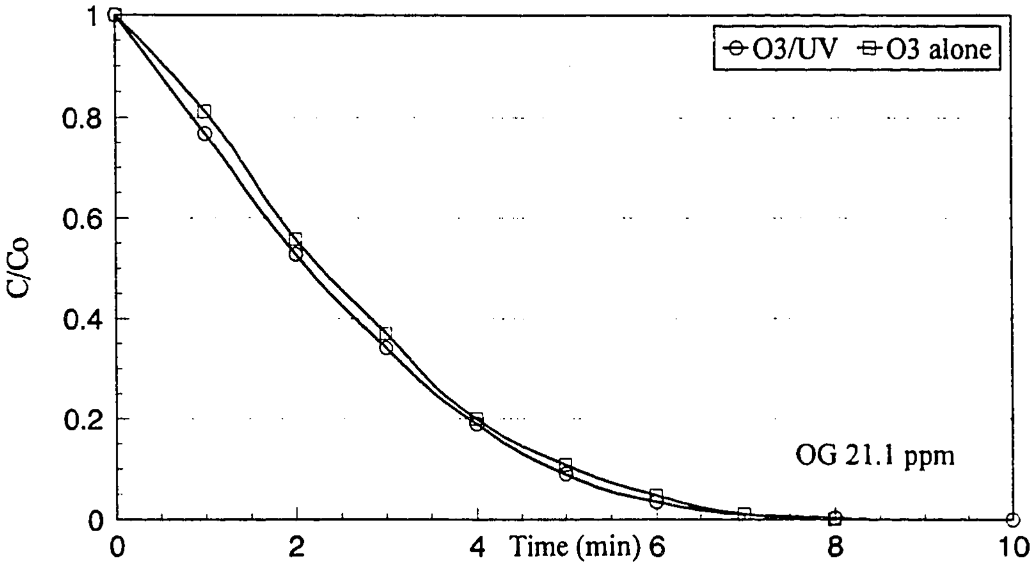


Figure 5.11 The Photolytic Ozonation of Acid Orange 10

5.3.6 Reaction Rate Constants Solved by Computer

Table 5.6 gives the reaction rate constants of Acid Orange 10 in each reaction which established the kinetic model. The reaction rate constants of the other 7 azo dyes could be checked in appendix.

Table 5.6 The Reaction Rate Constants of Acid Orange 10

Reaction	Rate Constant
$A + O_3 \xrightarrow{k_1} B_1$	0.1481 ± 0.0020 x 10^3
$B_1 + O_3 \xrightarrow{k_2}$ Product	0.2088 ± 0.0862 x 10^3
$A + OH\bullet \xrightarrow{k_4} B_2$	0.1036 ± 0.0063 x 10^{10}
$B_2 + OH\bullet \xrightarrow{k_5}$ Product	0.2785 ± 0.0351 x 10^{11}
$A + HO_2\bullet \xrightarrow{k_6}$ Product	0.5467 ± 0.0240 x 10^4

From a series of various and complex experiments, the rate constants and mass transfer coefficients could be obtained by simulating the experimental results. A kinetic model which described the contemplated experiments was developed and excersized by using the Rosenbrock Hillclimb Optimization Algorithm with the LSODE ODE Solver method. All the rate constants solved by computer could be applied to a commercial wastewater treatment plant by scaling up the CSTR results.

5.4 Phenol Decomposition by Different Oxidation Processes

5.4.1 Ozonation of Phenol

Phenolic compounds included phenol were characterized by presence of the OH donor group on the aromatic nucleus. These compounds reacted strongly with ozone. The mechanism at neutral or acidic pH was proved as an electrophilic attack of the oxidant on reactive carbons (ortho or para positions). First level intermediates of oxidation showed much more toxic than phenol itself. Furthermore, a sufficiently long retention time was allowed to degrade these intermediates. The reaction pathway described in Figure B.10 in Appendix.

From GC/MS analysis, it was found the major intermediate as hydroquinone showed in Figure B.1 to Figure B.3 in Appendix B. Figure 5.12 shows experimental and modeling data for ozonation of phenol.

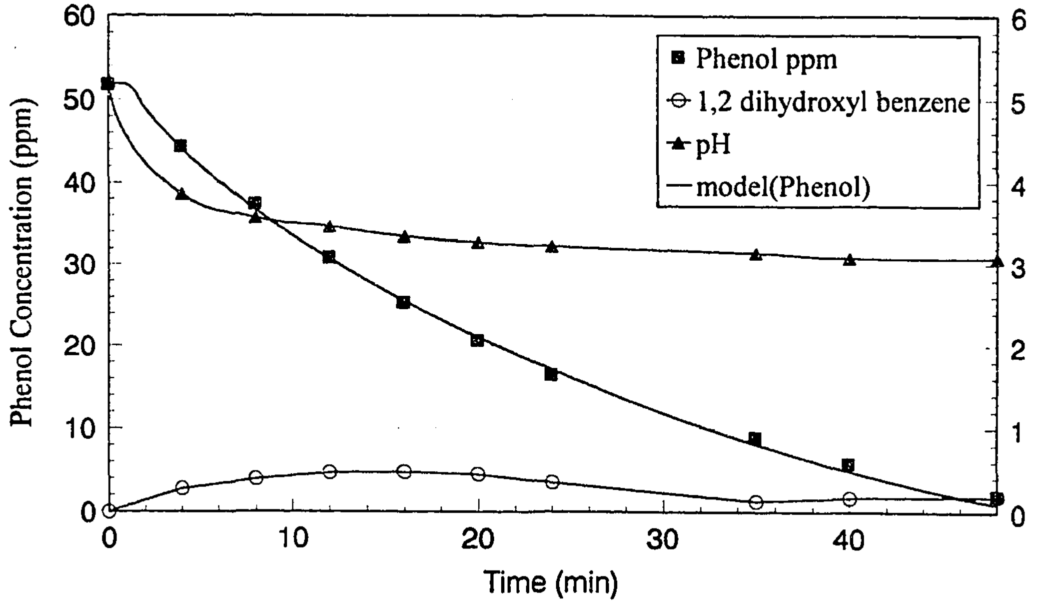


Figure 5.12 Phenol Decomposition by Ozonation

5.4.2 Photolytic Hydrogen Peroxide Oxidation

From GC/MS analysis, different oxidation products could be observed for photolytic hydrogen peroxide oxidation. Catechol and hydroquinone were the major intermediates. Meanwhile, catechol could reach higher concentration than hydroquinone. Except the catechol and hydroquinone, there were other more high molecular weight compounds in MS spectrum. They were 2,3-dihydro-1,4-benzodioxin-2-methanol, 2-phenoxy-phenol, 1,1'-biphenyl-2,2'-diol 2,6-bis(1,1-dimethylethyl)-naphthalene, (1,1-dimethylethyl)-2-methoxy phenol and 1,4-benzenedicarboxylic acid, as Figure B.7 ~ B.9., the reaction pathways are described in Figure B.11.

Figure 5.13 shows the experimental data and model fitting of the photolytic hydrogen peroxide of phenol.

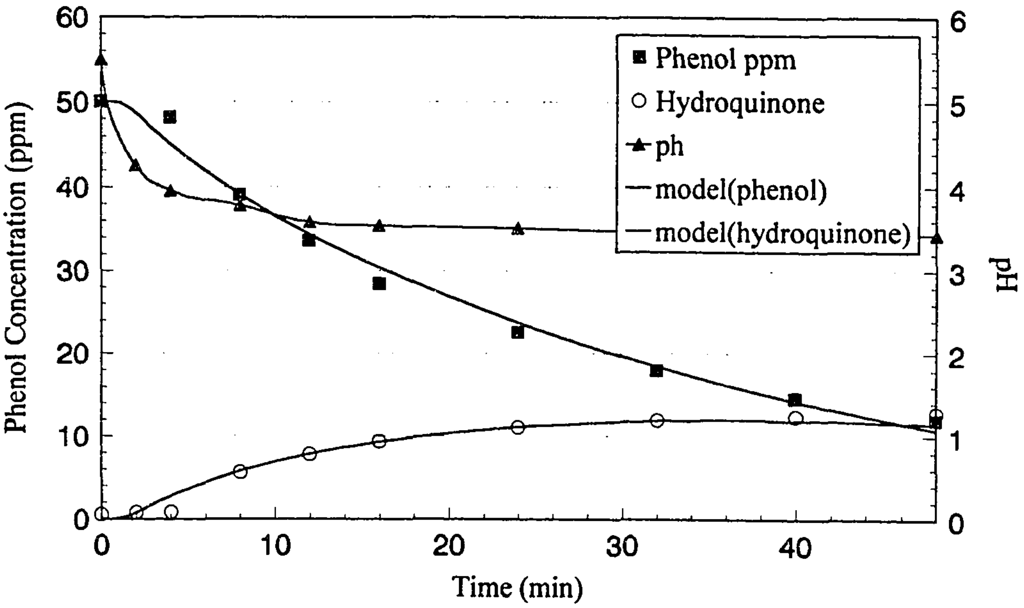


Figure 5.13 Phenol Decomposition by H_2O_2/UV System

5.4.3 Photolytic Ozonation of Phenol

From GC/MS analysis (Figure B.4 ~ B.6), the reaction pathway of photolytic ozonations was very similar to ozonation of phenol. However, some high molecular weight compounds but very low concentrations were found as intermediates. These compounds were 2-phenoxy-phenol, 1,1'-biphenyl-2,2'-diol, disooctyl ester 1,2-benzenedicarboxylic acid, and dicyclohexyl ester 1,2-benenedicarboxylic acid. The reason why high molecular weight compounds formed was hydroxyl free radical abstract of phenol to phenolic radical, then phenolic radical reacted with phenol to produce those compounds. Figure 5.14 shows the decomposition of phenol by photolytic ozonation.

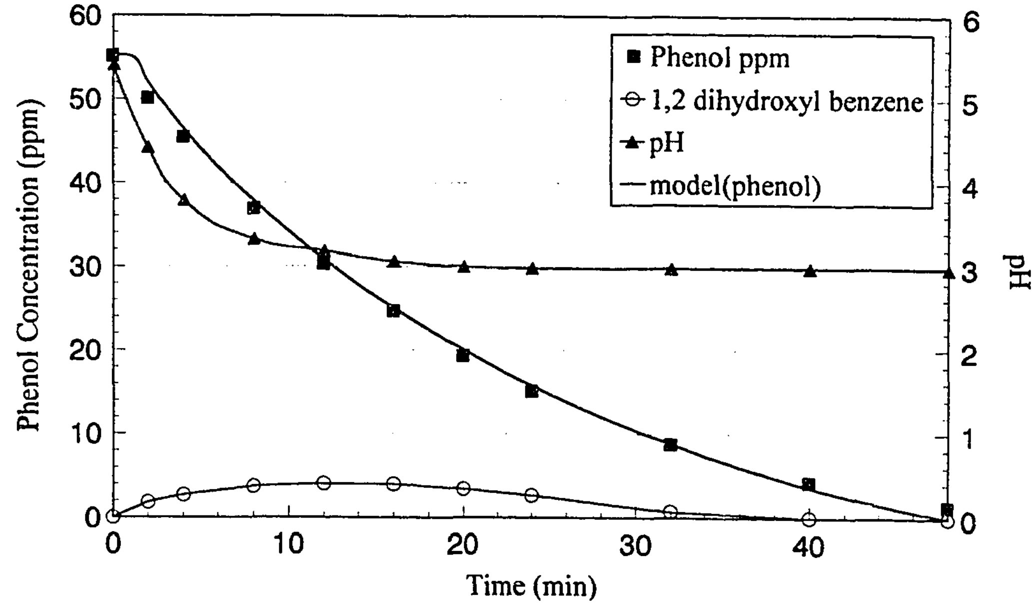


Figure 5.14 Phenol Decomposition by O_3/UV System

5.4.4 pH Effect on Phenol Decomposition by H_2O_2/UV System

The Effect of pH on H2O2/UV system can be shown in Figure 5.15 Two sets of experiments were run under pH 5.45 and pH 11.15. It can be observed that hydrogen peroxide decomposed very fast under pH 11.15 than pH 5.45. This effect causes lower free radical concentration and lower phenol decomposition rate.

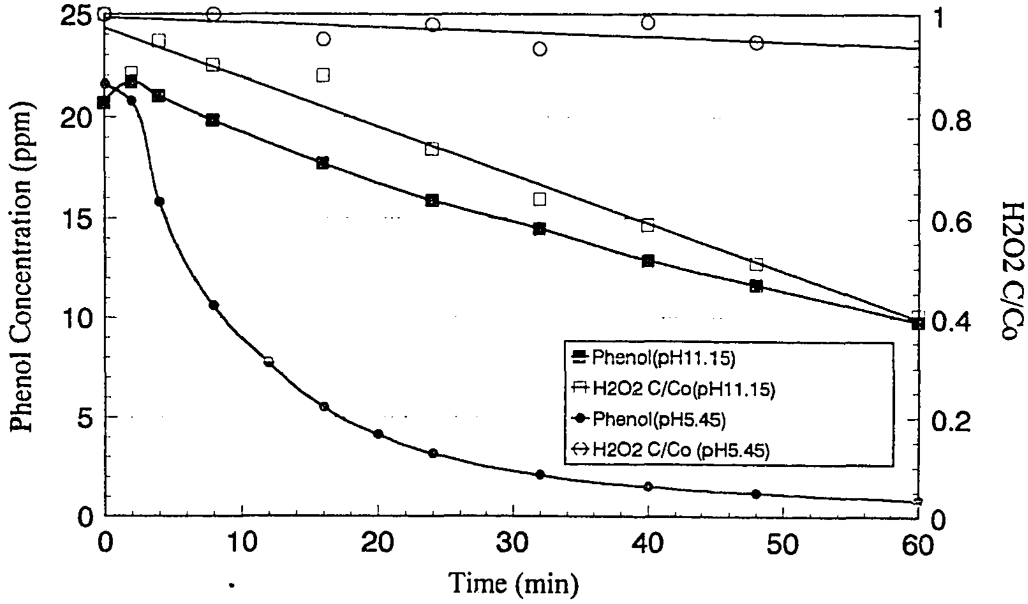


Figure 5.15 pH Effect on Phenol Decomposition by H_2O_2/UV System

5.4.5 The Rate Constants Obtained from Computer

Modeling are listed in Table 5.7. By checking with published references, all the values are consistent with the literature.

Table 5.7 Rate Constants Obtained from Computer Modeling

Reaction	Rate Constants
$Phenol + O_3 \rightarrow$ Hydroquinone, Catechol	1.3×10^3
Hydroquinone, Catechol + $O_3 \rightarrow B_3$	4.038×10^3
$B_3 + O_3 \rightarrow$ Product	1.252×10^3
$Phenol + OH\bullet \rightarrow$ Hydroquinone + Catechol	4.5×10^9
$Phenol + OH\bullet \rightarrow$ ph• (phenolic radical)	2.1×10^9
$ph\bullet + Phenol \rightarrow$ High molecular weight compounds	1.748×10^4
Hydroquinone, Catechol + $OH\bullet \rightarrow$ Organic acid	7.0×10^9
$Phenol + HO_2\bullet \rightarrow$ Products	8.551×10^4

5.5 Discussion

5.5.1 Comparison of Different Experiments

It was generally expected on the oxidation strengths of the reactants for gaining the different reaction rates in the experiments. By comparing the decomposition rates, ozonation and photolytic ozonation were the most effective reactions in degrading the azo dyes. The effects could be observed by the orders of photolytic hydrogen peroxide oxidation, then UV/N_2 and N_2 bubbling which did not decompose or strip out any of the azo dyes or phenol. Figure 5.16 shows the comparison of Acid Orange 10 decomposition in each type of experiment. The comparison of the other 7 azo dyes could be checked in appendix A.

