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Kinetic studies of photo-initiated oxidation of toxic organic pollutants including the formation and the destruction of intermediates

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New Jersey Institute of Technology, 1992

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KINETIC STUDIES OF PHOTO-INITIATED OXIDATION OF TOXIC ORGANIC POLLUTANTS INCLUDING THE FORMATION AND THE DESTRUCTION OF INTERMEDIATES

by

Yuan-Shen Li

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the degree of Doctor of Philosophy Department of Chemical Engineering, Chemistry, and Environmental Science May 1992

APPROVAL PAGE

Kinetic Studies of Photo-Initiated Oxidation of Toxic Organic Pollutants Including the Formation and the Destruction of Intermediates

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ABSTRACT Kinetic Studies of Photo-Initiated Oxidation of Toxic Organic

Pollutants Including the Formation and the Destruction of Intermediates

by

Yuan-Shen Li

The photo-initiated oxidation process, using hydrogen peroxide or ozone under ultraviolet radiation, has been proven to be an effective treatment method for toxic organic pollutants in wastewater. Most of the recent kinetic studies of the process were concentrated on the breakdown mechanisms of the pollutant itself. The formation and the destruction of intermediates were seldom investigated. Also the mechanisms and their reaction rate constants of free radical formation and destruction in the O₃/UV or H₂O₂/UV reactor were seldom studied.

The objective of this research is to study the kinetics of photo-initiated oxidation of toxic organic pollutants including the formation and the destruction of the intermediates. The reaction mechanisms and their rate constants of free radical formation and destruction in the ozone (O₃), O_3/UV , and H_2O_2/UV reactor were also studied. Three refractory pollutants, nitrotoluene, naphthalene and 2,4,6trichlorophenol were conducted in a 120 liter stainless reactor and the ultraviolet radiation source was provided by a low pressure mercury lamp located at the center of the reactor. The analysis of the concentration of pollutants and their intermediates were done by high performance liquid chromatograph (HPLC). The intermediates were identified by the GC/MS and HPLC. The kinetic models developed were verified by the experimental data taken from the reactor. The Rosenbrook Hillclimb Optimization Algorithm together with the Fourth-order Runge-Kutta method were used on a digital computer to calculate the reaction rate constants. By comparing the theoretical output concentration of pollutants with the experimental results in the CSTR processes, it is believed that the calculated rate constants and the proposed kinetic models can be practically used in the photolytic oxidation waste water treatment process.

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This dissertation is dedicated to my wife Ya-Ling Cheng

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CHAPTER 1 INTRODUCTION

In recent years the major emphasis in the waste-water treatments has shifted from the removal of conventional pollutants (e.q. Biological Oxygen Demand and Suspended Solid) to a variety of the hazardous/toxic chemical pollutants. Chemicals which are referred as hazardous/toxic are being found more and more in our environments. The sources of the toxic chemical pollutants are mostly from the industrial processes. Although the flow of the waste waters from the industrial processes may be small, the high concentration and the increasing volume give great pressure on the natural environment. In order to reduce the concentration of the toxic pollutants to a low residual level, many waste water treatment methods have been proposed, such as the physical/chemical treatments: precipitation, coagulation, filtration, activated carbon adsorption oxidation and biological treatment methods.

Oxidation is one of the chemical treatment methods used for the degradation of the chemical pollutants from water solutions. Four chemical oxidants are commonly used in the U.S.A. : chlorine, chlorine dioxide, bromine chloride and ozone. Chlorination is one of the most commonly used methods for the water and waste water treatment because chlorine can destroy the pathogenic as well as other harmful organisms that may endanger human health. However, chlorination is effectiveless to those toxic and refractory chemical pollutants and has been found that many organic constituents in waste water may react with chlorine to form toxic compounds. Chlorination has also been found to produce trihalomethanes which are suspected of being carcinogens in water treatment. Because of the potential hazards associated with chlorination by-products, other methods for the treatment of water and waste water are considered as alternatives to chlorination. Among the alternatives, biological unit processes and advance oxidation methods such as ozone, ozone with ultraviolet

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radiation, hydrogen peroxide, hydrogen peroxide with ultraviolet radiation and other combinations have been receiving much attention. With proper analysis and environmental control, almost all waste water which have concentrations below a certain value can be treated biologically. But for some highly toxic pollutants, they may kill biomass at a higher concentration. Also, the degradation rate is so low that it takes time to degrade to a low concentration. Ozone was first used to disinfect water supplies in the France in the early 1900s. Its use there increased and eventually spread into several European countries. A common use for ozone in this process is to control taste-, odor, and color-producing agents. Recently, advances in ozone generation and solution technology have made the use of ozone more competitive economically, for waste water disinfection. Ozone can also be used in waste water treatment for odor control and in advanced waste water treatment for the removal of some soluble refractory toxic chemicals. In the early 1970's, the combination of ultraviolet (UV) radiation with ozonation had been shown to increase the rate of ozone oxidations in an aqueous solution. A later series of experiments demonstrated that ozone/UV combination caused oxidations to proceed more rapidly than does the use of ozone alone, especially for compounds normally refractory to the use of ozone alone (1). This is due to the decomposition of ozone under UV radiation which can produce more powerful oxidants, such as hydroxyl radical (OH·) and hydrodioxy radical (HO_2) , and a constant intensity of ultraviolet radiation is used to activate those compounds and accelerate the reaction. The ozone, hydroxyl radicals and hydrodioxy radicals are the species responsible for the strong germicide activity of ozonated solutions.

While ozone/UV treatment process is undoubtedly effective on a wide range of compounds, it has a number of disadvantages. Ozone is an unstable gas and must be

generated on-site and used immediately. An ozone contacting device must be provided which can achieve adequate mass transfer of ozone. An oxidant which may be as effective as ozone but is better suited for use in small treatment system is hydrogen peroxide. As one of the strongest oxidants, hydrogen peroxide (H₂O₂), when dissolved in an aqueous solution and when its exposed to the ultraviolet radiation, it can also produce the same free radicals, hydroxyl radical, and hydrodioxy radical, same as the ozone under the ultraviolet radiation. For some pollutants, the decomposition rate in the H₂O₂/UV process is more effective than in the O₃/UV process. This phenomena depends on which radical predominates the reaction pathway. In H₂O₂/UV treatment process, the predominant radical is hydroxyl radical. While in O₃/UV process, the hydrodioxy radical is the predominant radical.

In the ozone treatment process, several investigators have reported that ozonation can produce some toxic mutagenic and/or carcinogenic compounds. Whether toxic intermediates are formed during ozonation depends on ozone dose, contact time, and precursor pollutants (2). Very little research has been done in the O_3/UV and H_2O_2/UV processes. It is believed that the formation of toxic intermediates are dependent on the contact time, the precursor pollutants, the intensity of ultraviolet radiation, and the ozone or hydrogen peroxide dose.

The topic of this research involves the study of the degradation of o-nitrotoluene $(C_7H_7NO_2)$, naphthalene $(C_{10}H_8)$ and 2,4,6-trichlorophenol using O₃, O₃/UV and H₂O₂/UV processes. Also during the pollutant degradation period, to investigate the formation and the destruction of the intermediates. We intended to propose reasonable kinetic reaction models for the degradation of these compounds and intermediates using O₃, O₃/UV and H₂O₂/UV. Before study, the degradation of those pollutants, mechanisms and their reaction rate constants of free radicals formation and destruction in a H₂O₂/UV reactor and in a O₃/UV reactor will also be

investigated. By using the Rosenbrook Hillclimb Optimization Algorithm (3) with the Fourth-Order Runge-Kutta method on a digital computer, we can obtain the reaction rate constants for the different kinds of reaction mechanisms and the mass transfer coefficients between liquid and gas phase for the reaction of O₃ alone, O₃/UV and H₂O₂/UV in the photo-reactor and O₃, O₃/UV and H₂O₂/UV with these three compounds.

In order to demonstrate the feasibility of the O_3/UV and the H_2O_2/UV processes in waste water treatment, constant flow stirred tank reactor (CSTR) experiments were also conducted. By using the reaction rate constants and the mass transfer coefficients which are obtained from the batch reactor reaction from a series of experiments, the theoretical output concentration for CSTR can also be predicted. Comparison of the theoretical data and the experimental data in the CSTR process, has shown good aggrement. We believe, that these kinetic models and the rate constants for the pollutants and intermediates in different treatment processes can be used in practical waste water treatment.