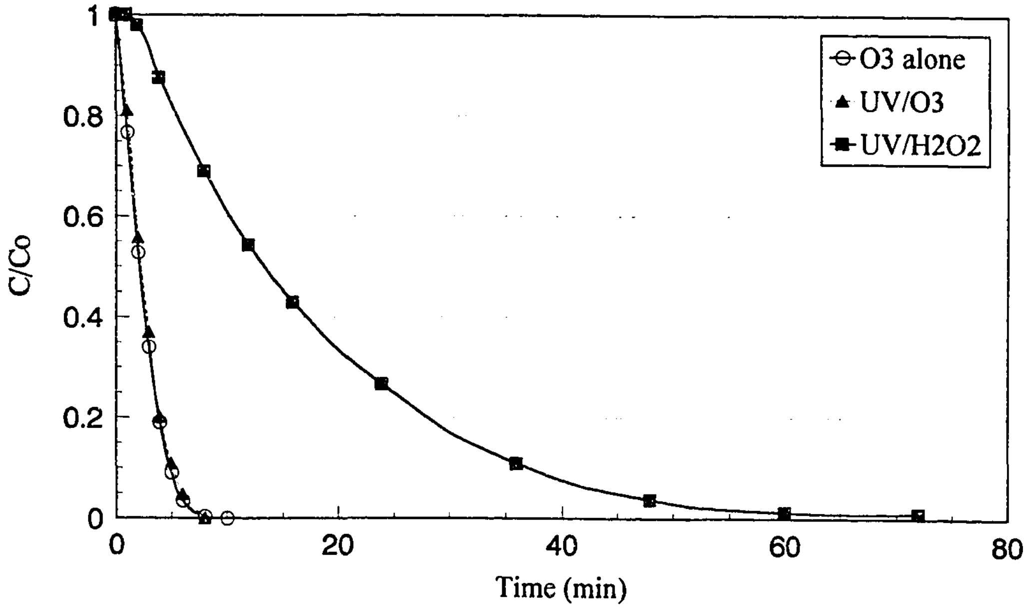


Figure 5.16 The Comparison of Acid Orange 10 Decomposition in Each Type of Experiment

A. Ozonation and Photolytic Ozonation

Comparison of ozonation only and photolytic ozonation showed that there was little enhancement for the combination of UV light into ozonation. The major conclusions for the decomposition of the azo dyes by ozonation or photolytic ozonation could be acquired as follows :

- Azo dyes could be effectively degraded by ozonation.
- UV light was absorbed by azo dyes in water. UV could attach 0_3 to produce free radicals (OH• and HO_2•) weakly. The dominant reaction was ozonation in photolytic ozonation for azo dyes.

B. Photolytic Hydrogen Peroxide Oxidation

Azo dyes could be decomposed very slightly by H_2O_2 only. However, when hydrogen peroxide was irradiated with UV light, then the decomposition rates increased substantially. Although the reaction rates of photolytic hydrogen peroxide oxidation were slower than photolytic ozonation azo dyes. Yet, it was still a powerful method for degrading azo dyes.

As described in Chapter 2, hydrogen peroxide had a number of advantages which coincided with limitations for using ozone as a oxidant. From the kinetic model, it could be seen that photolytic hydrogen peroxide oxidation was the basis of photolytic ozonation and the differences between these two methods were the distributions of OH• and HO_2• free radicals. Based on the computer simulation, it could be concluded that :

- The rates of photolytic ozonation which could be faster or slower than photolytic hydrogen peroxide oxidation depending on the target chemicals.
- Hydrogen peroxide was produced and consumed in the photolytic ozonation reaction.
- In photolytic hydrogen peroxide oxidation reactions, hydrogen peroxide was decomposed very slowly. In photolytic ozonation, however, ozone was continuously bubbled into the liquid phase and decomposed by UV light to produce free radicals, so the concentrations of ozone, hydrogen peroxide, OH• and HO_2• in liquid phase reached steady state values.

C. Effects of Stripping, and UV radiation

From the N_2 bubbling and UV/N_2 systems (see 5.4.1 and 5.4.2), they were nearly significant concentration changes or less than 1% disappearance after 60-minute observation. For azo dyes, it was observed no significant rate effects by comparing N_2

bubbling and UV/N_2 systems with O_3, OH• and HO_2• reactions. From the experimental results, the conclusions were as follows :

- Stripping by bubbling nitrogen had no effect on azo dyes.
- UV radiation can hardly photodecompose azo dyes.

5.5.2 The Effect of pH in H_2O_2/UV reaction

The decomposition of azo dyes with photolytic hydrogen peroxide oxidation showed in Figure 5.8 at the different pH. The reaction rates of photolytic hydrogen peroxide oxidation increased with decreasing pH. The effects of pH on the reaction rates may follow the mechanism of basic catalyzed decomposition of hydrogen peroxide during the mixing procedure and photolytic reaction.

The photolytic hydrogen peroxide oxidation was worked as soon as UV light was turned on effectually and powerfully. At basic condition, hydrogen peroxide was decomposed to water by basic catalyzed decomposition before the UV light was turned on. Meanwhile, no free radical was produced in this period. For this reason, under UV irradiation, the initial concentration of hydrogen peroxide was lower than under acidic condition.

During the photolytic hydrogen peroxide oxidation, hydrogen peroxide was decomposed by UV radiation to produce OH• and HO_2• free radicals. At the same time, hydrogen peroxide was also decomposed by basic catalyzed decomposition to produce unreactive H_2O and O_2. Consequently, lower pH value can prevent hydrogen peroxide decomposition to stable compounds and therefor reaches a higher reaction rate. The pH effect in photolytic hydrogen peroxide oxidation is summarized as follows

- A higher reaction rate in photolytic hydrogen peroxide oxidation is achieved at lower pH, because hydrogen peroxide decomposes in basic solution.
- Hydrogen peroxide decomposes to free radicals only under the UV radiation.
- In basic solution, hydrogen peroxide decomposes to unreactive H_2O and O_2 during both of the mixing procedure and photolytic reaction period.
- In the treatment of wastewater treatment, the wastewater effluent can be pretreated to acidic condition before flowing into photolytic hydrogen peroxide oxidation process.

5.5.3. The Effect of Hydrogen Peroxide Dosage

Hydrogen peroxide dosage (molar fraction of hydrogen peroxide per azo dyes) can have a pronounced effect on different reaction rates. Higher hydrogen peroxide initial concentration causes higher reaction rate. The results in Figure 5.9 shows this effect. But when the initial concentration of hydrogen peroxide is increased to a limit (between 60 ml to 80ml/100l), the change of reaction rate becomes not significant. By a series of experiments, an optimum initial concentration of hydrogen peroxide can be determined.

Hydrogen peroxide dosage can also be expressed as molar fraction of hydrogen peroxide to azo dyes. From the relation of molar fraction and azo dye decomposition rate, a economic hydrogen peroxide dosage may be obtained for different initial concentration of azo dye. That approach is more useful for wastewater treatment applications.

In this group of experiments, the reaction rate increases as hydrogen peroxide dosage increases, until a optimum dosage is reached where the reaction rate changes very slowly. That is when hydrogen peroxide initial concentration increases, the production of hydroxyl radical also increasing at the same time. At high H_2O_2 concentration, free radicals tend to react with each other rather than diffuse away to react with the azo dyes.

These free radical termination produces H_2O and O_2 which have essentially no effect on increasing reaction rate.

From the kinetic model study, the following conclusions are enumerated :

- Decomposition rate of azo dyes increases with increasing hydrogen peroxide concentration. This is a consequence of the increasing in concentration of free radicals such as OH• and HO_2• with dosage of hydrogen peroxide in H_2O_2/UV reaction.
- Hydrogen peroxide dosage reaches an upper limit when the reaction rate increases not significantly. This rate saturation seems to be caused by free radical termination reactions.
- When hydrogen peroxide dosage increases to the optimum upper limit, the termination of free radicals becomes more and more important and eliminates the advantage of increasing hydrogen peroxide dosage.
- The reaction rate constants for free radical termination reactions are very large, so the concentration of free radicals tends to approach a steady state.

5.5.4 The Role of Mass Transfer in Ozonation

In this study, it has been shown that the mass transfer of ozone from gas phase to liquid phase performs a very important role in ozonation, when the reaction rate of ozone and azo dye is very fast. Because the mass transfer of ozone becomes the rate determination step, that means whenever the ozone comes into liquid phase it reacts with azo dye immediately.

Although ozone in liquid phase may produce free radicals, the concentration of free radicals is very small (less than 10^{-15} M) as compared to ozone concentration in the liquid phase (about x 10^{-2} M), therefor the effect of free radicals in the reaction is neglected.

The following conclusions are reached based on these results :

- The decomposition rate increases with increasing ozone mass transfer rate from the gas phase to the liquid phase.
- Because the ozone mass transfer is very important in this reaction, for the first one minute, ozone gas feed is supplied only part of the capacity and then increased proportional to bubbling time. After one minute, the mass transfer of ozone is considered as supplied to full capacity.
- The saturation concentration of ozone decreases with increasing temperature. So temperature is a very important parameter in this experiment.

5.5.5 Oxidants in UV Induced System

In photolytic ozonation, ozone concentration in liquid phase is very small, because of ozone decomposition by UV radiation. Most of ozone is decomposed into free radicals such as $OH\cdot$ and $HO_2\cdot$ and produces hydrogen peroxide. Then hydrogen peroxide is also decomposed by UV radiation or reacted with hydroxyl radicals to form hydroperoxide radical. All these oxidants have powerful ability to decompose azo dyes.

Azo dyes in photolytic oxidation system are decomposed by those oxidants. For different reaction rate constants with oxidants, the decomposition curve of different azo dyes are quite different. Because the concentration of those oxidants are hard to determine by analysis, the reference data from literature is used in computer simulation to solve for rate constants and oxidants' concentrations.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

From the experimental results and kinetic modeling, the following conclusions are obtained.

1. Advance oxidation processes such as photolytic ozonation and photolytic hydrogen peroxide oxidation are powerful methods for the decomposition of azo dyes.
2. Stripping and UV radiation alone cannot effectively decompose azo dyes.
3. The azo dyes studied in this project have similar decomposition properties.
4. Hydrogen peroxide decomposition by UV radiation to produce hydroxyl radicals and hydroperoxide radicals is the basic mechanism of advanced oxidation processes.
5. The kinetic model proposed in this study shows excellent agreement with experimental results, and the rate constants obtained from computer simulation may prove very useful for scale-up to a commercial wastewater treatment process.
6. UV radiation intensity, pH effect, hydrogen peroxide dosage effect can enhance the decomposition rate.
7. The mechanism of these AOPs is very complex. Some of reactions which achieve a very small effect on decomposition of azo dyes are neglected (i.e. stripping, UV radiation only) in this kinetic study. The light intensity model is introduced into the overall model to improve the accuracy of the prediction.

8. Phenol performs as a model compound to test the reaction mechanism model. The results show excellent agreement with experimental data, reaction pathways, and intermediates were also identified by GC/MS analysis.

6.2 Recommendation

In order to understand the mechanism well, some investigation should be considered in future studies :

1. High pH will cause hydrogen peroxide decomposition and decrease the decomposition rate of pollutants in photolytic hydrogen peroxide oxidation. The decomposition of hydrogen peroxide at different pH should be studied to determine the H^+ contribution to the reaction kinetics.
2. Measuring the concentration of intermediate products may improve the kinetic model. By using GC/MS, the concentration and identity of intermediates can be obtained.
3. The effect of UV light in photolytic ozonation and photolytic hydrogen peroxide has to be studied for different light source and different reactor size to estimate the best geometry for a reactor.

APPENDIX A

DECOMPOSITION OF EIGHT AZO DYES

In this appendix, the curves for the decomposition of eight studied azo dyes are given in Figure A.1 to Figure A.7, pH effect and sensitivity analysis are also included in Figure A.8 to Figure A.10