CHAPTER 2 REVIEW OF PREVIOUS STUDIES

2.1 Ozone Properties

Ozone (O_3) is an unstable, blue colored gas having a pungent characteristic odor, but at the concentration at which it is ordinary produced this odor is not noticeable. The most efficient method of producing ozone today is by electric discharge. Ozone is generated either from air or pure oxygen when a high voltage is applied across the gap of narrowly spaced electrodes. The high energy corona created by this arrangement dissociates one oxygen molecule, which reforms with two other oxygen molecules to create two ozone molecules. Thus the structure of the ozone molecule is that of an obtuse angle, where a central oxygen atom is attached to two equidistant oxygen atoms. Ozone gas is slightly soluble in water, and even more in other liquids. especially at low temperatures. In an acid solution, ozone has an oxidation potential 2.07 volts and of 1.24 volts in basic solution at 20 °C, thereby making it capable of oxidizing many organic and inorganic chemicals. Rosenthal (4) reported that the halflife period of ozone in distilled water is about 20 minutes at 20 °C. When it is sparged into water, saturation is difficult to achieve. This is because in water solution. ozone may react directly with the dissolved substances or it may decompose to form secondary oxidants such as hydroxyl radical (OH·) and hydroperoxide radical (HO₂·). Ozone is used commercially in the purification of drinking water, the preparation of chemicals, the treatment of industrial wastes, the deodorization of air and sewage gases and the preservation of goods in cold storage.

2.2 The Decomposition of Ozone in Water

The decomposition of ozone in an aqueous solution has been thoroughly studies for many years. However, prediction of the reaction mechanism and the reaction kinetics of the decomposition of ozone in water are still uncertain. This is because in water solution ozone may react directly with dissolved substance or it may decompose to form secondary oxidants, such as $OH \cdot$ and $HO_2 \cdot$, which then react with solutes immediately. These different reaction pathways produce different products, each having a different kind of kinetics and reaction mechanisms.

Peleg (5) proposed that the kinetics of ozone decomposition in water solution is between first order and second order, depending on the pH value and the temperature. Stumm (6) pointed out that at pH ranging between 7.6 to 10.4 and temperature from 1.2 °C to 19.8 °C the reaction order with respect to ozone is first order reaction. Rothmund and Burgstaller (7) found that it is second order reaction with respect to ozone at the pH range 2 to 4 at 0 °C. Hewes and Davison (8) summarized the reference literature and suggested that the decomposition of ozone in water is a second order reaction at pH 2 to 4 with the rate insensitive to pH, at pH 6 the reaction order is 2/3 to 2, at pH 8 it is first order reaction and above pH 6 the reaction rate increases rapidly with pH.

One reaction mechanism, suggested by Weiss (9) showed that the decomposition of ozone in water, at a given pH value, was catalyzed by the hydroxyl ion (OH-) for the initial reaction. The overall reaction mechanism which he suggested was :

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

$$O_3 + HO_2 \cdot \rightarrow 2O_2 + OH \cdot$$

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

$$2HO_2 \cdot \rightarrow O_3 + H_2O$$

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

From this mechanism above, Weiss calculated that the kinetics of ozone decomposition was 3/2 order with respect to the ozone concentration.

Alder and Hill (10) on the basis of their kinetics studies, suggested the following first order reaction mechanism :

$$O_3 + H_2O \rightarrow HO_3^+ + OH^-$$

 $HO_3^+ + OH^- \Leftrightarrow 2HO_2^-$
 $O_3 + HO_2^- \rightarrow HO^- + 2O_2$
 $HO^+ + HO_2^- \rightarrow H_2O + O_2$

Peleg (11) referred the previous studies and proposed the following more reasonable reaction mechanism for the ozone decomposition in an aqueous solution :

$$O_{3} + H_{2}O \rightarrow O_{2} + 2OH$$

$$O_{3} + OH \rightarrow O_{2} + HO_{2}$$

$$O_{3} + HO_{2} \rightarrow 2O_{2} + OH$$

$$OH \rightarrow HO_{1} \rightarrow H_{2}O_{2}$$

$$OH \rightarrow HO_{2} \rightarrow H_{2}O + O_{2}$$

$$OH \rightarrow HO_{1} \rightarrow O^{-} + H_{2}O$$

$$O^{-} + O_{2} \rightarrow O_{3}^{-}$$

$$HO_{2} \rightarrow HO_{2} \rightarrow H_{2}O_{2} + O_{2}$$

Staehelin and Holgne (12) also proposed a more complicated reaction mechanism for the decomposition of ozone in the pure water and in the presence of organic solutes. Tomiyasu and co-workers (13) reported the kinetics and the reaction mechanism of ozone decomposition in an basic aqueous solution. All of the above mentioned investigators generally agreed that the decomposition of ozone in an aqueous solution can produce hydroxyl radical and be catalyzed by these hydroxyl radicals. Thus, we can write the overall reaction mechanism of ozone decomposition in an neutral aqueous solution as follows :

$$O_3 + H_2O \rightarrow 2 \text{ OH} \cdot + O_2$$
$$O_3 + OH \cdot \rightarrow O_2 + HO_2 \cdot$$
$$O_3 + HO_2 \cdot \rightarrow 2O_2 + OH \cdot$$

$$OH \cdot + OH \cdot \rightarrow H_2O_2$$
$$OH \cdot + HO_2 \cdot \rightarrow H_2O + O_2$$
$$HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$$

2.3 The Ozone Oxidation of Organic Chemicals

Ozone oxidation can generally be classified into two types : mass transfer controlled and chemical reaction rate controlled (14). Mass transfer controlled oxidation with ozone occurs so rapidly that rate is limited only by the speed at which ozone can be added to the solution. However, for those highly volatile organic chemicals the mass transfer controlled reaction is as important as the chemical reaction rate control. Thus, this reaction still should be considered during the ozone oxidation. Previous researchers neglected this effective which may cause a serious error during the reaction kinetic study. Thus, we put this reaction control in our ozone oxidation mechanism which will propose in chapter 4. As for the chemical reaction rate controlled, Hoigne and his co-workers (15) stated that there are two types of ozonation reaction : the direct reaction of ozone with the organic compound and the free radicals of ozone which involve hydroxyl radical and hydroperoxide radical.

During ozonation, some of the added ozone may react directly with the solute. However, part of the added ozone decomposes to form hydroxyl free radicals and hydroperoxide free radicals before its reaction with the oxidized solute. Ozone in acidic solution has an oxidation potential of 2.07 volts and of 1.24 volts in an basic solution. The oxidation potential of the hydroxyl free radical is 2.87 volts and the hydroperoxide is 1.7 in acidic solution. Those are all extremely reactive oxidants.

The quantitative of formation of the free radicals is dependent on pH value (16). A higher pH value can increase the formation of hydroxyl free radical and hydroperoxide free radical. Thus, there may be several reaction pathways contributing to the oxidation of organic chemicals. Singer and Gurol (17) used ozone to treat phenol solution at pH 3.0 found that muconic acid is the predominant intermediate and the concentration of other intermediates, catechol and hydroquinone, is small. This is contrary to the observations of Eisenhauer (18). Eisenhauer who run the same experiment at higher pH value found that catechol and hydroquinone are the major intermediates. Thus it is very important to maintain the pH at a certain value.

Many chemistry researchers reported the papers about the initial ozone direct attack organic chemicals. They found that ozone molecule has an obtuse apex angle and that it should be consider a hybrid of the following resonating structure:

 $0 = 0 - 0 \leftrightarrow 0 - 0 = 0 \leftrightarrow 0 - 0 - 0 \leftrightarrow 0 - 0 - 0$

The first step is the electrophic attack by a terminal oxygen atom and the second step is the central oxygen atom completes the attack on the other carbon atom.

Hydroxyl radical and hydroperoxide radical initiate oxidation by three main types of reaction : (1) radical addition reaction (2) hydrogen abstraction reaction (3) electron transfer reaction (19). Because these two radicals do not react very selectively with the dissolved materials, their reactions always lead to a great variety of intermediate products.

2.4 Photolytic Ozonation : O3/UV

The ozone in combination with ultraviolet radiation (O_3/UV) process for the oxidation of refractory and toxic organic or inorganic was developed in the 1970's. In recent years, this combination process has been shown to increase the rate of many ozone oxidation in an aqueous solution, especially for those chemicals that do not react directly with ozone.

UV radiation at 180 - 400 nm provides 72 - 155 Kcal/mole (20) energy. For many organic chemicals, this radiation supports enough energy to reach the excited

state, when it is easier to be decomposed by oxidants. This energy also accelerates the decomposition of ozone and produces other oxidizing free radicals, hydroxyl radical and hydroperoxide radical from ozone.

At present a detailed investigation of the mechanisms of ozonation in the presence of UV radiation, and the proposed mechanisms are speculative. Prengle and Mauk (20) proposed the following steps for the reaction of ozone under the UV radiation :

(1) production of highly oxidizing photolytic species from ozone.

(2) production of free radicals and excited state photolytic species from the parent compound.

(3) reaction with water species OH• and H•.

Those reaction steps did not tell us the detailed reaction mechanisms of O_3/UV reaction. Gray and co-workers (21) also proposed the following simple O_3/UV reaction mechanism :

$$O_3 \xrightarrow{h\nu} O_2 + O(^1D)$$

 $O + H_2O \longrightarrow 2HO$

In the water - rich gas phase, the process involves dissociation into an oxygen molecule and an oxygen atom in the ${}^{1}D$ state. The latter may react with a water molecule to produce two hydroxyl radicals. They also determined the ozone mass transfer coefficients between the gas phase and the liquid phase at different ozone gas flow rate and the experimental results of the concentration of ozone in the liquid phase with and without irradiation with 254-nm UV radiation. This reaction mechanisms is too simple to explain all of the reaction. For example, it did not mention the decomposition reaction of ozone which had already dissolved into water.

Prengle (22) presented a overall reaction mechanisms of the O_3/UV photo oxidation of M species containing sulfur, phosphorous and halogen in an aqueous solution in a simplified process.

$$O_{3} \longrightarrow hv \rightarrow O_{2}^{*} + O \cdot$$

$$O \cdot + H_{2}O \longrightarrow 2OH \cdot$$

$$O_{3} + OH \cdot \longrightarrow HO_{2} \cdot + O_{2}$$

$$M \longrightarrow hv \rightarrow M^{*}$$

$$M \longrightarrow hv \rightarrow R. + O_{2}$$

$$M^{*} + \{hv, O \cdot, OH \cdot, HO_{2} \cdot \} \longrightarrow R., I, H$$
The overall reaction is given as :

M, M*, R., I + {hv, O·, OH·, HO₂.} \rightarrow CO₂, H₂O, SO₄²⁻, PO₄²⁻, Cl⁻

Prengle used trihalomethane as the M species, As a result of UV radiation, the overall oxidation rate was enhanced.

Although the above listed reactions have different kinds of reaction mechanisms, many investigator (21) believe that there have in common a chain reaction which is introduced by UV protons that decompose ozone into an oxygen molecule and an oxygen radical. The oxygen radical may immediately react with the water molecule to produce two hydroxyl radicals. Hydroxyl radicals continue to be produced and consumed in a complex radical reaction mechanism. The hydroperoxide radicals which are produced from the reaction of ozone with hydroxyl radical also involved in the chain reaction. The O₃/UV treatment process may also involve the formation of excited organic species which may subsequently react with hydroxyl radicals and hydroperoxide radicals. Since the concentration of ozone is very small in this process, the effective of ozone on the pollutants is also small.

Gurol and Vatistas (22) did a comparative study of oxidation of phenolic compounds by UV O3 and O3/UV at different pH values. They obtained the following results :

(1) The ozone molecular is the predominant oxidation in an acid solution.

(2) In a basic solution, in the absence or presence of UV radiation, free radicals reaction are the major pathway to the oxidation of phenolic compounds.

(3) The overall removal of the phenols and the total organic carbon (TOC) are increased with increasing pH value during ozonation, with or without UV radiation.

(4) For a specific pH value, the ozone/UV process has the highest removal rate for the phenol and the TOC chemicals, followed by ozone alone, and then UV light alone.

Our experimental result also match above conclusion.

2.5 Photolytic Hydrogen Peroxide

Hydrogen peroxide is a weak acidic, colorless and rather unstable liquid It is completely miscible with water. Hydrogen peroxide is also a strong oxidant and can oxidize some of the organic chemicals.

While the ozone/UV treatment is undoubtedly effective on a wide range of compounds, it still has a number of disadvantage. Ozone is unstable gas and must be generated on-site and used immediately. An ozone contacting device must be provided which can achieve an adequate mass transfer of ozone into the liquid phase. An oxidant which may be as effective as ozone, but is better suited for use in a small treatment system, is hydrogen peroxide, H_2O_2 , plus UV radiation. Malaiyandi and co-worker (23) found that this method could reduce the TOC content of distilled water by about 88 % and of tap water by 98 %. Sundstrom used this process effectively destruct the halogenated aliphatics (24). They also compared the reaction rate with UV, H_2O_2 , H_2O_2/UV at different temperature and had the following result : (1) H_2O_2/UV process has the highest efficiency as compared to other methods.

(2) The rates of decomposition is increased when the hydrogen peroxide concentration and the temperature are increased and the rate of decomposition is highly on the structure of organic compounds dependent.

Weir et al. (25), in 1987, studied on the destruction of benzene by H2O2/UV process. They point out that :

(1) Reaction rate increasing when hydrogen peroxide concentration or UV radiation intensity increased.

(2) At higher pH value, benzene decomposed slowly which probably caused by hydrogen peroxide's base catalyzed decomposition.

The chemistry of the H_2O_2/UV reaction involves the generation of hydroxyl radicals and other reactive species by the photochemical reaction of UV light on hydrogen peroxide. The detail reaction mechanisms are still not clear. Hochanadel (25) first proposed a simple but useful mechanism for the H_2O_2/UV reaction.

$$H_{2}O_{2} \longrightarrow \frac{h\nu}{2} \rightarrow 2OH \cdot$$

$$H_{2}O_{2} + OH \cdot \longrightarrow H_{2}O_{2} + HO_{2} \cdot$$

$$2HO_{2} \cdot \longrightarrow H_{2}O_{2} + O_{2}.$$

:

Later Yoshiro Ogata (26) proposed a very similar reaction mechanism as follows

$$H_{2}O_{2} \longrightarrow \frac{h\nu}{2} \rightarrow 2OH$$

$$H_{2}O_{2} + OH \rightarrow H_{2}O_{2} + HO_{2} \rightarrow$$

$$HO_{2} + H_{2}O_{2} \rightarrow OH + H_{2}O + O_{2}$$

$$2HO_{2} \rightarrow H_{2}O_{2} + O_{2}$$

Basically hydrogen peroxide produces two hydroxyl radical under suitable working condition. Then a series of chain reactions happen among the hydrogen peroxide, hydroxyl radical and hydroperoxide radical. Since the hydroxyl radical is produced first by the hydrogen peroxide decomposition, we should not neglect the reactions between two hydroxyl radical and hydroxyl radical with hydroperoxide radical. Thus, we propose a two step chain reaction mechanism for the hydrogen peroxide with ultraviolet radiation.. The detail mechanism is in chapter 4, reaction mechanism and kinetic model.

2.6 The Reaction Intermediates

The intermediates which are produced from the pollutants were seldom studied, specially the reaction kinetic study in the O_3/UV and H_2O_2/UV process. Sundstrom (24) used benzene as the target pollutant and found that phenol, catechol, resorcinol and hydroquinone were produced from benzene. But the power of ultraviolet source and the reactor he used are so small that a total annular volume of 285 ml of reactor and 5.3 watts of ultraviolet source, which could not be used in the industrial wastewater treatment for any practical purposes. The reaction rate constant which he calculated is only for the target pollutant, not including the intermediates. For some of the intermediates which have a quite high concentration, we should also consider the competitive reaction between the intermediates and the target pollutant.

CHAPTER 3 EXPERIMENTAL EQUIPMENTS AND PROCEDURES

3.1 Experimental Equipment

A schematic diagram of the apparatus used in the experiments is shown in Figure 3.1. The detail descriptions are as follows :

3.1.1 The Reactor

The vertical cylindric type reactor is made of #304 stainless steel. The outside diameter is 13 inches and the length is 55 inches, which gives approximately 104 liters of hold-up volume. There are nine vertical sample ports evenly spaced in three rows. All the tubes connected to the reactor are of #304 stainless steel. The ultraviolet light source residue in the reactor with an annular space of about 3.5 inches between the lamp and the reactor well. A pH electrode which connects to the pH controller is located in the center of the reactor. There are two pumps used in this reactor. One pump, of 1/2 horse power rating, is used to recycle the solution in order to have maximum mixing. Another pump is used for feeding the pollutant solution to the reactor from a reservoir tank. The flow rate of the pollutant solution into the reactor is measure by a rotameter.

Ozone, oxygen or nitrogen introduced through the bottom of the reactor through a four-head sparger of medium porosity. The exhaust gas is vented from the top of the reactor into the laboratory hood. Complete mixing of the solution is achieved by recycling the solution and bubbling nitrogen gas into the reactor. The acid or basic solution is pumped into the reactor from the reservoir by the pH controlling pump to maintain a constant pH value. Hydrogen peroxide and pollutants are fed into the reactor from a port which is at the top of the reactor.