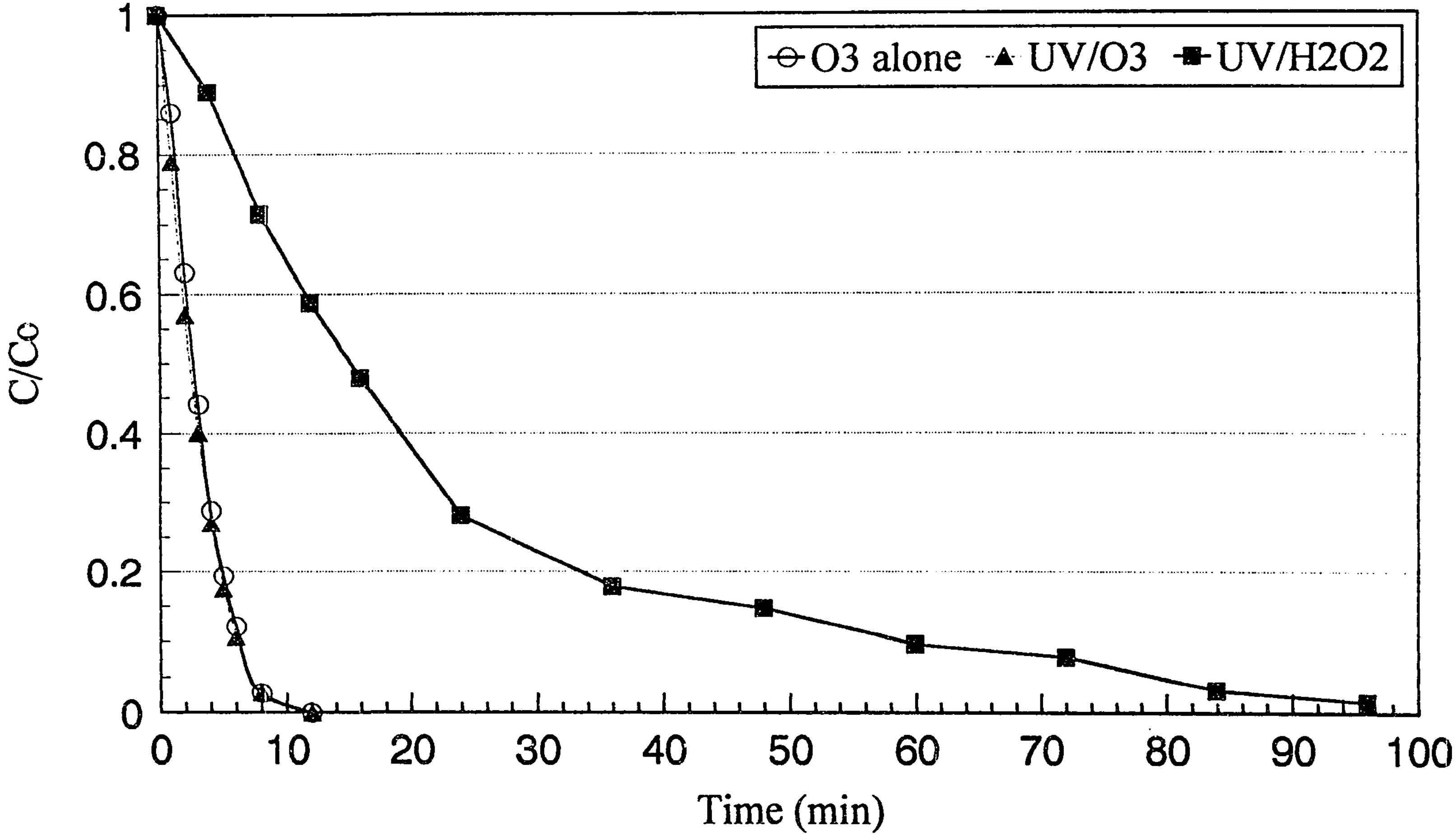


Figure A.1 Acid Black 1 Decomposition by Different Processes

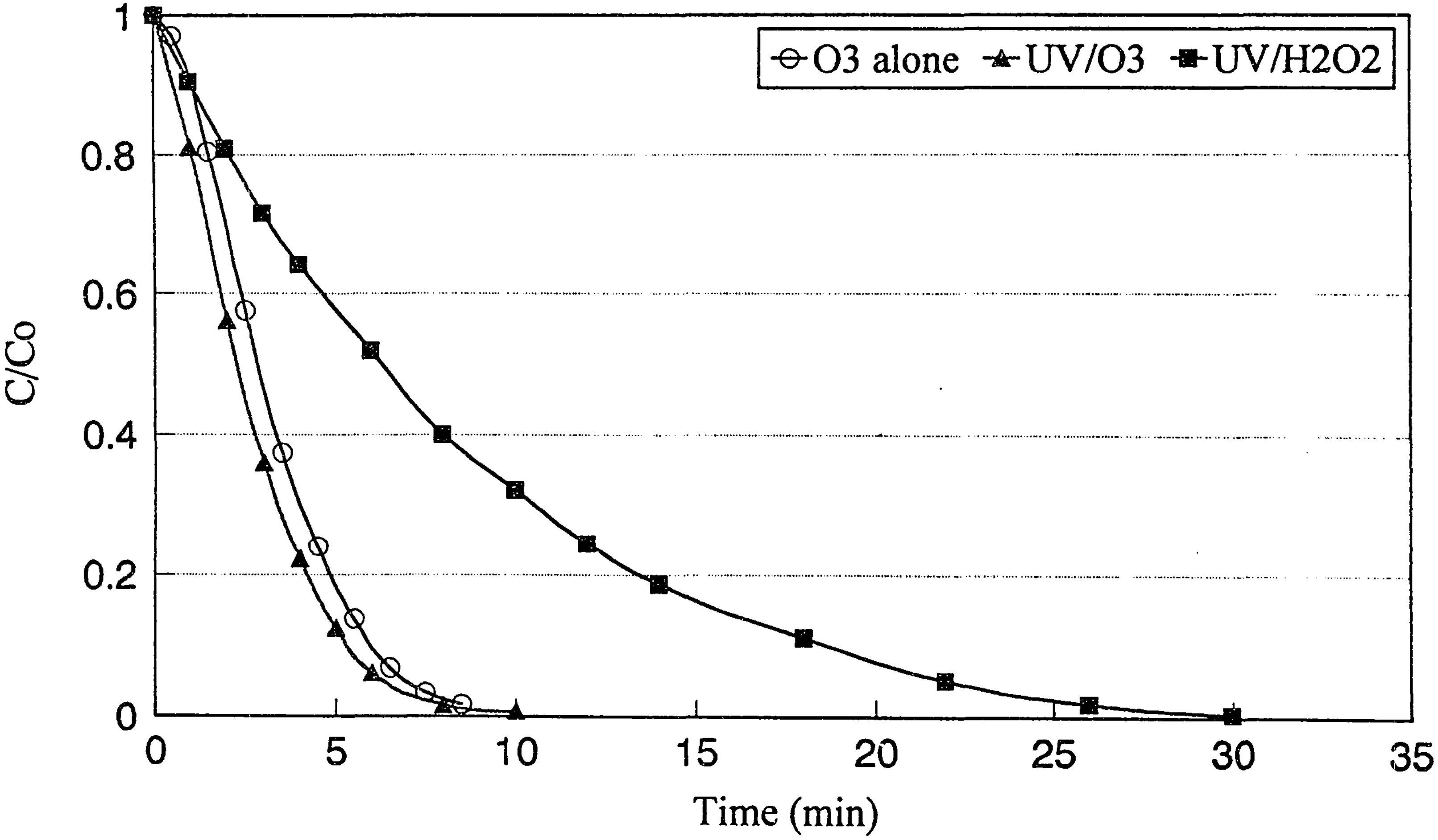


Figure A.2 Acid Red 1 Decomposition by Different Processes

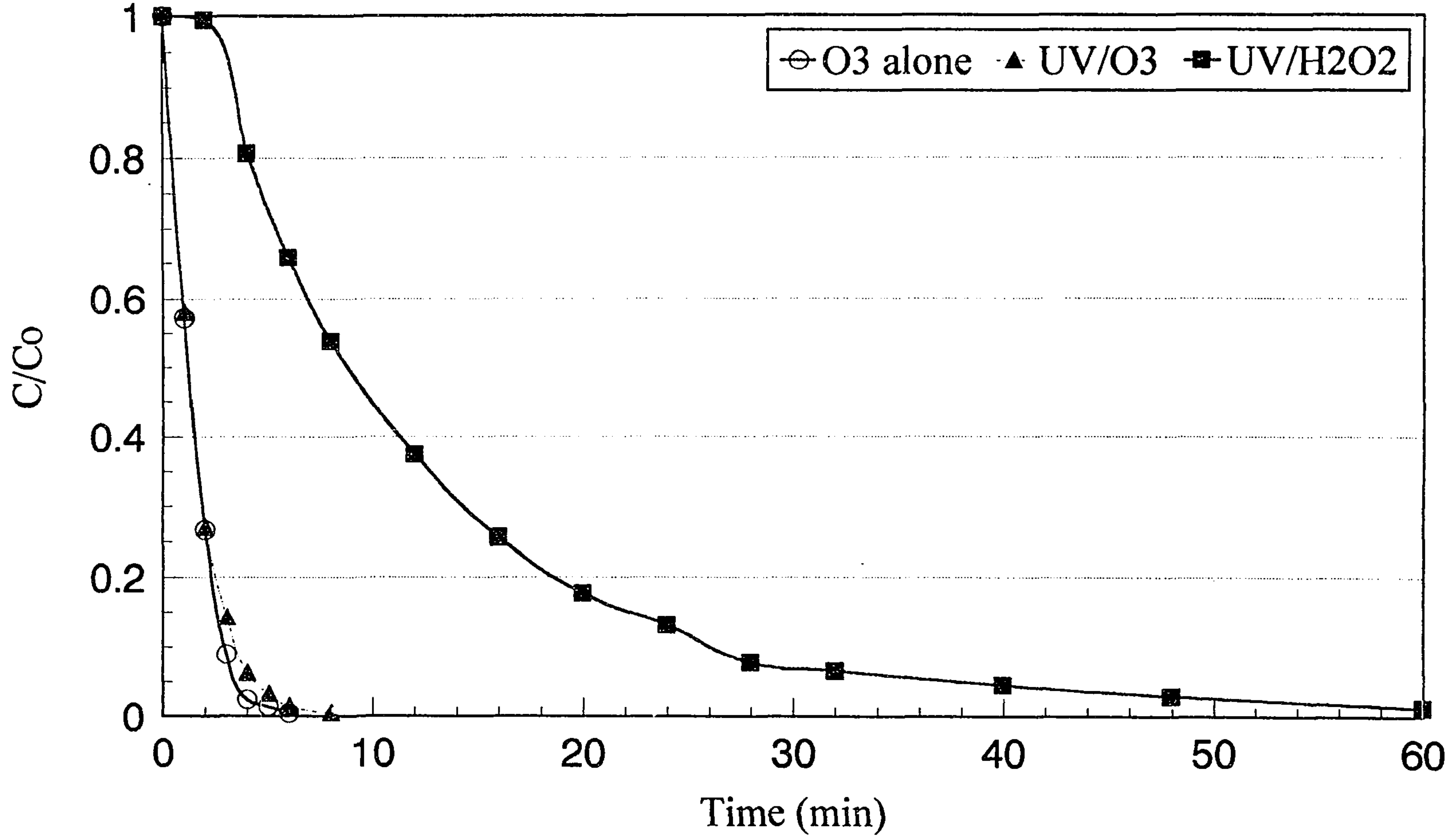


Figure A.3 Acid Red 14 Decomposition by Different Processes

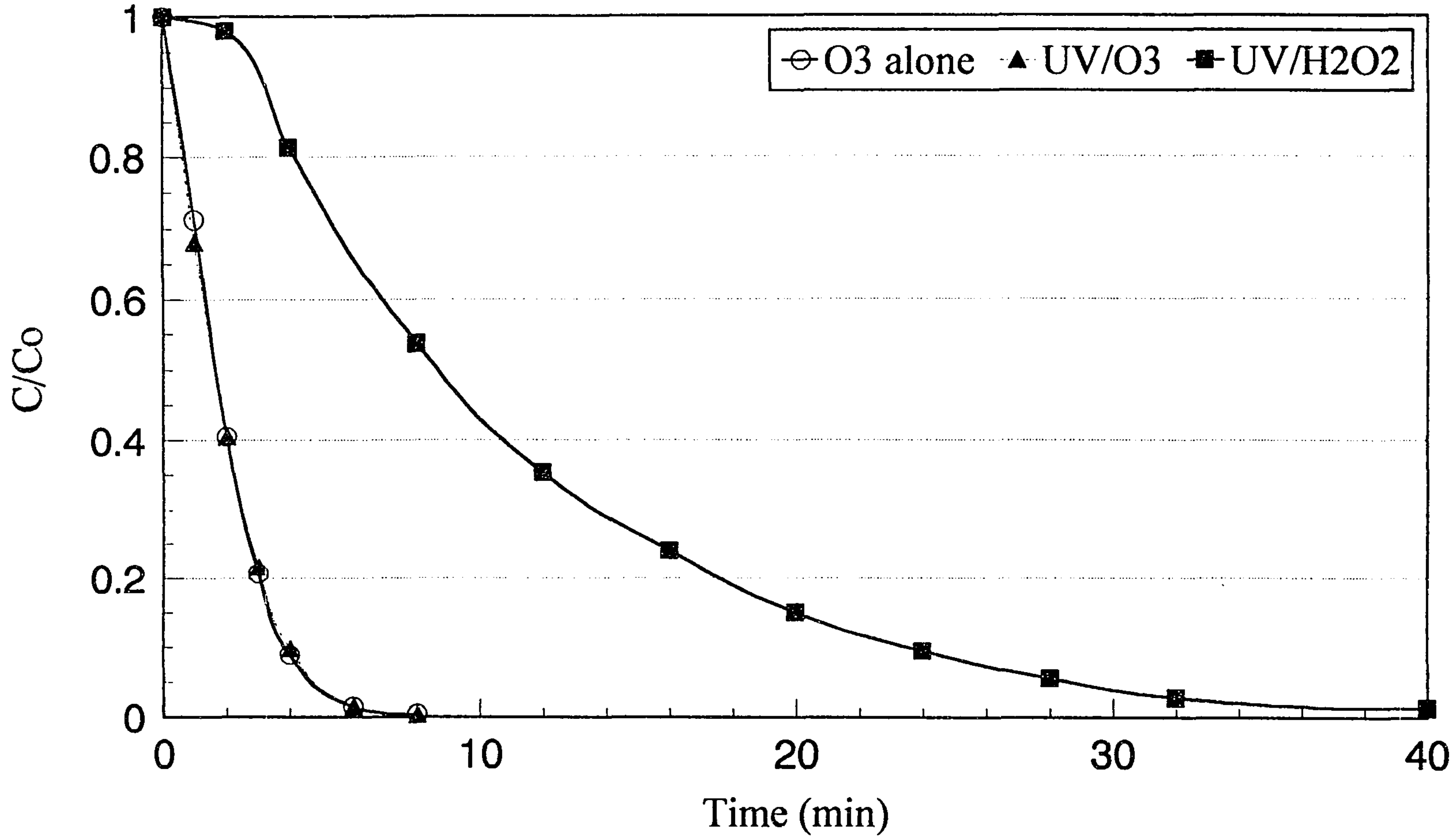


Figure A.4 Acid Red 18 Decomposition by Different Processes

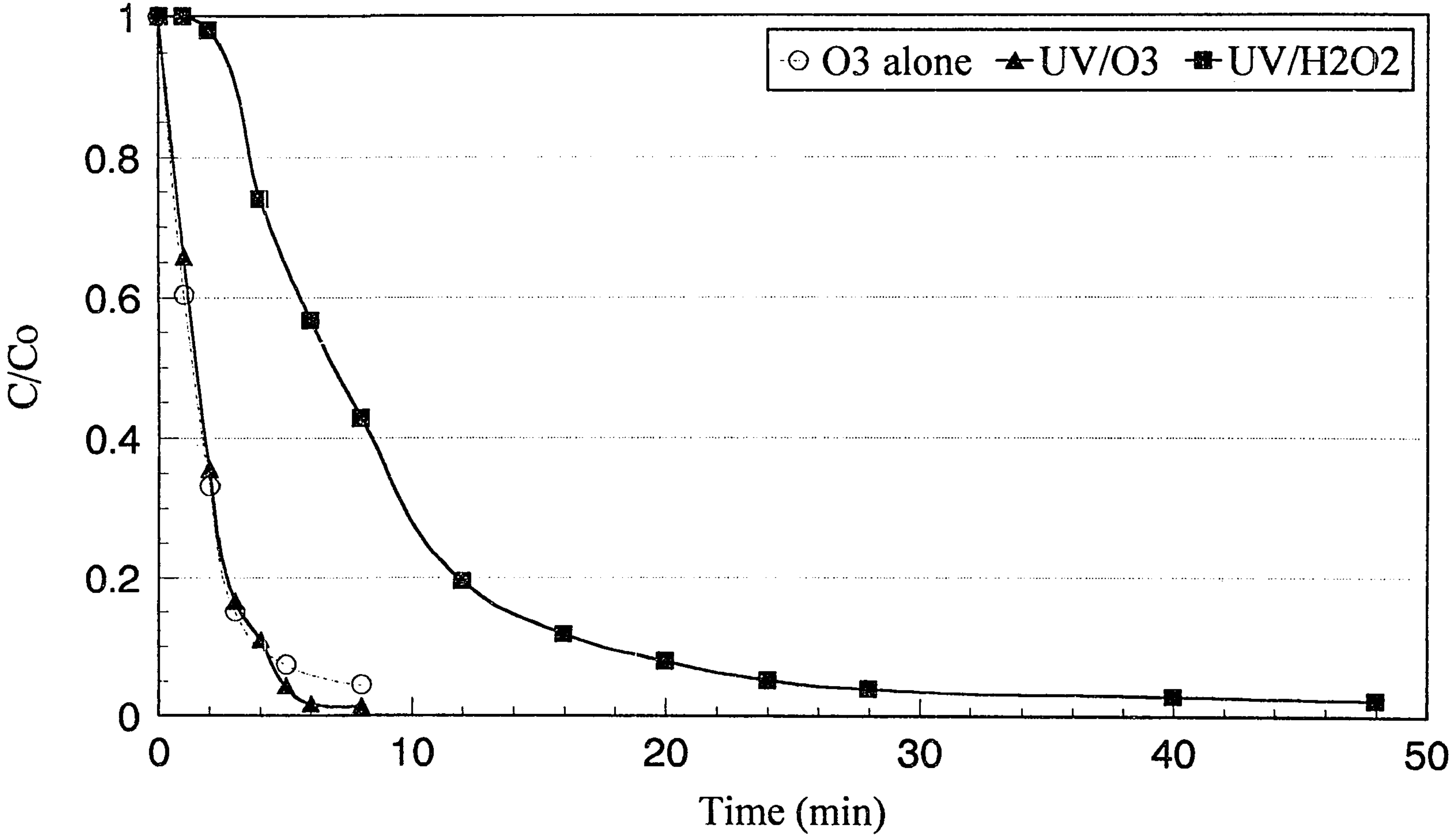


Figure A.5 Acid Yellow 17 Decomposition by Different Processes