3.1.2 Ozone Generator

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Ozone is produced by a T-816 Ozone Generator which manufactured by the Welsbach Ozone System Corporation, Philadelphia, PA. This generator has a capacity for producing a minimum of 16 grams of pure, dry ozone per hour. It is a corona discharge type and cooled by water. Ozone output flow-rate is adjustable by a ball valve. The power is set at 110 W and 99.6 % pure, dry oxygen was used for ozone generation in this experiment.

3.1.3 Ultraviolet Light Source

The ultraviolet light source lamp was purchased from the Canrad - Hanovia Inc., Newark, NJ. It is a low pressure mercury vapor lamp with an arc length of 25 inches and has a power rate of 5000 watts. The lamp is a clear fused quartz tube with tungsten electrodes at both sides, filled with precisely measured amounts of mercury and inert argon gas. It is encased in two concentric wells made of quartz glass. The inner well, which houses the mercury lamp is connected to a nitrogen gas feed line to avoid an explosion hazard. Nitrogen if fed with a flow rate of under 100 cm3/min. The outer well is used to circulate the cooling water. Cooling water flow rate is kept at about 4 - 8 gallons per minutes. The power supplied to the lamp can be set to 300, 200 or 125 watts/inch levels. Experiments are conducted at the 200 watts/inch power level for the UV lamp. Output wavelength of the lamp is around 254 nm. A detail structure of the UV lamp is in Figure 3.2, Appendix I.

3.1.4 pH Control System

A Cole Parmer Co. pH control system model 5654-12 is used to keep the solution in the reactor at a constant value. This system includes inbuild pH indicator and recorder, adjustable controlling pump, basic solution reservoir, and pH electrode which is installed inside the reactor.

3.1.5 High Performance Liquid Chromatograph (HPLC)

A LDC / Millton Roy Co. made HPLC which includes Spectro Monitor III with variable UV/VIS detector, Constra Metric III & I, and Gradient Master, is used to determine the calibration curves and calculate the concentration for the pollutants.

Analysis of the nitrotoluene and the naphthalene is conducted by using a 25 cm x 4.6 cm Zorbax ODS column,lot no. 7288B, which purchased from Phenomenex Co. with mobile phase gradient from 62 % acetonitrile in water to 100 % acetonitrile in water at 1.0 ml/min, and the flow rate of the mobile phase was 2.4 ml/min. The absorption wave length of the UV/VIS detector is set at 254 nm for these two chemicals. 2,4,6-trichlorophenol was measured by a 25 cm x 4.6 cm C8 column, LOT NO. 23826, with mobile phase 75 % methanol and 1 % acetic acid in water, and the flow rate is 1.0 ml/min. The absorption wave length of the detector is 280 nm.

3.1.6 UV/VIS Spectrophotometer

A Varian DMS 200 UV-Visible spectrophotometer is used to determine the absorbance of the hydrogen peroxide mixture and the ozone solution at a certain wavelength, 260 nm and 352 nm.

3.1.7 Gas Chromatograph with Mass Detector (GC/MS)

The identification of the intermediates are done by the HP 5998 mass spectrometry couple with HP 5890 Gas chromatograph. All the samples were extracted by dichloromethane before inject into the instrument and 1 ul sample is injected into the GC/MS. A 25 m x 0.21 mm crosslink methyl-silicone capillary column was installed in the gas chromatograph.

3.2 Experiments

3.2.1 Reagents and Chemicals

Distilled water is used in all experiments and the following chemicals are used as target pollutants :

1. O-Nitrotoluene (C7H7NO2)



Yellow liquid; m.w. 137.13; b.p. 225° C; solubility 652 mg/l at 30° C in water.

2. Naphthalene (C₁₀H₈)



White solid; m.w.128; b.p.101.7^o C; d 1.162

3. 2,4,6-Trichlorophenol (C₆H₃OCl₃)



needle solid; m.w. 197.46 m.p.197.46° C; b.p. 244.5° C ; solub. 800 mg/l
3.2.2 Sample Collection and Analysis

One sample port, located in the center of the reactor, is used for sample collection. In order to eliminate the collection of the dead volume in the sample port, each sample jar was rinced twice with effluent solution from the reactor just prior to the sample collection. A 20 ml sample is collected and filtered before inject into the HPLC. The sample volume injected into the HPLC is 20 ul which was controlled by a sampling loop. In order to avoid of analysis error, each sample was measured two times.

3.2.3 Standard Solution

The pollutant solution was prepared precisely as in a closed flask as a standard solution. After completely dissolvies in distilled water, using HPLC analyzes to get the area reference concentration. By plotting the area versus concentration figure from the different sets of data, a straight line can be obtained. From the straight line, we know the pollutants concentration for each area which we read from the HPLC integrator. Standard solution stored for more than three days were discarded. Efforts have been made to maintain HPLC conditions as constant as possible. The calibration curves for three pollutants were plotted from Figure 3.3 to Figure 3.5.

3.2.4 Sample Preparation for GC/MS Analysis

The method which we used in the sample preparation for GC/MS analysis is follow the EPA standard method in series 625. The procedure is as follows :

- 1. Transfer 200 ml of the sample into a 500 ml separatory funnel.
- Put 50 ml of the dichloromethane (DCM) into the funnel, then shake it for about 5 minutes. After it settles down, transfer the bottom part solution into a beaker.
 Repeat this procedure three times.

3. By use of a hot water bath to concentrate the collected solution to about 5 ml and ready to be analyzed.

3.2.5 Ozone Concentration Analysis

A sensitive spectrophotometric method was used to determine the ozone concentration in water (25). The procedure was as follows :

- 1. 5 ml of the sample solution are introduced in a test tube containing 5 ml of 2 % neutral potassium, dissolve 13.61 g potassium dihydrogen-phosphate, 14.2 g anhydrous disodium hydrogen phosphate and 20.0 g potassium iodide in 1000 ml distilled water.
- 2. After about 30 minutes the intensity of the absorbance at 352 nm is read using cells of 20 mm light path.
- 3. Calibration curve, Figure 3.6, was plotted from reading of a series of freshly prepared standards. The stock iodine solution 0.01 N (1 ml = 240 μ g of ozone) is dilute to different portions with neutral potassium iodide. Then read the intensity of the absorbance at 352 nm for those standard solutions.

3.2.6 Hydrogen Peroxide Concentration Analysis

The concentration of hydrogen peroxide in the reactor was measured by a spectrophotometric method. (26) The procedure is as follows :

- A 80 ml of a sample solution is transferred into a 100 ml volumetric flask and 1 ml of the sodium hexametaphosphate solution, 10 g/l, 1 ml of the Co⁺⁺ reagent, 4 g/l are added into the flask. The mixture was made up to 100 ml with the saturated bicarbonate solution.
- 2. The absorbance was measured at 260 nm using a 10 mm quartz cell by comparison with a blank-reagent solution.

3. The standard solution ,3 % hydrogen peroxide, was diluted to different portion to make a calibration curve, Figure 3.7.

3.2.7 Calibartion Curve Between Ozone and Hydrogen Peroxide

We used photometric methods for analysis of ozone and hydrogen peroxide. We find that there some relationship exists between the concentration of ozone and the concentration of ozone. The calibration curve was prepared as described below :

- 1. 4 beakers were taken each containing 2 liters of water.
- 2. Ozone was sparged into those beakers at the same time. After 1 minute, shut down the ozone supply in the first beaker and turned off the ozone supply to the others in each addition 1 minute.
- 3. By use hydrogen peroxide and ozone analysis methods to measure those four solutions.
- 4. Plotted ozone concentration versus hydrogen peroxide concentration from the analysis result, in Figure 3.8.

3.2.8 Batch Experiments

Two experimental trials were performed for each pollutant in the batch experiments. The first step towards the batch experiment comprises of pumping the uniform pollutant solution into the reactor. Then recycle was started followed by the introduction of the nitrogen at a flow rate of 10 l/min into the reactor. The UV light source, if needed, was activated. Before switching the UV light source power on, cooling water and nitrogen flow for the UV lamp started at a safe level. Setting the power rate at 125 W/inch first, after 30 seconds power rate was increased 200 W/inch. Timing of the experiment began about 20 seconds later. The N₂ alone and

the N₂/UV processes belong to above mode batch experiment. Another batch mode experiments were the H_2O_2 and $N_2/H_2O_2/UV$ processes.

The pollutants solution were prepared just as previous batch experiment. But before the UV light power on, we add exact amount of the H_2O_2 into the reactor. The amount of the H_2O_2 was added to the reactor in the experiment was the stoichiometric amount needed for oxidation of the compound to carbon dioxide, water or halide ion. For example, the balanced chemical reaction for 2,4,6-trichlorophenol is

 $C_6H_3OCl_3 + 11 H_2O_2 \rightarrow 6 CO_2 + 11 H_2O + 3 HCl$ (2.1)

Thus, the initial concentration of the H_2O_2 , which would be added to the reactor was 11. times of the initial concentration of the 2,4,6-trichlorophenol.

After 1 minute mixing of the H_2O_2 with solution, we began to the following procedure as the N_2 or the N_2/UV process. Sample collection was down as frequently as possible and all the samples were subjected to analysis as soon as possible after collection in order to avoid of any possibility of chemical evaporation.

3.2.9 Semi-Batch Experiments

In the semi-batch reactor, pollutants were added batch-wise initially. The experiment was then conducted with a constant flow of the second reactant, oxygen or ozone. Three experiments were conducted in the semi-batch experiments. There are the O_2/UV , the O_3 alone and the O_3/UV experiments.

In the ozone alone experiment, cooling water and oxygen flow to the ozone generator before the ozone generator power on. Oxygen flow rate was regulated at 9 psig and controlled by a ball valve for a flow rate of 10 l/min. In the O_3/UV experiment, the UV light source power was turned on after introducing the O_3 into the reactor.

3.2.10 CSTR Experiments

The O_3/UV and the H_2O_2/UV experiments were introduced in the CSTR experiments. The pollutant solution was dissolved in a reservoir tank before feeding to the reactor. In the O_3/UV experiment, UV light was turned on after O_3 flow was started. After 5 minutes feeding of the pollutant solution to the reactor was started from the reservoir at a certain flow rate which controlled by a flow-meter. In the H_2O_2/UV process, hydrogen peroxide was dissolved in the reservoir. The quantity of the hydrogen peroxide was also followed the stoichiometric relationship with pollutant as shown in equation 2.1. Then the feed and UV light turn on at the same time. The experiment was terminated when the feed solution was exhausted.



The schematic diagram of the experimental apparatus

Figure 3.1

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Calibration curve of ozone in water

CHAPTER 4 REACTION MECHANISM AND KINETIC MODELS

4.1 Introduction

Use of ozone with UV radiation process or hydrogen peroxide with UV radiation to treat waste water has been demonstrated effectively; however, the detail reaction mechanism is not clear yet. Based on previous research and chemical properties, we designed a series of experiments and propose following reaction mechanism and kinetic models for these processes. Then, a optimization program would be used to calculate the reaction rate constants and give a best fit to the experimental data.

The reaction kinetic models for the each experimental mode were initially developed by Dr. C. .R. Huang in 1983 and revised in 1984, 1988, 1991 (28, 29, 30, 31). In order to distinguish the effects of the different processes and get the reaction rate constants, at least 9 experiments are run for each chemical, i.e. (1) bubbling with nitrogen, (2) nitrogen plus UV radiation, (3) oxygen plus UV radiation, (4) ozone alone, (5) ozone and oxygen plus UV radiation. (6) hydrogen peroxide only, (7) hydrogen peroxide plus UV radiation, (8) CSTR for ozone plus UV radiation and (9) CSTR for hydrogen peroxide plus UV radiation. Three basic kinetic model for the ozone and the hydrogen peroxide under the UV radiation was also proposed.

The reaction kinetic models set up for each experiments are based upon the following assumptions :

(1) The reaction in each of the mechanism was considered as a first order reaction.

(2) Assume complete mixing by both bubbling and pumping circulation.

4.2 H₂O₂ With UV Radiation

The purpose of this experiment is to determine decomposition rate of H_2O_2 with UV radiation. At the same time we can calculate the reaction rate constants which are the reactions between free radicals or free radicals with hydrogen peroxide.

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A two steps reaction mechanism is proposed as follows :

(I) Region I ($0 \le t \le t1$)

$$\begin{array}{l} H_2O_2 \xrightarrow{Kf} 2 \text{ OH} \cdot \\ H_2O_2 + \text{OH} \cdot \xrightarrow{K_{13}} HO_2 \cdot + H_2O \\ H_2O_2 + HO_2 \cdot \xrightarrow{K_{14}} H_2O + O_2 + OH \cdot \end{array}$$

With initial conditions :

At
$$t = 0$$
 $C_{H_2O_2} = C_{H_2O_2 i}$
 $C_{OH*} = 0$
 $C_{HO_2*} = 0$

Here t1 is a value measured after 20 minutes.

The material balance for H_2O_2 , $OH \cdot$ and $HO_2 \cdot$ is as follows :

$$\frac{dC_{H2O2}}{dt} = -K_f C_{H2O2} - K_{13} C_{H2O2} C_{OH} - K_{14} C_{H2O2} C_{HO2}.$$

$$\frac{dC_{OH}}{dt} = 2K_f C_{H2O2} - K_{13} C_{H2O2} C_{OH} + K_{14} C_{H2O2} C_{HO2}.$$

$$\frac{dC_{HO2}}{dt} = K_{13} C_{H2O2} C_{OH} - K_{14} C_{H2O2} C_{HO2}.$$

Those unknown reaction rate constants was calculated by use of the Rosenbrock Hill Climb Optimization Program with the Fourth Order Runge-kutta method to give the best fit to the experimental data.

(II)Region II (t1 < t < t2)

In this region, those free radicals will react each other. Thus, we add two more reactions schemes

OH• + OH•
$$\xrightarrow{K_{15}}$$
 H₂O₂
OH• + HO₂• $\xrightarrow{K_{16}}$ H₂O + O₂
Initial conditions :

At t = t1 CH2O2, COH. and CHO2. can be calculated from the previous region.

The material balance for each species becomes :

$$\frac{dC_{H2O2}}{dt} = -K_f C_{H2O2} - K_{13} C_{H2O2} C_{HO2} - K_{14} C_{H2O2} C_{HO2} + K_{15} C_{OH.}^2$$
(4.1)

$$\frac{dC_{OH}}{dt} = 2K_{f}C_{H_{2}O_{2}} - K_{13}C_{H_{2}O_{2}}C_{HO_{2}} + K_{14}C_{H_{2}O_{2}}C_{HO_{2}} - 2K_{15}C_{OH}^{2} - K_{16}C_{OH}C_{HO_{2}}.$$
(4.2)

$$\frac{dC_{HO2}}{dt} = \kappa_{13} C_{H_2O_2} C_{HO_2} - \kappa_{14} C_{H_2O_2} C_{HO_2} - \kappa_{16} C_{OH} C_{HO_2}.$$
(4.3)

In this region, the unknown constants are K_{15} and K_{16} . We used the same method to find the optimal value.

(III) 0 < t < t2

Finally, we can put these 5 reaction mechanisms together and use K_f , K_{13} , K_{14} , K_{15} , K_{16} obtained before as initial guessed values for regression analysis.

The final reaction mechanisms are as follows :

$$\begin{array}{l} H_2O_2 & \longrightarrow Kf & 2 \text{ OH} \cdot \\ H_2O_2 + \text{ OH} \cdot & \longrightarrow \frac{K_{13}}{\longrightarrow} & HO_2 \cdot + H_2O \\ H_2O_2 + HO_2 \cdot & \longrightarrow \frac{K_{14}}{\longrightarrow} & H_2O + O_2 + \text{ OH} \cdot \\ \text{OH} \cdot + \text{ OH} \cdot & \longrightarrow \frac{K_{15}}{\longrightarrow} & H_2O_2 \\ \text{OH} \cdot + HO_2 \cdot & \longrightarrow \frac{K_{16}}{\longrightarrow} & H_2O + O_2 \end{array}$$

The material balances for each species are as the mechanisms in region II.

4.3 Saturation of Ozone in Water

Ozone was sparged into the water and the mass transfer coefficient which from gas phase to liquid phase can be calculated as follows :

 O_3 (g) $\rightarrow O_3$ (l)

...

The mass balance for ozone is

$$\frac{dC_{O3}}{dt} = K_{LO3}a (C_{O3}s - C_{O3})$$

With initial condition C_{O3} (t = 0) = 0

The above equation can be solved by Laplace Transform method. The concentration of ozone which dissolved in the water can be express as follows :

$$C_{O3} = C_{O3}s [1 - exp(-K_{LO3}a x t)]$$

Here a is the ration of interface area and volume of mixture.

Thus, the mass transfer coefficient can be obtained from the experimental data.