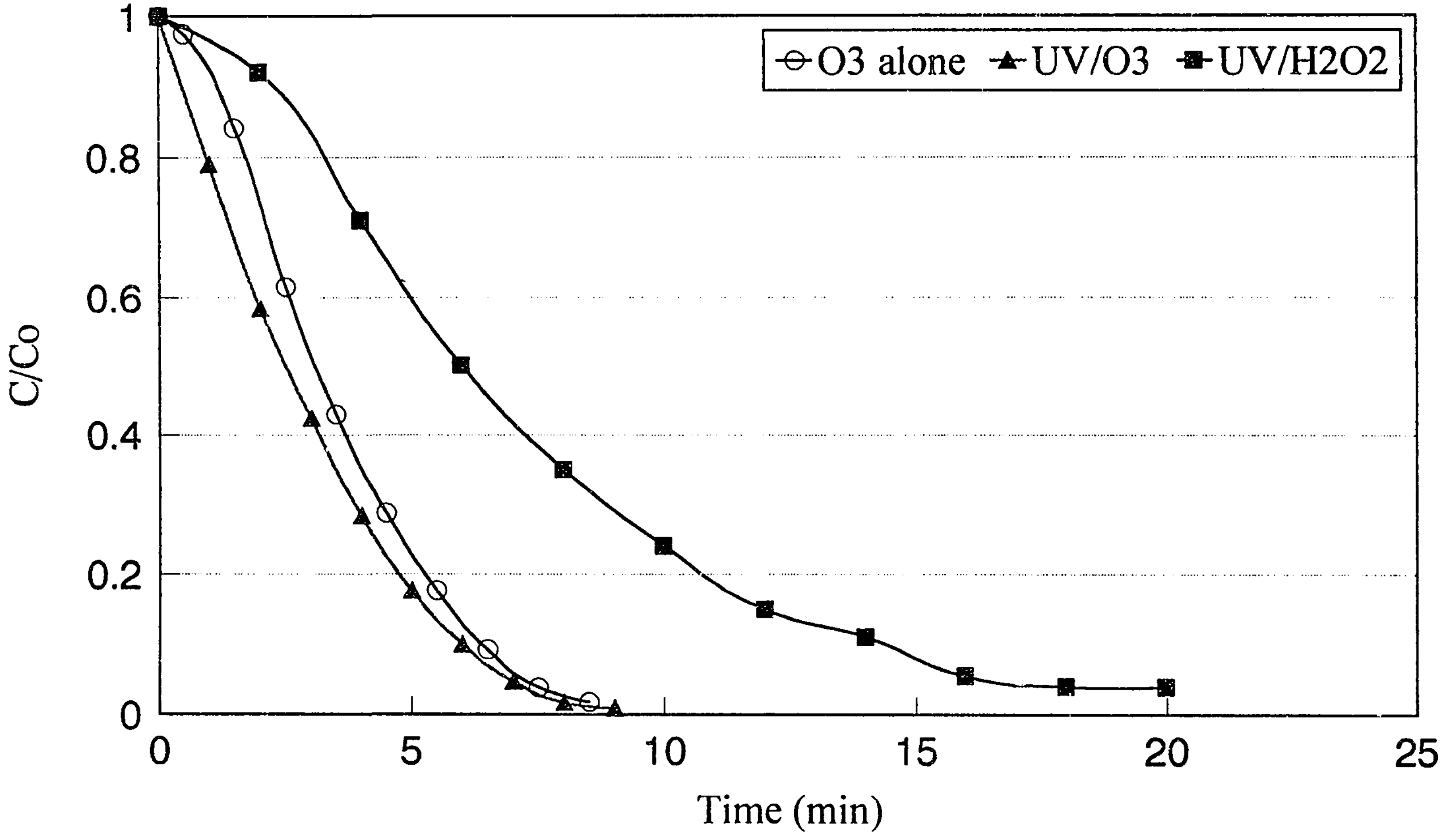


Figure A.6 Acid Yellow 23 Decomposition by Different Processes

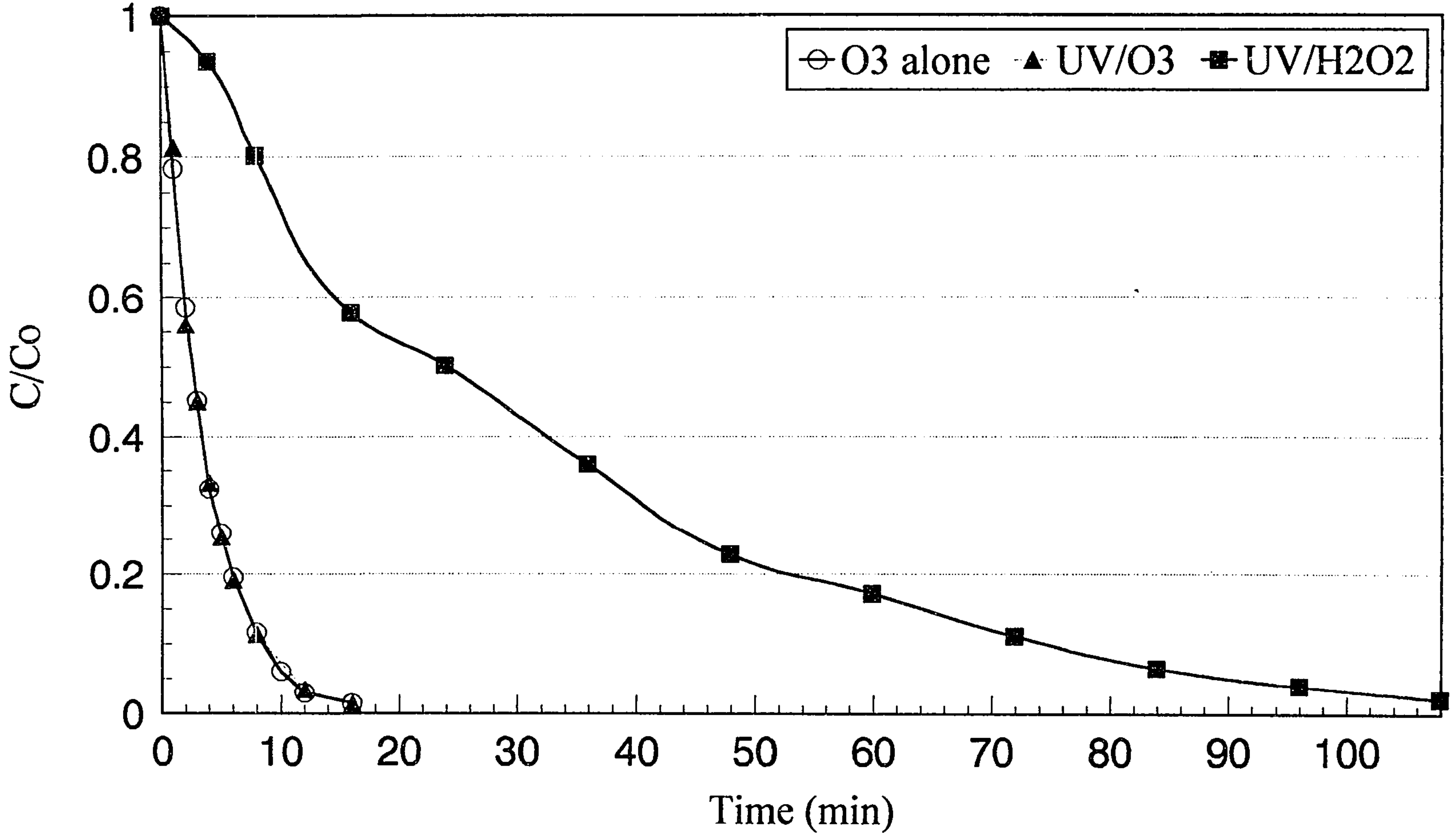


Figure A.7 Direct Yellow 4 Decomposition by Different Processes

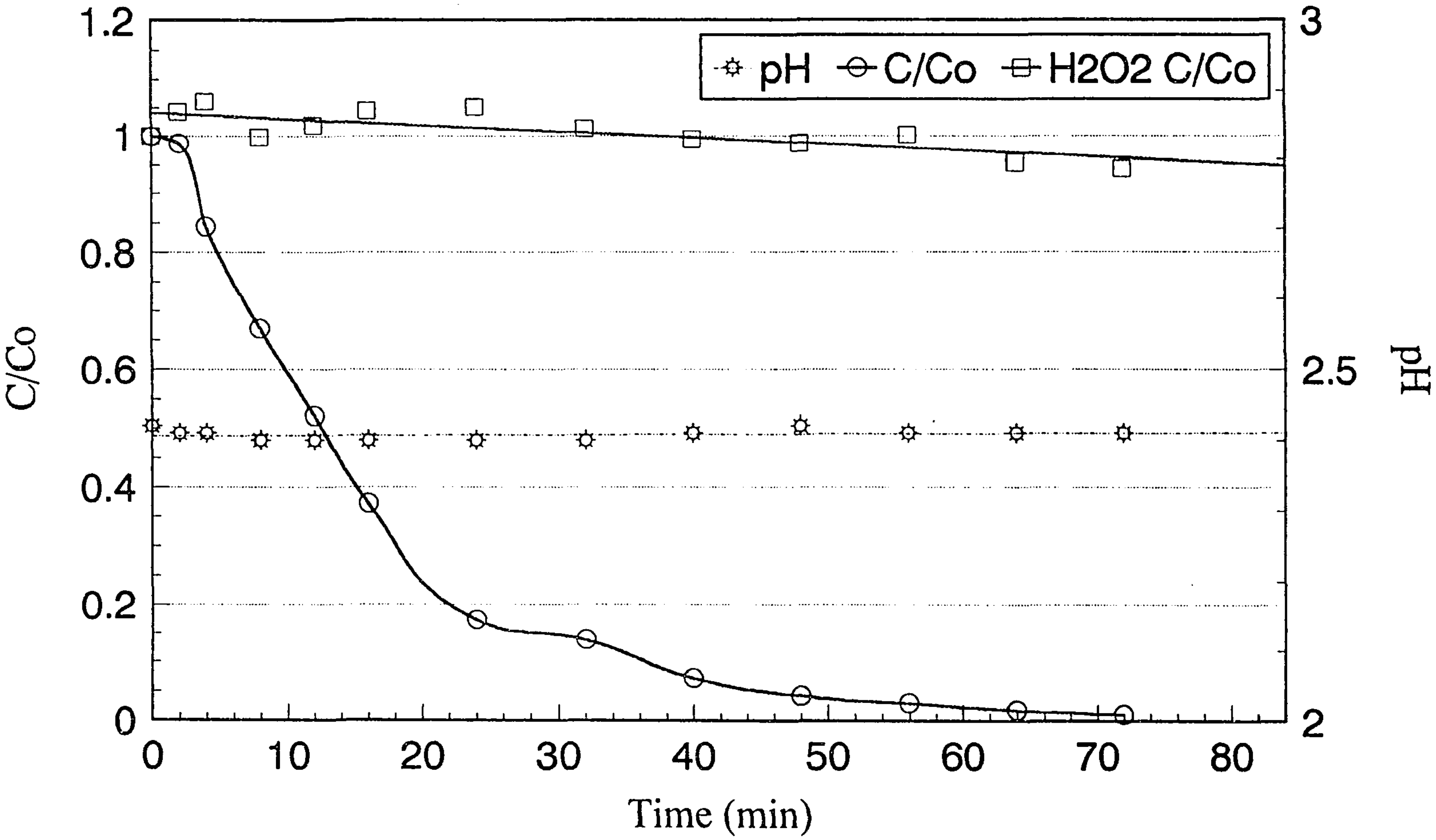


Figure A.8 Acid Orange 10 Decomposition in UV/H2O2 System, pH=2.40, OG 20 ppm, H2O2 60 ml

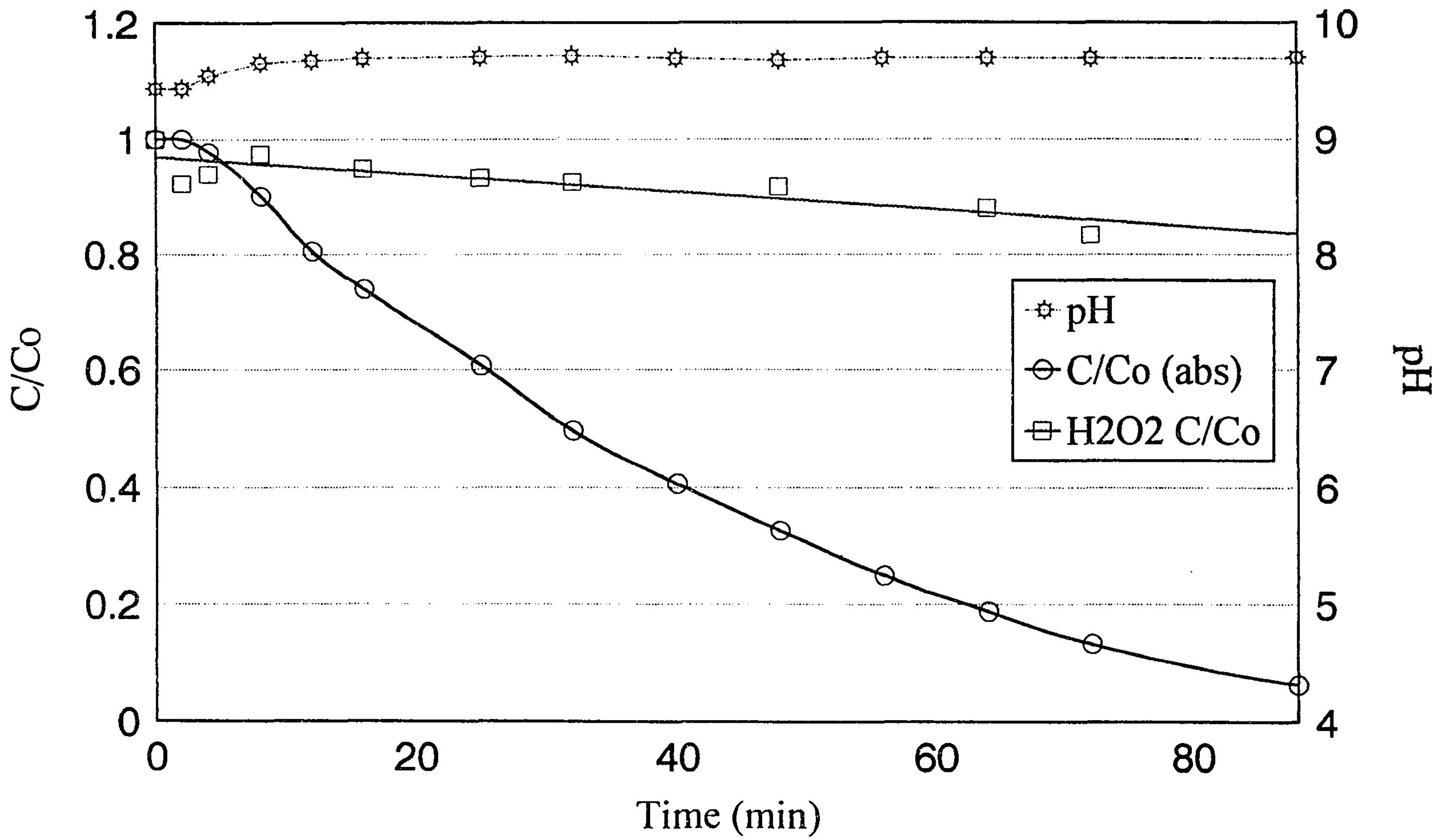


Figure A.9 Acid Orange 10 Decomposition by UV/H2O2 System, pH=9.7, OG 20 ppm, H2O2 60 ml

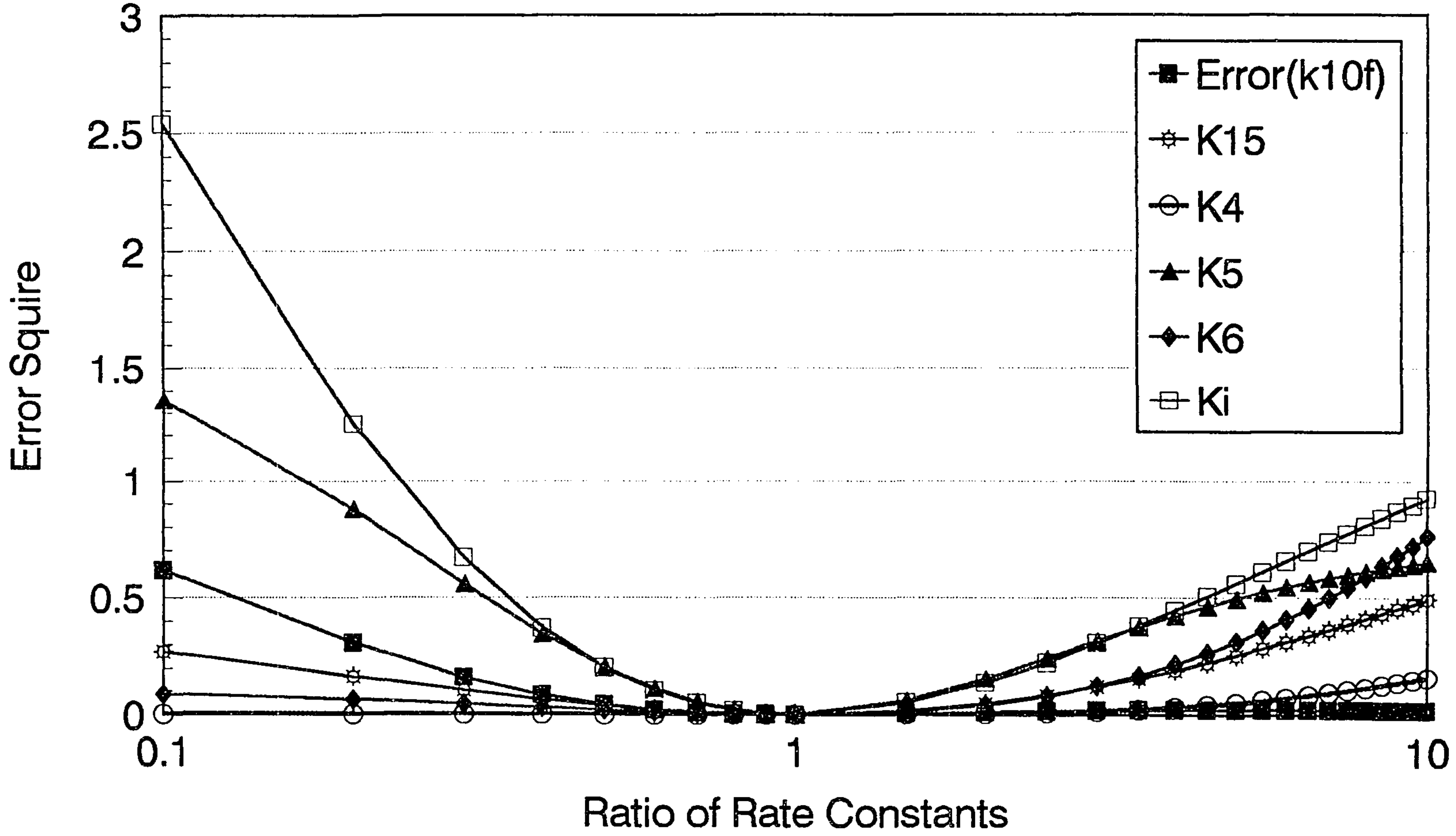
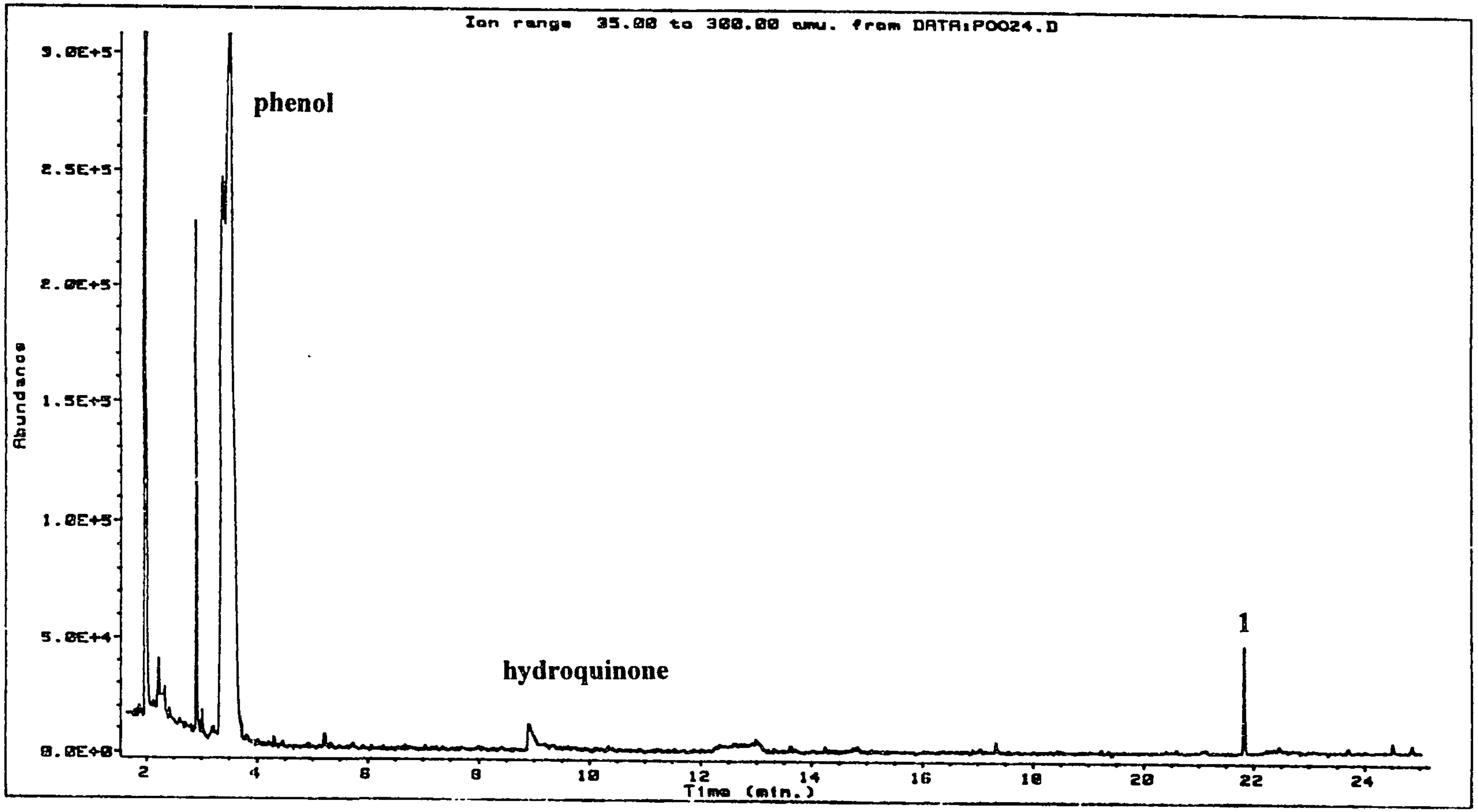


Figure A.10 Senstivity Analysis of Acid Orange 10 Decomposition by UV/H2O2 System