4.4 The Effect of UV Radiation in Water Saturated With Ozone

There are two cases in this model. (1). After ozone is saturated in water, turn off the ozone source and turning on the UV radiation at the same time. (2) After ozone is saturated in water, turn on the UV radiation and keep supply the ozone. For the first case, since there no ozone supply, ozone would be decomposed to two hydroxyl radicals immediately. The two hydroxyl radicals would react together and become hydrogen peroxide. The following reactions were just like the reactions of hydrogen peroxide under the UV radiation.

The whole reaction mechanisms are as follows :

$$03 + H2O \xrightarrow{hv} 2OH. + O2 \qquad (very fast)$$

$$OH. + OH. \xrightarrow{K_{15}} H_2O_2 \qquad (fast)$$

$$H_2O_2 \xrightarrow{Kf} 2 OH \cdot$$

$$H_2O_2 + OH \cdot \xrightarrow{K_{13}} HO_2 \cdot + H_2O$$

$$H_2O_2 + HO_2 \cdot \xrightarrow{K_{14}} H_2O + O_2 + OH \cdot$$

$$OH \cdot + HO_2 \cdot \xrightarrow{K_{16}} H_2O + O_2$$

The material balance for H_2O_2 , OH• and HO_2 • was same as equation 4.1 ,4.2 and 4.3 and the initial conditions are

t = 0
$$C_{H_2O_2} = 0$$
$$COH \cdot = C_{O_3}s$$
$$C_{HO_2} = 0$$

Those reaction rate constants, K_f , K_{13} , K_{14} , K_{15} , K_{16} were calculated in the previous model, hydrogen peroxide with UV radiation. Thus, we were able to predict the hydrogen peroxide concentration in this case.

In the second case, ozone sparged into the solution continuously after turn on UV radiation, most of the saturated ozone be decomposed to hydroxyl radicals and the undecomposed ozone would react with those redicals, hydroxyl radical and hydroxyl peroxide radical. Thus, the total reaction scheme would be sketched as follows :

$$O_{3} + H2O \longrightarrow \frac{h\nu}{2}OH + O_{2}$$

$$O_{3} + OH \longrightarrow \frac{K_{8f}}{2}O_{2} + HO_{2}$$

$$O_{3} + HO_{2} \longrightarrow \frac{K_{12}f}{2}O_{2} + OH$$

$$OH \longrightarrow OH \longrightarrow \frac{K_{15}}{2}H_{2}O_{2}$$

$$H_{2}O_{2} \longrightarrow \frac{Kf}{2}OH$$

$$H_{2}O_{2} + OH \cdot \xrightarrow{K_{13}} HO_{2} \cdot + H_{2}O$$

$$H_{2}O_{2} + HO_{2} \cdot \xrightarrow{K_{14}} H_{2}O + O_{2} + OH \cdot$$

$$OH \cdot + HO_{2} \cdot \xrightarrow{K_{16}} H_{2}O + O_{2}$$

Ozone mass transfer :

$$O_{31} \longrightarrow K_{LO3a} O_{3g}$$

Oxygen mass transfer :

$$O_{21} \xrightarrow{K_{LO2a}} O_{2g}$$

The material balance for each species is as follows :

$$\begin{aligned} \frac{dC_{H2O2}}{dt} &= -K_f C_{H2O2} - K_{13} C_{H2O2} C_{HO2} \cdot -K_{14} C_{H2O2} C_{HO2} \cdot + K_{15} C_{OH}^2 \\ \frac{dCo3}{dt} &= -K_{IO3} I C_{O3} - K_{8f} C_{O3} C_{OH} \cdot - K_{12f} C_{O3} C_{HO2} \cdot + K_{LO3} a (C_{O3} s_{-C_{O3}}) \\ \frac{dC_{OH} \cdot}{dt} &= 2K_f C_{H2O2} - K_{13} C_{H2O2} C_{HO2} \cdot + K_{14} C_{H2O2} C_{HO2} \cdot - 2K_{15} C_{OH}^2 \cdot K_{16} C_{OH} \cdot C_{HO2} \cdot - K_{8f} C_{O3} C_{OH} \cdot + 2K_{IO3} I C_{O3} \\ \frac{dC_{HO2} \cdot}{dt} &= K_{13} C_{H2O2} C_{HO2} \cdot - K_{14} C_{H2O2} C_{HO2} \cdot - K_{16} C_{OH} \cdot C_{HO2} \cdot - K_{12f} C_{O3} C_{HO2} \cdot - K_{16} C_{OH} \cdot C_{HO2} \cdot - K_{12f} C_{O3} - K_{12f}$$

$$\frac{dC_{O2}}{dt} = -K_{IO2I}C_{O2} + K_{LO2}a(C_{O2}s - C_{O2}) + K_{IO2}bC_{O2}*$$
$$\frac{dC_{O2}*}{dt} = K_{IO2I}C_{O2} - K_{IO2b}C_{O2}*$$

Initial conditions :

$$t = 0$$
 $C_{O3}, C_{O2}, C_{H2O2}, C_{O2}^*, C_{OH}, C_{HO2} = 0$

The unknown parameter in the above equations were $K_{IO3}I$, K_{8f} , and K_{12f} which could be decided in this experiment.

4.5 Bubbling with Nitrogen

The purpose of this experiment was to estimate the evaporation effects of the chemicals due to the nitrogen bubbling. We can calculate the mass transfer coefficient between the bulk liquid stream and the liquid film and the Henry's constant for the specific pollutant.

Two film theory was used to produce the following material balance equation in the different phases. It was assumed that the resistance between the gas film and the gas bulk is negligible because a well mixed system was postulated, that is, the concentration of species A in the gas film (Cag') is equal to the concentration in the bulk gas phase (Cag). The mass transfer diagram is in the Figure 4.1. It was further assumed that the concentration of the liquid film at the gas-liquid interface (Cas) satisfies the Henry's Law relationship with Cag', that is,

Cag = Cag' = M*Cas

With the above assumption, the mass balance for reactant A in the liquid phase was

input - out = accumulation

0 - V * K_{LA}a * (C_a - C_as) = V
$$\frac{dCa}{dt}$$
 (4.4)

 $K_{LA}a$ is the mass transfer coefficient between the bulk liquid stream and the liquid film.

The mass balance of reactant A in the gas phase is

0 -
$$(C_{ag}Qg + K_{LA}a * V * (C_{as} - C_{a}) = \frac{dC_{ag}}{dt}$$
 (4.5)

Henry's Law gives :
$$C_{ag} = M * C_{as}$$
 (4.6)

The initial conditions are

$$t = 0 Cag = 0$$
$$Ca = Cas$$

We can solve the simultaneous equation (4.4), (4.5) and (4.6) with the initial conditions and give the relationship between the concentration of species A in the liquid phase and the time .

$$C_{a} = \frac{K_{LAa} + M_{2}}{M_{2} - M_{1}} * e^{(M_{1} * t)} - \frac{K_{LAa} + M_{1}}{M_{2} - M_{1}} * e^{(M_{2} * t)}$$

Where

$$M1 = \frac{-C_1 + (C_1^2 - 4C_2)}{2}$$
$$M2 = \frac{-C_1 - (C_1^2 - 4C_2)}{2}$$
$$C1 = K_{LA}a + \frac{K_{LA}a}{E * M} + \frac{Q_g}{E * V}$$
$$C2 = \frac{K_{LA}a * Q_g}{E * V}$$

The values of $K_{LA}a$ and M could be optimized with the aid of the optimization program, so as to give the best fit to the experimental data.

Figure 4.1

Mass transfer between gas phase and liquid phase

4.6 Reaction with UV Radiation

The purpose of this experiment was to determine the effects of UV radiation on the chemicals. There are two types of experiments, one with nitrogen bubbling and another one without nitrogen bubbling. In order to compare the different reaction effects on the pollutant and to get the complete mixing, we performed this experiment at the condition with nitrogen bubbling.