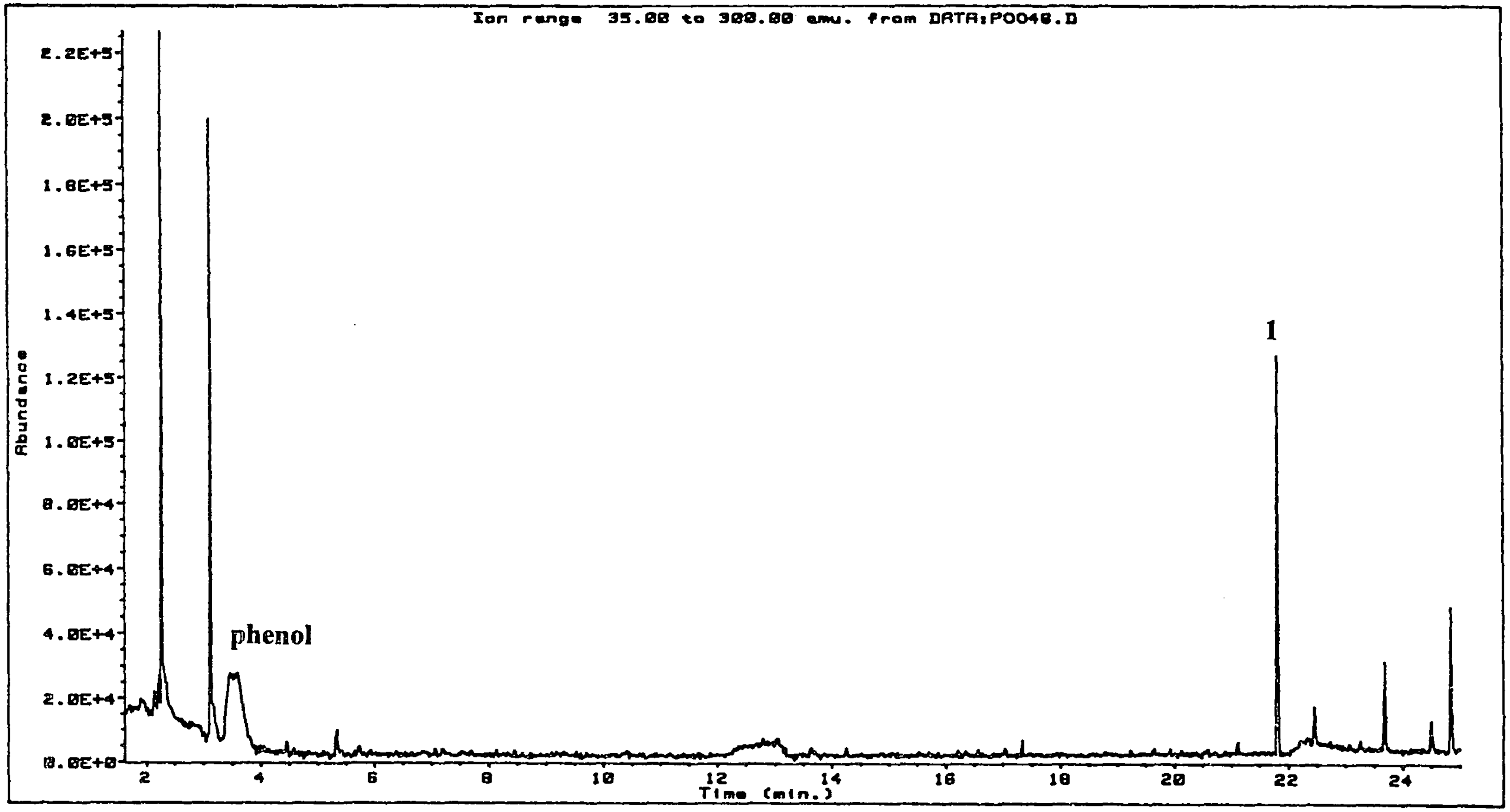
APPENDIX B

OXIDATION OF PHENOL AND ITS REACTION PATHWAYS

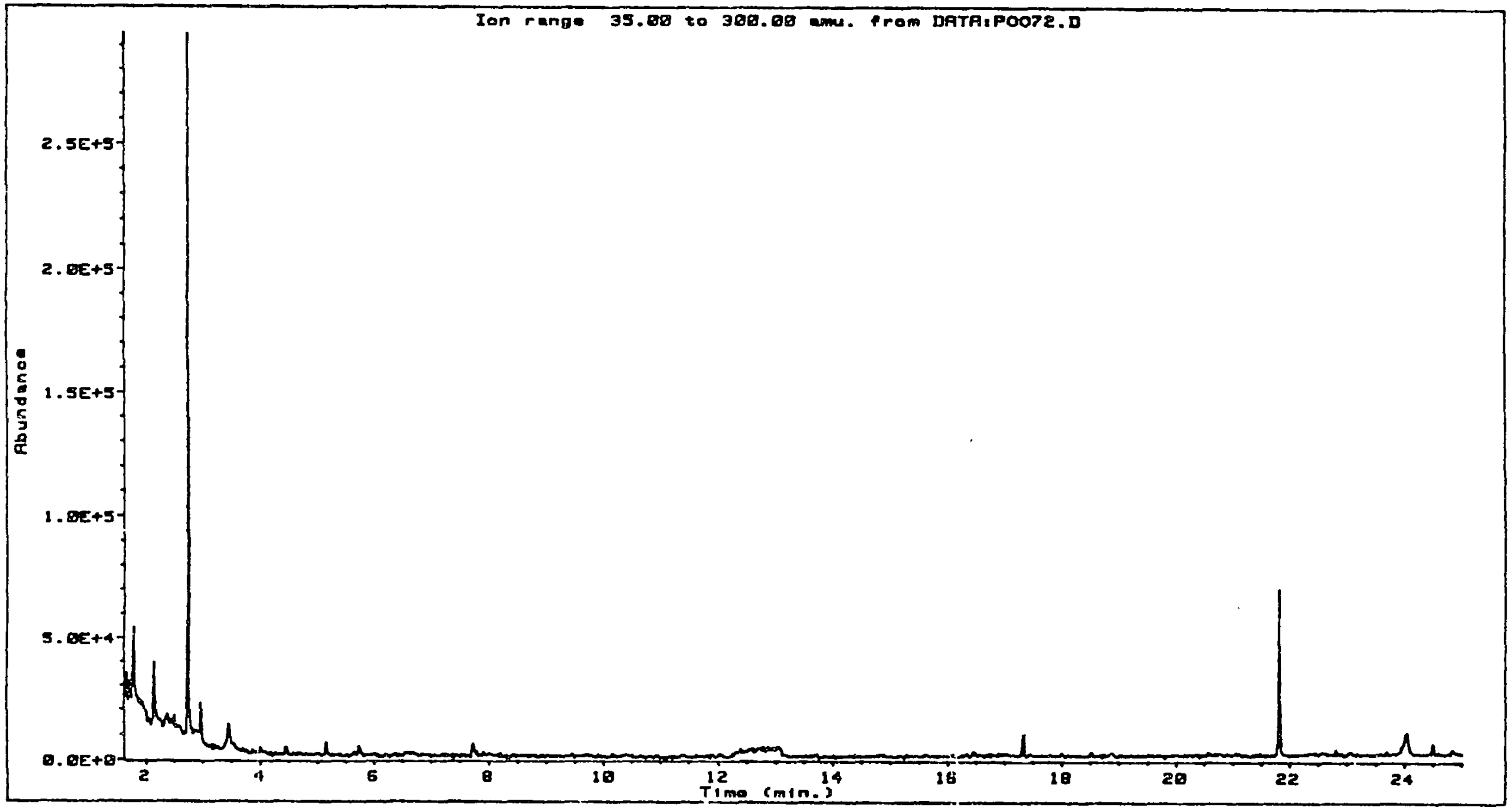
In this appendix, the Total Ion Chromatograph for phenol decomposition in three different processes are given in Figure B.1 to Figure B.9, reaction pathways and mass spectrum of intermediates are also included in Figure B.10 to Figure B.17



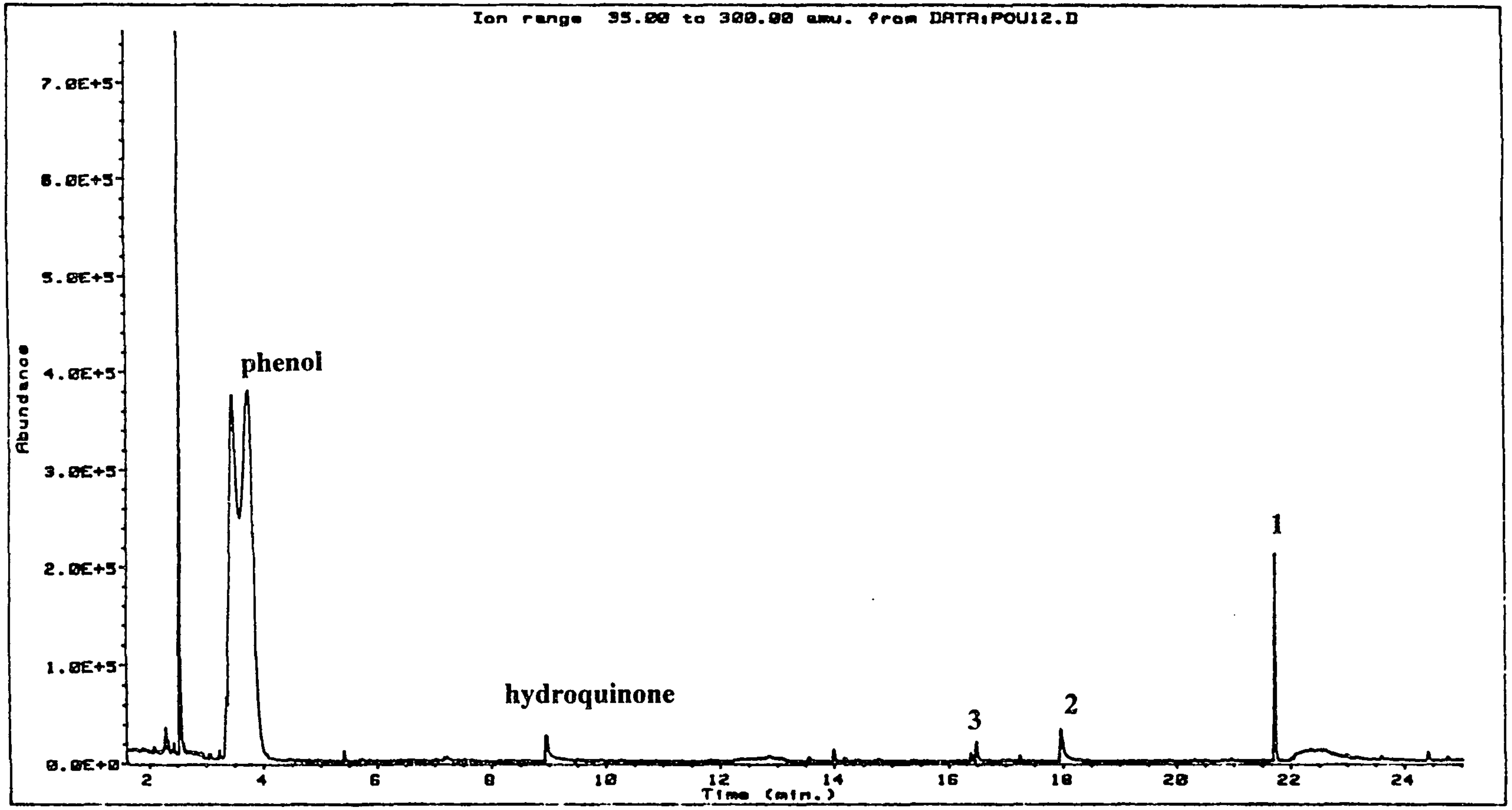
Figures B.1 The GC/MS Total Ion Chromatograph for Phenol Decomposition by O_3 Reaction at 24 Minutes



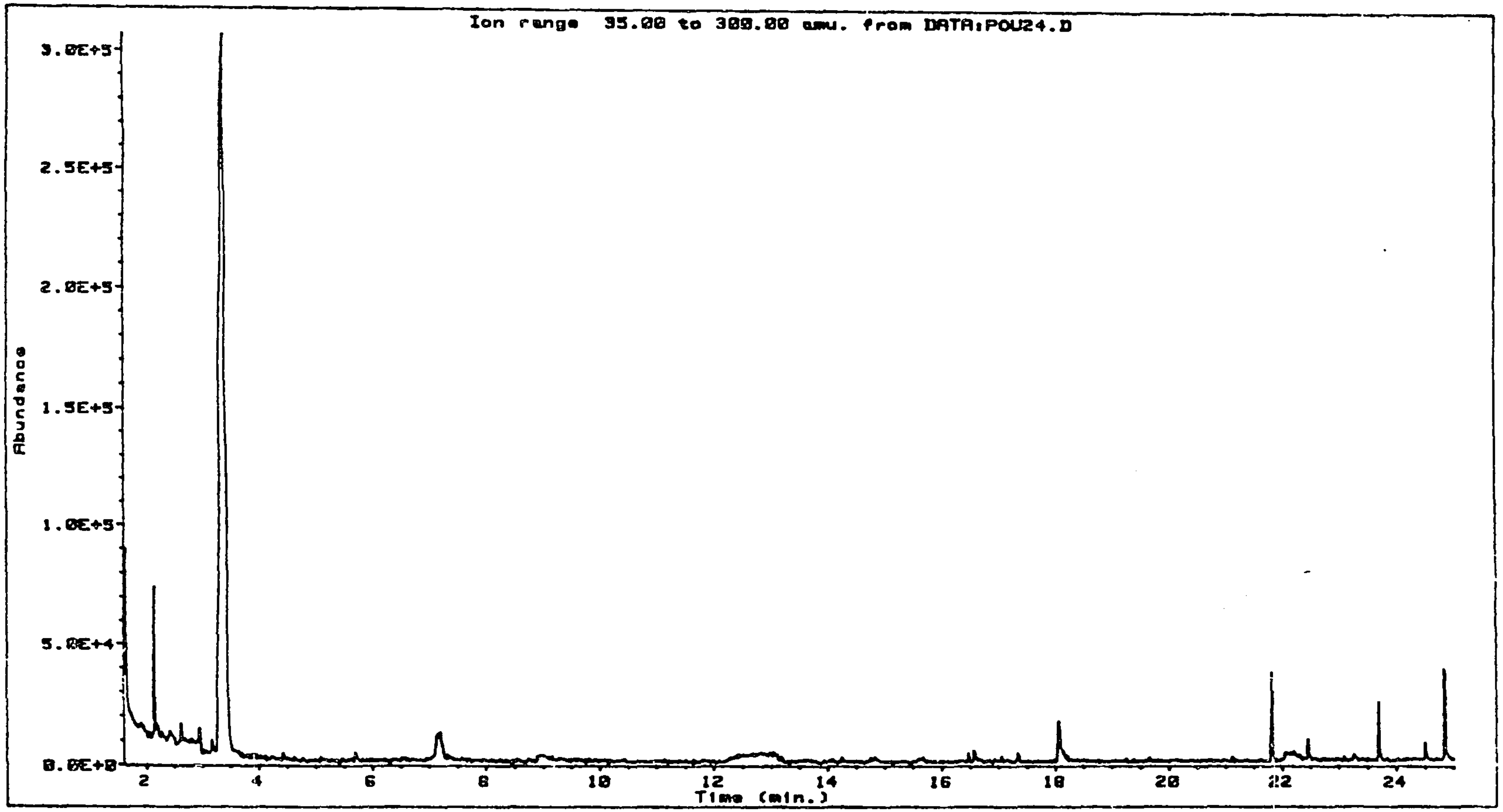
Figures B.2 The GC/MS Total Ion Chromatograph for Phenol Decomposition by O_3 Reaction at 48 Minutes



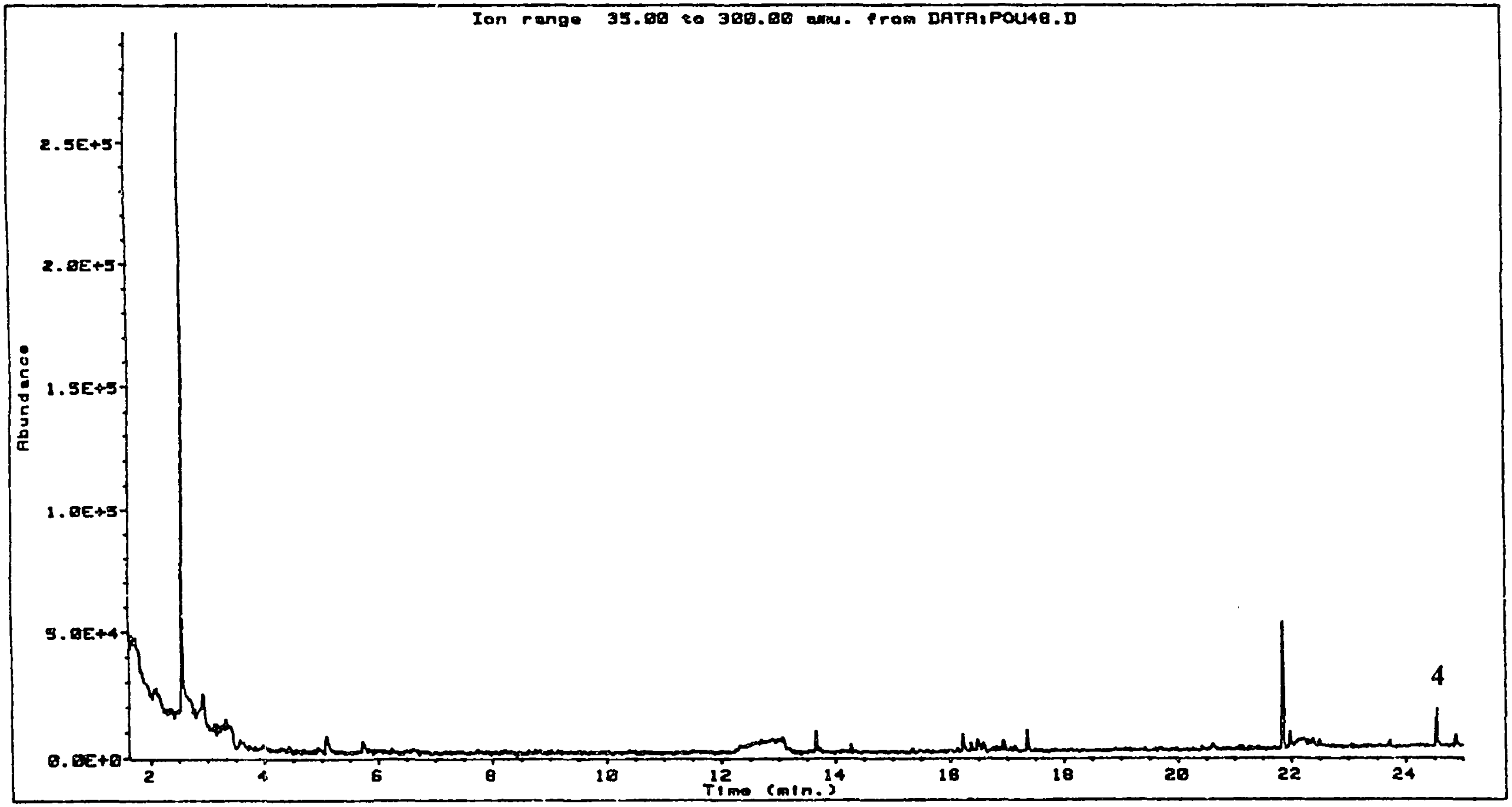
Figures B.3 The GC/MS Total Ion Chromatograph for Phenol Decomposition by O_3 Reaction at 72 Minutes



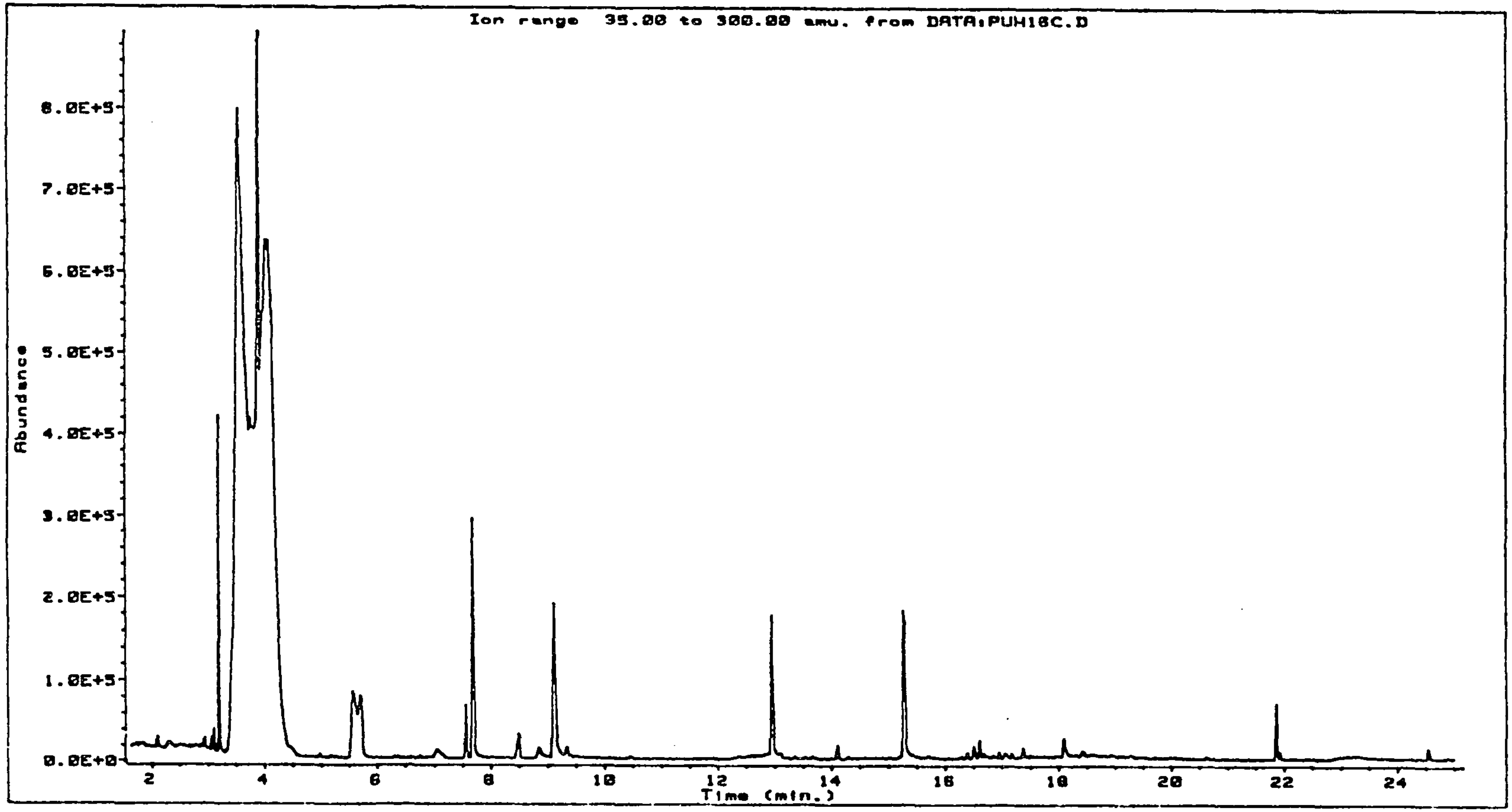
Figures B.4 The GC/MS Total Ion Chromatograph for Phenol Decomposition by O_3/UV Reaction at 12 Minutes



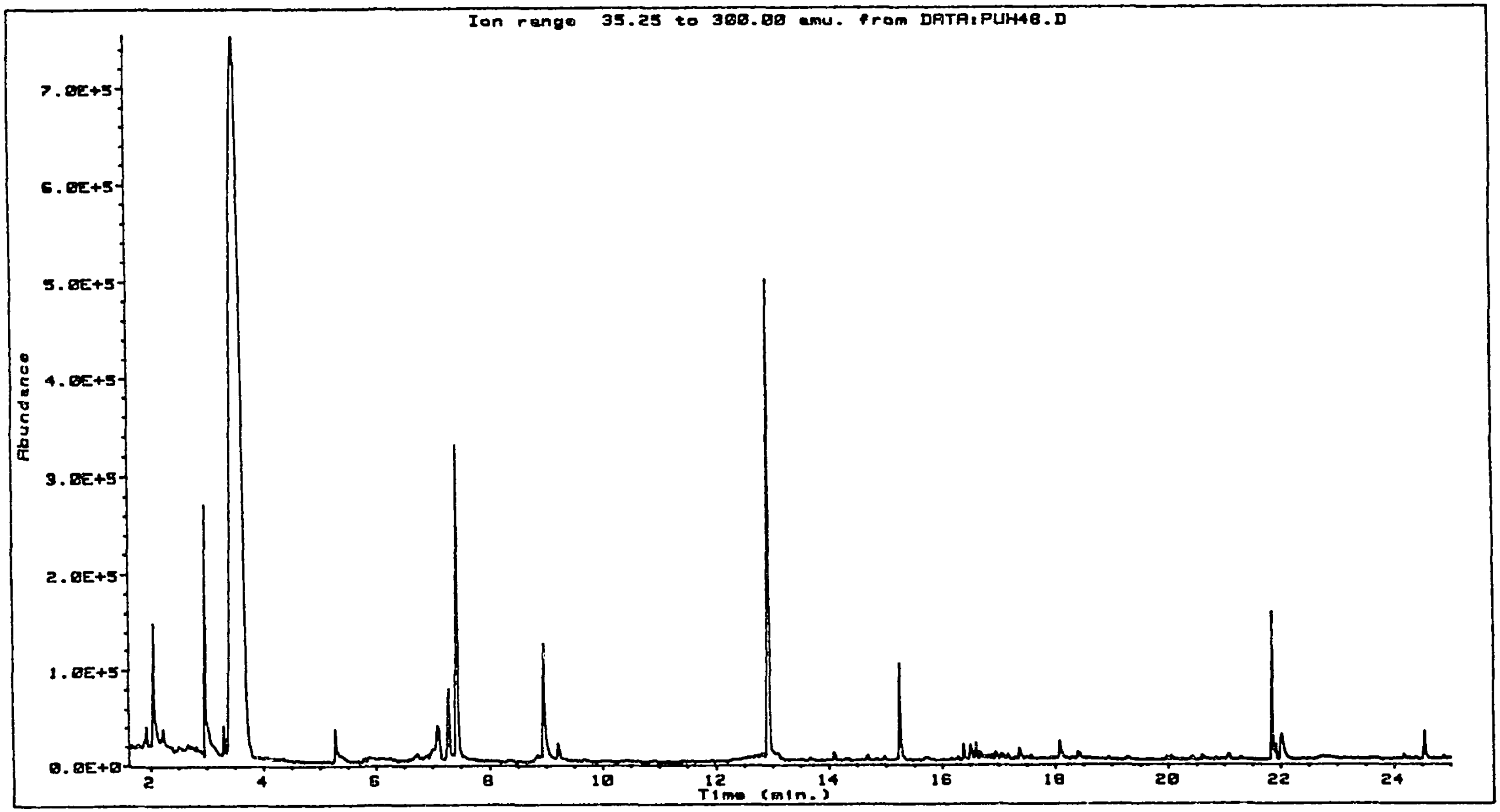
Figures B.5 The GC/MS Total Ion Chromatograph for Phenol Decomposition by O_3/UV Reaction at 24 Minutes



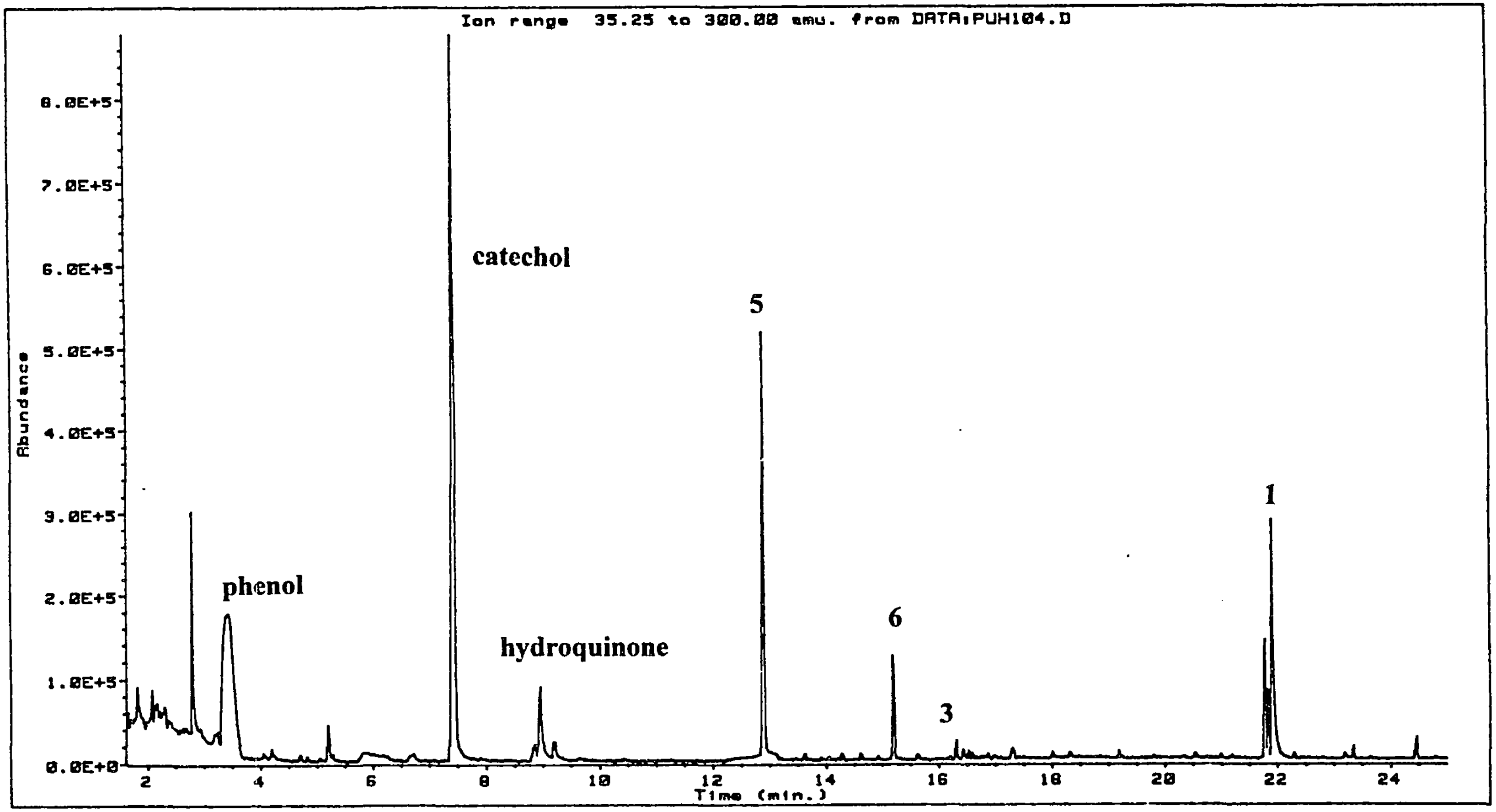
Figures B.6 The GC/MS Total Ion Chromatograph for Phenol Decomposition by O_3/UV Reaction at 48 Minutes



Figures B.7 The GC/MS Total Ion Chromatograph for Phenol Decomposition by UV/H_2O_2 Reaction at 16 Minutes



Figures B.8 The GC/MS Total Ion Chromatograph for Phenol Decomposition by UV/H_2O_2 Reaction at 48 Minutes



Figures B.9 The GC/MS Total Ion Chromatograph for Phenol Decomposition by UV/H_2O_2 Reaction at 104 Minutes