The reaction mechanisms for these two types are as follows :

(1) With nitrogen

At this condition, evaporation and decomposition occur at the same time.

$$A + hv \xrightarrow{K_{IA}I} A^* \xrightarrow{K_2} A_1$$
$$A_1 + hv \xrightarrow{K_{IA}II} Decompose Products$$

Substrate mass Balance

Al— $\frac{K \iota_A a}{\longrightarrow}$ Ag

The material balance for each species is as follows :

$$\frac{dC_a}{dt} = -K_{IA}IC_a + K_3C_{a*} + k_{LA}a(C_{ag}/M - C_a)$$

$$\frac{dC_{a*}}{dt} = -K_2C_{a*} + K_{IA}IC_{a-}K_3C_{a*}$$

$$\frac{dC_{a1}}{dt} = K_{IA}IC_{a-}K_{IA1}IC_{a1}$$

$$\frac{dC_{ag}}{dt} = -\frac{C_{ag}*Q_g}{V*E} - \frac{k_{LA}a(C_{ag}/M - C_a)}{E}$$

Initial conditions :

$$t = 0$$
 Ca = Cao
Cag, Ca*, Ca1 = 0

(2) Without Nitrogen bubbling

$$A + hv \xrightarrow{K_{IA}I} A^* \xrightarrow{K_2} A1$$
$$A_1 + hv \xrightarrow{K_{IA}II} Decompose$$

The material balance for A, A^* and A1 are as follows :

$$\frac{dC_a}{dt} = -K_{IA}IC_a + K_3C_{a*}$$
$$\frac{dC_{a*}}{dt} = -K_2Ca* + K_{IA}IC_a - K_3C_{a*}$$
$$\frac{dC_{a1}}{dt} = K_{IA}IC_a - K_{IA1}IC_{a1}$$

Initial conditions :

$$t = 0 Ca = Cao$$
$$Ca^*, Ca1 =$$

0

These simultaneous differential equations were solved by the fourth order Runge-Kutta method. The reaction rate constants, $K_{IA}I$, K_2 , K_3 and $K_{IA1}I$ also can be determined by using the Rosenbrock Hill Climb Optimization Algorithm. The $K_{LA}a$ value was calculated from the previous experiment. If the decomposition of pollutants by this process is slow, we may neglect the intermediate A1.

4.7 Reaction with Oxygen and UV Radiation

This experiment was designed to determined the interaction between the pollutant and the activated oxygen (O_2^*) .

The reaction mechanism is as follows :

$$O_2 + hv \xrightarrow{K_{102}I} O_2^*$$

 $A + hv \xrightarrow{K_{1A}I} A^* \xrightarrow{K_2}$ Decompose Product
 $A + O_2^* \xrightarrow{K_6}$ Decompose Products

Oxygen mass transfer $O_{21} \xrightarrow{K_{LO2a}} O_{2g}$ Substrate mass transfer $Al \xrightarrow{K_{LAa}} Ag$

Material balance for each species is as follows :

$$\frac{dC_{a}}{dt} = -K_{IA}IC_{a} + K_{3}C_{a^{*}} - K_{6}C_{a}C_{O2}^{*} + K_{LA}a(C_{ag}/M - C_{a})$$
$$\frac{dC_{a^{*}}}{dt} = -K_{2}C_{a^{*}} + K_{IA}IC_{a} - K_{3}C_{a^{*}}$$

$$\frac{dC_{02}}{dt} = -K_{IO2I}C_{O2} + K_{LO2}a(C_{O2}s - C_{O2}) + K_{IO2}bC_{O2}*$$
$$\frac{dC_{02}*}{dt} = K_{IO2I}C_{O2} - K6C_aC_{O2}* - K_{IO2b}C_{O2}*$$
$$\frac{dC_{ag}}{dt} = -\frac{C_{ag}*Q_g}{V*E} - \frac{K_{LA}a(C_{ag}/M - C_a)}{E}$$

Initial conditions :

$$t = 0$$
 Ca = Cao
CO2 = CO2o = 0.11
Ca*, CO2*,Cag = 0

The rate constants K_{IO2I} , K_{IO2} b and K_6 were determined by this experiment. By comparing this experimental result with the nitrogen bubbling with UV radiation experiment, we found that the O_2^* effect on the decomposition of pollutant was very small. Thus, we did not consider the intermediates which were produced from pollutant by this reaction.

4.8 Reaction with Hydrogen Peroxide

In this experiment we were able to study the effect of hydrogen peroxide effects on the chemicals. The reaction mechanism is very simple.

$$A + H_2O_2 \xrightarrow{KH_2O_2} decompose product$$

The material balance for each species is as follows :

$$\frac{dC_a}{dt} = -\kappa_{H_2O_2}C_aC_{H_2O_2}$$
$$\frac{dCH_2O_2}{dt} = -\kappa_{H_2O_2}C_aC_{H_2O_2}$$

In our experiments, we found that the three pollutants we chose could not be decomposed by the hydrogen peroxide. Thus K_{H2O2} is equal to zero.

4.9 Photolytic Hydrogen Peroxide

Hydrogen peroxide can serve as a source of hydroxyl radical in aqueous solution under UV radiation. In section 4.2, H_2O_2 with UV radiation, we discuss the reaction between hydrogen peroxide and UV radiation which did not involve the reaction of pollutant and the intermediates that produced by the pollutant. In this section, we would consider the competitive reaction between the pollutant and the intermediates. Those reaction rate constants, K_f , K_{13} , K_{14} , K_{15} , K_{16} , was calculated in section 4.2 and used in this model.

The reaction mechanism is as follows :

$$H_{2}O_{2} \xrightarrow{Kf} 2 OH$$

$$H_{2}O_{2} + OH \cdot \xrightarrow{K_{13}} HO_{2} \cdot + H_{2}O$$

$$H_{2}O_{2} + HO2. \xrightarrow{K_{14}} H_{2}O + O_{2} + OH$$

$$OH \cdot + OH \cdot \xrightarrow{K_{15}} H_{2}O_{2}$$

$$OH \cdot + HO_{2} \cdot \xrightarrow{K_{16}} H_{2}O + O_{2}$$

$$O_{2} + hv \xrightarrow{K_{102}I} O_{2} *$$

$$A + hv \xrightarrow{K_{14}I} A^{*} \xrightarrow{K_{2}} Decompose Product$$

$$A + O_{2} * \xrightarrow{K_{6}} Decompose product$$

$$A + OH \cdot \xrightarrow{K_{4}} A1$$

$$A1 + HO_{2} \cdot \xrightarrow{K_{44}} Decompose Product$$

$$A + HO_{2} \cdot \xrightarrow{K_{5}} A2$$

$$A2 + OH \cdot \xrightarrow{K_{55}} Decompose Product$$

The material balance for each species is as follows :

$$\begin{aligned} \frac{dC_a}{dt} &= -\kappa_{IA}IC_a + \kappa_3C_{a^*} - \kappa_6C_aC_{O2}^* - \kappa_4C_aC_{OH} - \kappa_5C_aC_{HO_2}.\\ \frac{dC_{a^*}}{dt} &= -\kappa_2C_{a^*} + \kappa_{IA}IC_{a} - \kappa_3C_{a^*}\\ \frac{dC_{a1}}{dt} &= \kappa_4C_aC_{OH} - \kappa_{44}C_{a1}CHO2.\\ \frac{dC_{a2}}{dt} &= \kappa_5C_aC_{HO_2} - \kappa_{55}C_{a2}C_{HO_2}.\\ \frac{dC_{H2O2}}{dt} &= -\kappa_fC_{H2O_2} - \kappa_{13}C_{H2O_2}C_{HO_2} - \kappa_{14}C_{H2O_2}C_{HO_2}. + \\ & \kappa_{15}C_{OH}^2. \end{aligned}$$

$$2K_{15}C_{OH}^2 - K_{16}C_{OH}C_{HO_2} - K_4C_aC_{OH} - K_{55}C_{a2}C_{OH}$$

$$\frac{dC_{HO2}}{dt} = K_{13} C_{H_2O_2} C_{HO_2} - K_{14} C_{H_2O_2} C_{HO_2} - K_{16} C_{OH} -$$

$$K_5C_aC_{HO_2}$$
. - $K_{44}C_{a1}C_{HO_2}$.

$$\frac{dC_{O2}}{dt} = -K_{IO2I}C_{O2} + K_{LO2}a(C_{O2}s - C_{O2}) + K_{IO2}bC_{O2}*$$
$$\frac{dC_{O2}*}{dt} = K_{IO2I}C_{O2} - K_{6}C_{a}C_{O2}* - K_{IO2b}C_{O2}*$$

With initial conditions :

t = 0 Ca = Cao, Ca1 = 0, Ca2 = 0

$$C_{O2} = C_{O20} = 0.11$$
, $C_{H2O2} = C_{H2O20}$
 C_{OH} , C_{HO2} , Ca*, C_{O2} * = 0

From above simultaneous equations, four unknown reaction rate constants, K_4 , K_{44} , K_5 and K_{55} . should be calculated. In this experiment we have three sets of experimental data for pollutant and its intermediates. The optimized rate constants would give us the best fit to the three experimental data which are the decomposition of pollutant and the formation and the destruction of the intermediates.