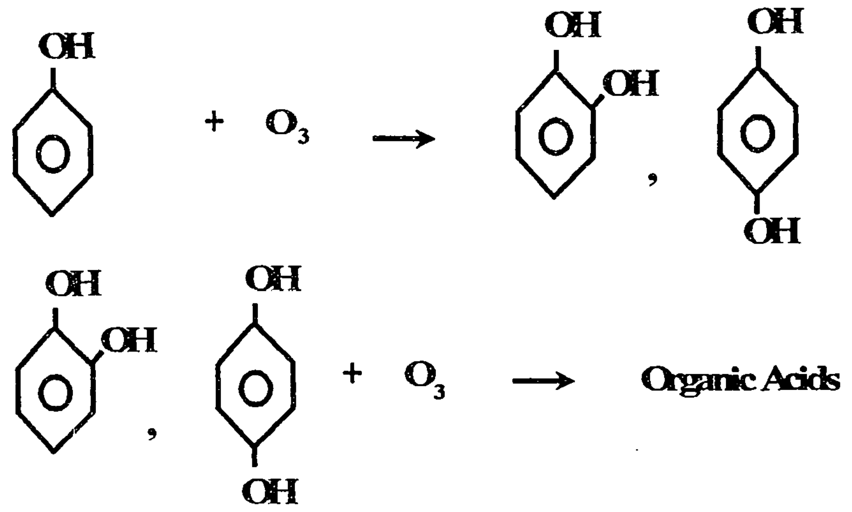


Figure B.10 Reaction Pathway of Phenol Decomposition by Ozonation

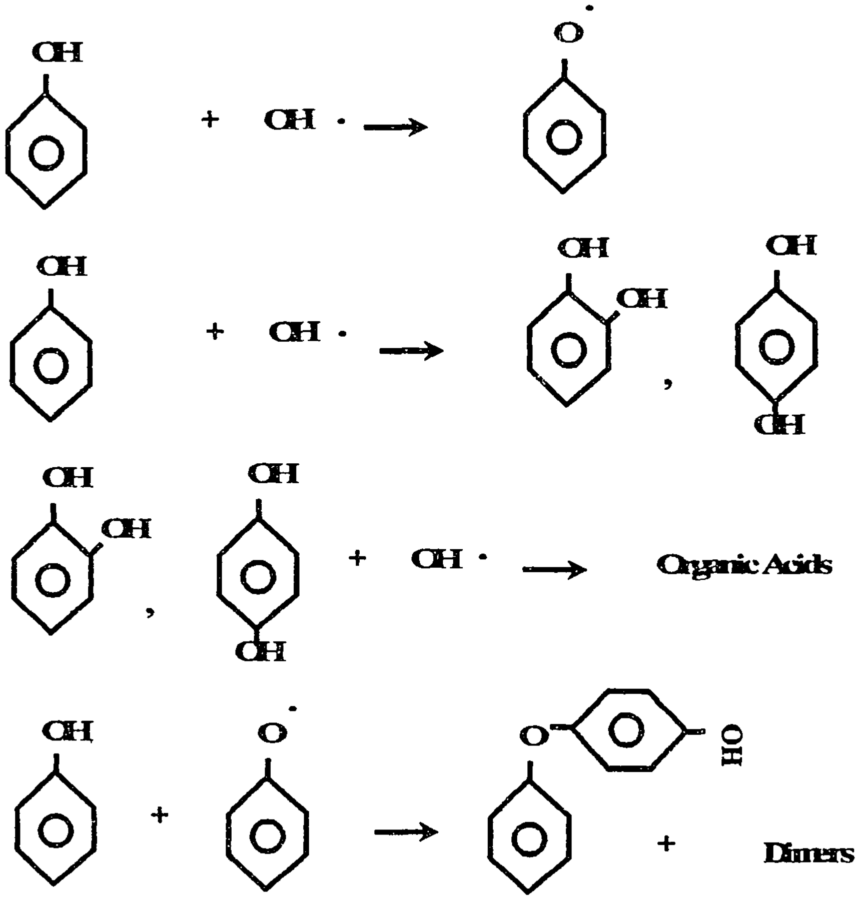


Figure B.11 Reaction Pathway of Phenol Decomposition by Hydroxyl Radicals

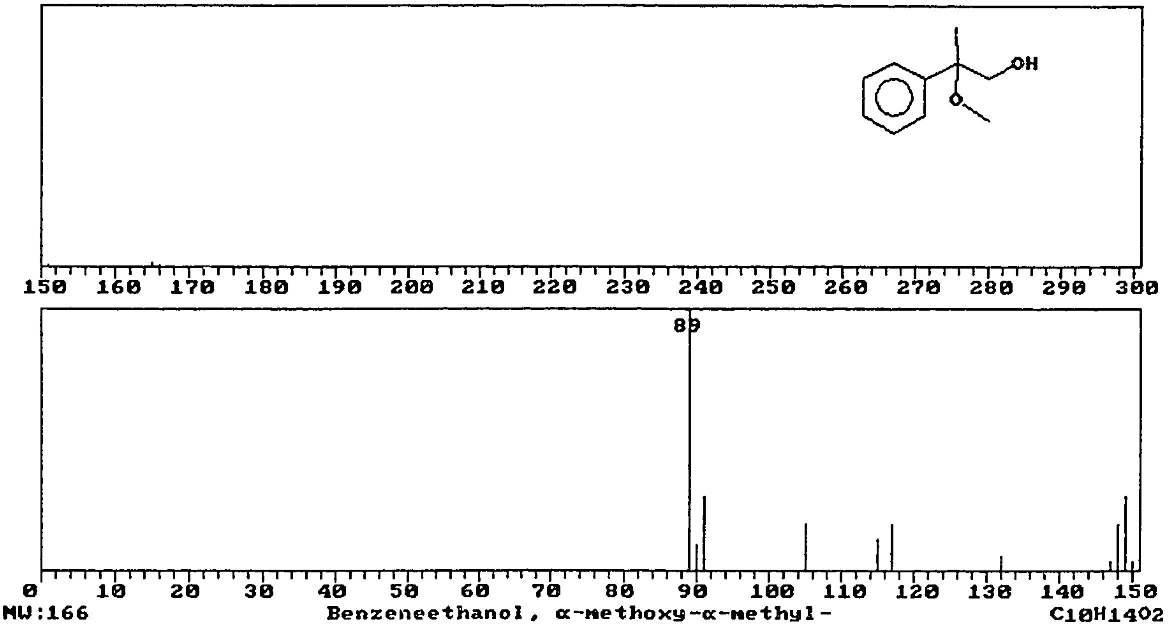


Figure B.12 Mass Spectrum of α-methoxy-α-methyl Benzeneethanol (Marked 1)

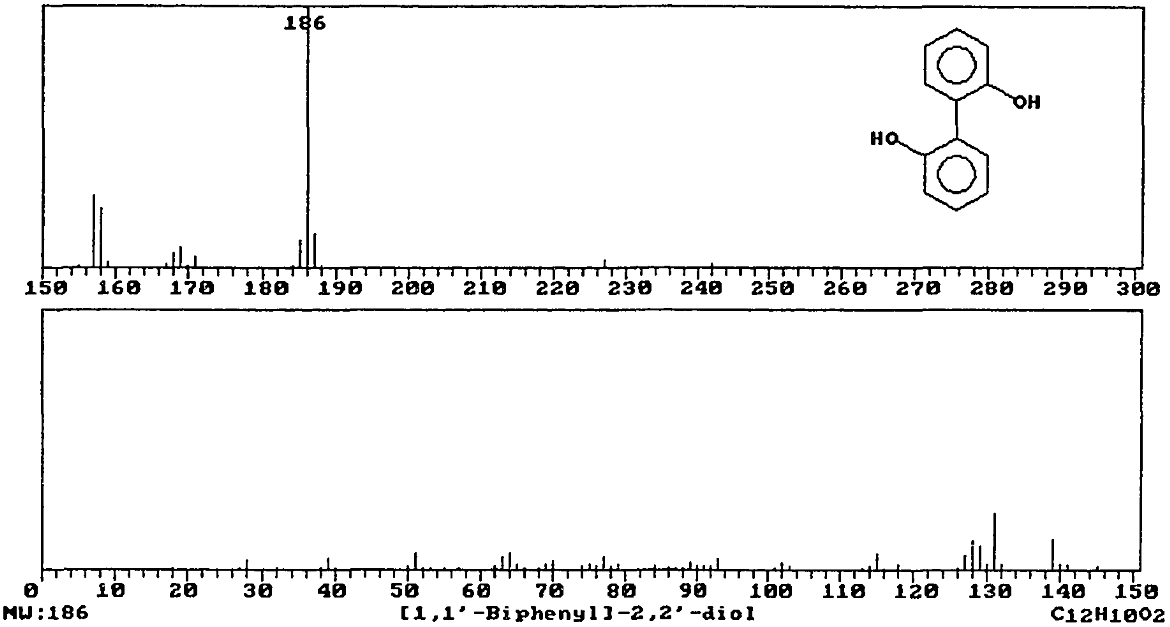


Figure B.13 Mass Spectrum of 1,1'-Biphenyl-2,2'-diol (Marked 2)

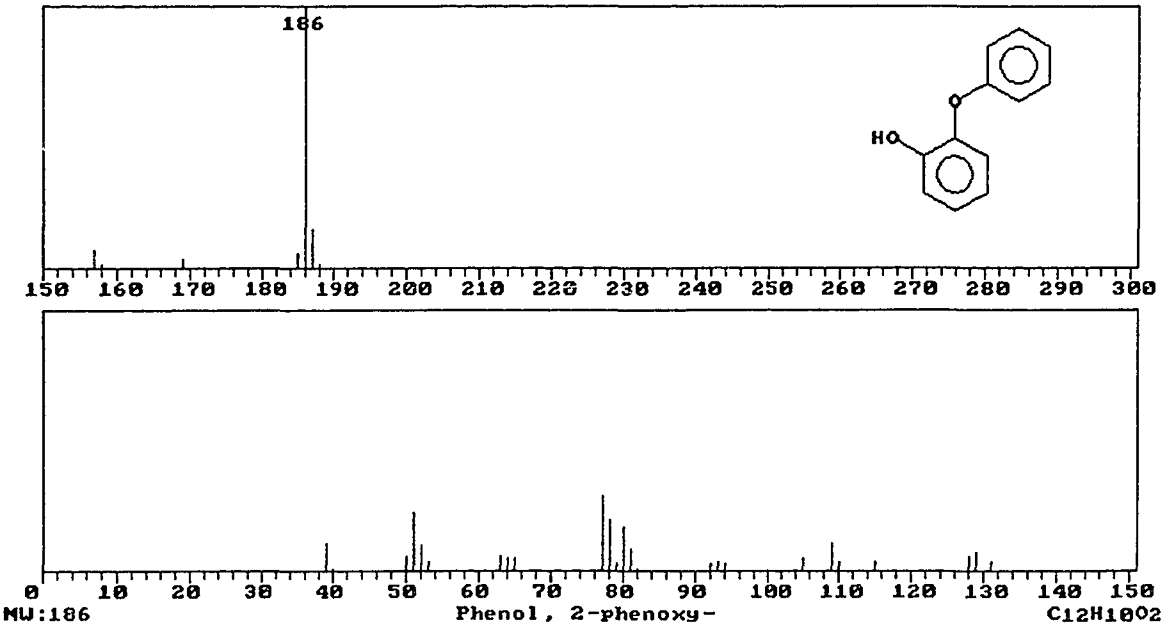


Figure B.14 Mass Spectrum of 2-Phenoxy-phenol (Marked 3)

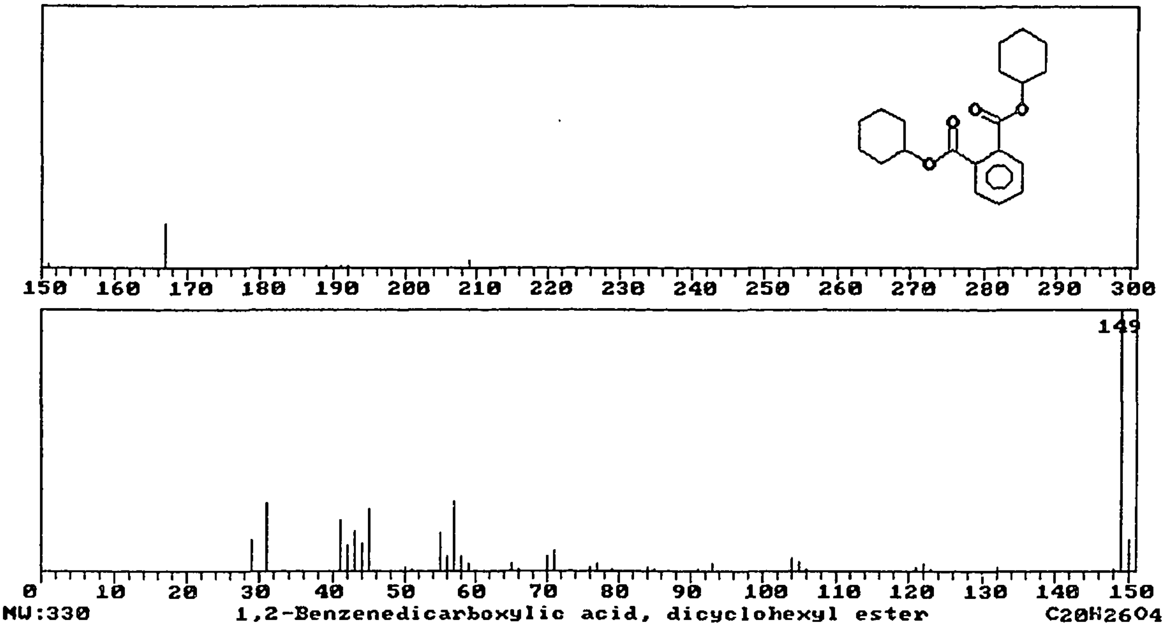


Figure B.15 Mass Spectrum of 1,2-Benzenedicarboxylic acid, dicyclohexyl ester (Marked 4)

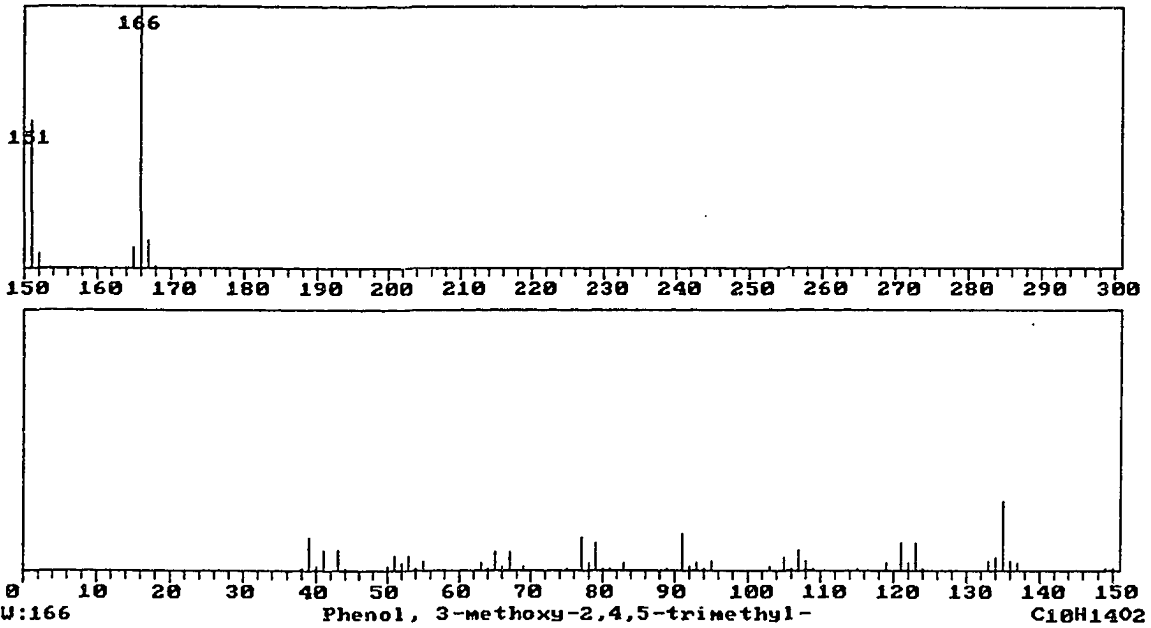


Figure B.16 Mass Spectrum of 3-methoxy-2,4,5-trimethyl-phenol (Marked 5)

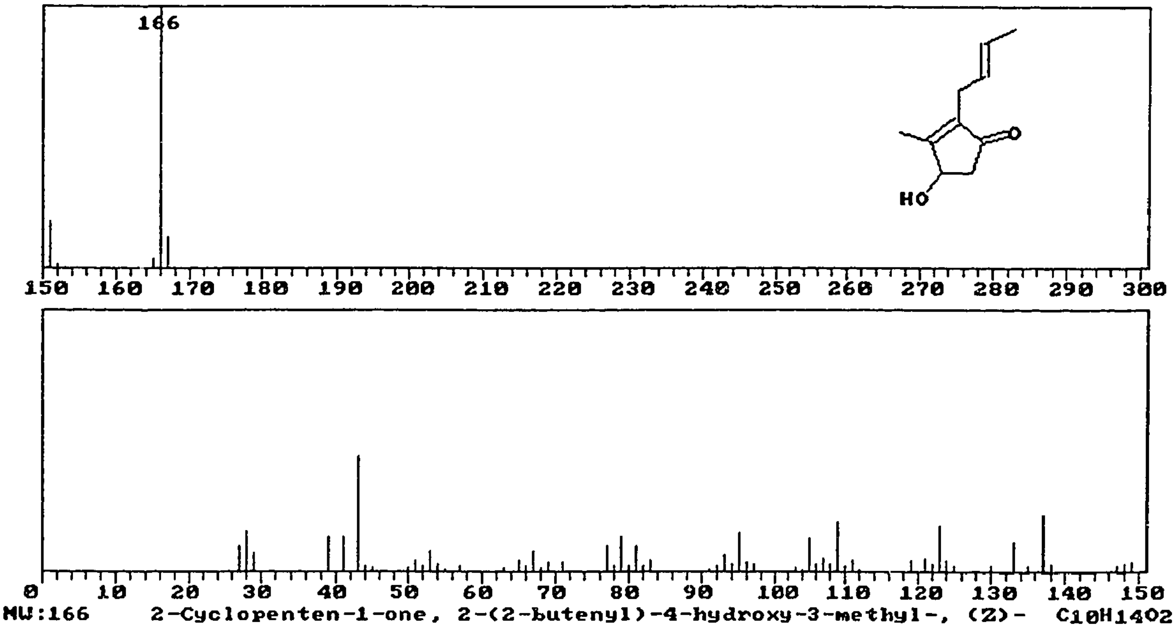


Figure B.17 Mass Spectrum of 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one (Marked 6)

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