4.10 Reaction with Ozone

Ozone is a quite strong oxidant and after getting dissolved in water would produce the hydroxyl radicals and the hydroperoxide radicals, in very small amounts. The reaction mechanism is as follows :

$$0_{3} + H_{2}O \xrightarrow{K7f} 2OH. + O_{2}$$

$$0_{3} + OH. \xrightarrow{K8f} HO_{2}. + O_{2}$$

$$0_{3} + HO_{2}. \xrightarrow{K12f} OH. + 2O_{2}$$

$$0_{1} + OH \xrightarrow{K_{15}} H_{2}O_{2}$$

$$OH \xrightarrow{K_{16}} H_{2}O + O_{2}$$

$$A + O_{3} \xrightarrow{K_{1}} Decompose$$

$$A + OH \xrightarrow{K_{4}} Decompose$$

$$A + HO_{2} \xrightarrow{K_{5}} Decompose$$

Ozone mass transfer

$$O_{31} \xrightarrow{Klo3a} O_{3g}$$

Substrate mass transfer

Al
$$\xrightarrow{K \sqcup A a}$$
 Ag

From the experimental result we found that most of the pollutant was decomposed by the oxidation of ozone and hydroxyl radicals. The concentration of the intermediate, A2, was very small. Thus, in the above reaction mechanism we did

not consider the intermediates which was produced by attact of hydroperoxide radicals on the pollutant.

The material balance for ozone and pollutant are as follows :

$$\begin{aligned} \frac{dCa}{dt} &= -K_1 Ca C_{O3} - K_4 Ca C_{OH} - K_5 Ca C_{HO_2} + K_{LA} a (Cag/M - Ca) \\ \frac{dCo_3}{dt} &= -K_1 C_a C_{O3} - K_{8f} C_{O3} C_{OH} - K_{12f} C_{O3} C_{HO_2} - K_{7f} C_{O3} + K_{LO3} a (C_{O3} s - C_{O3}) \\ \frac{dC_{OH}}{dt} &= 2K_{7f} CO_3 - 2K_{15} C_{OH}^2 - K_{8f} C_{O3} C_{OH} - K_{16} C_{OH} - C_{HO_2} - K_{4} C_a C_{OH} + K_{12f} C_{O3} C_{HO_2}. \end{aligned}$$

$$\frac{dC_{HO2}}{dt} = K_{8f}C_{O3}C_{OH} - K_{16}C_{OH} - K_{HO2} - K_5C_aC_{HO2} - K_{12f}C_{O3}C_{HO2}$$

$$\frac{dCag}{dt} = -\frac{Cag * Qg}{V * E} - \frac{k_{LA}a(Cag / M - Ca)}{E}$$

Initial conditions :

- ---

$$t = 0$$
 Ca = Cao
C_{O3}, C_{OH}., C_{HO2}. = 0

The unknown values are K_1 , K_{7f} , K_{8f} , and K_{12f} which also could be determined by the optimization method.

4.11 Photolytic Ozonation

In this experiment, the combined effect of all the radicals created by the ozone under the UV radiation was determined. The reaction is faster and more effective than the previous experiments. From section 4.4 we know that the concentration of ozone in the liquid phase was very small at this condition. Thus, the predominate decomposition of the pollutant become the hydroxyl radical and the hydroperoxide radical. This could be proved by that the intermediates which produced from the pollutant are same as the intermediates at the hydrogen peroxide under the UV radiation. In this mechanism we still include the ozonation effect, but the contribution is small. Thus we did not consider the intermediate which produced by direct ozonation.

The whole reaction mechanism is as follows :

$$O_{3} + H_{2}O \longrightarrow \frac{K_{103}I}{K_{8f}} O_{2} + 2OH \cdot$$

$$O_{3} + OH \cdot \longrightarrow \frac{K_{8f}}{K_{8f}} O_{2} + HO_{2} \cdot$$

$$O_{3} + HO_{2} \cdot \longrightarrow \frac{K_{12}f}{K_{12}} 2O_{2} + OH \cdot$$

$$OH \cdot + OH \cdot \longrightarrow \frac{K_{15}}{K_{12}} H_{2}O_{2}$$

$$OH \cdot + HO_{2} \cdot \longrightarrow \frac{K_{16}}{K_{12}} H_{2}O + O_{2}$$

$$H_{2}O_{2} \longrightarrow \frac{Kf}{K_{12}} 2 OH \cdot$$

$$H_{2}O_{2} + OH \cdot \longrightarrow \frac{K_{13}}{K_{13}} HO_{2} \cdot + H_{2}O$$

$$H_{2}O_{2} + HO_{2} \longrightarrow \frac{K_{14}}{K_{12}} H_{2}O + O_{2} + OH \cdot$$

$$O_{2} + hv \longrightarrow \frac{K_{102}I}{K_{12}} O_{2}^{*}$$

$$A + hv \longrightarrow \frac{K_{14}I}{K_{12}} A^{*} \longrightarrow \frac{K_{2}}{K_{2}} Decompose Product$$

$$A + O_{2}^{*} \longrightarrow \frac{K_{6}}{K_{4}} Decompose Product$$

$$A + OH \cdot \longrightarrow \frac{K_{44}}{K_{44}} Decompose Product$$

$$A + HO_{2} \cdot \longrightarrow \frac{K_{5}}{K_{5}} A_{2}$$

$$A_{2} + OH \cdot \longrightarrow \frac{K_{55}}{K_{5}} Decompose Product$$

Ozone mass transfer :

 $O_{31} \xrightarrow{KLO3a} O_{3g}$ Oxygen mass transfer : $O_{21} \xrightarrow{KLO2a} O_{2g}$ Substrate mass transfer : $A1 \xrightarrow{KLAa} Ag$

The material balance for each species is as follows :

$$\frac{dC_{HO2}}{dt} = \kappa_{13}C_{H2O2}C_{HO2} - \kappa_{14}C_{H2O2}C_{HO2} - \kappa_{16}C_{OH}C_{HO2}.$$

$$\kappa_{5}C_{a}C_{HO2} - \kappa_{44}C_{a1}C_{HO2} - \kappa_{12f}C_{O3}C_{HO2}.$$

$$\frac{dC_{O2}}{dt} = -\kappa_{IO2I}C_{O2} + \kappa_{LO2}a(C_{O2}s - C_{O2}) + \kappa_{IO2}bC_{O2}*$$

$$\frac{dC_{O2}*}{dt} = \kappa_{IO2I}C_{O2} - \kappa_{6}C_{a}C_{O2}* - \kappa_{IO2b}C_{O2}*$$

$$\frac{dC_{ag}}{dt} = -\frac{C_{ag}*Q_{g}}{V*E} - \frac{\kappa_{LAa}(C_{ag}/M - C_{a})}{E}$$

Initial conditions :

t = 0 Ca = Cao,
$$C_{O2} = C_{O20} = 0.11$$

 C_{O3} , Ca*, C_{O2} *, C_{OH} , C_{HO2} , = 0

The reaction constants, K8f, K12f, KIO3I, were determined in this experiment.

4.12 CSTR Process

The rate constants and the mass transfer coefficients which were calculated from the previous experiments were used in the CSTR process. The reaction mechanism of the CSTR process was the same as the mechanism in the batch reaction. The only difference is the mass balance for the pollutant.

A mass balance can be given as follows :

accumulation of A = input - output - decomposition by reaction.

Two experiments are conducted in the CSTR process, O_3/UV process and H_2O_2/UV process.

4.12.1 For O3/UV Process

The reaction mechanism was same as the O3/UV process in the semi-batch reaction. The material balance was as follows :

$$\begin{split} \frac{dC_a}{dt} &= \frac{Q}{V} x Cao - \frac{Q}{V} x Ca - r_a \\ r_a &= -\kappa_{IA} IC_a + \kappa_3 C_{a^*} - \kappa_6 C_a CO_2^* - \kappa_4 C_a C_{OH} \cdot - \kappa_5 C_a C_{HO_2} \cdot - \kappa_1 C_a C_{O3} \\ \frac{dC_{a^*}}{dt} &= -\kappa_2 C_{a^*} + \kappa_{IA} IC_a \cdot \kappa_3 C_{a^*} \\ \frac{dC_{a1}}{dt} &= \kappa_4 C_a C_{OH} \cdot - \kappa_{44} C_{a1} C_{HO_2} \cdot \\ \frac{dC_{a2}}{dt} &= \kappa_5 C_a C_{HO_2} \cdot - \kappa_{55} C_{a2} C_{OH} \cdot \\ \frac{dC_{a2}}{dt} &= -\kappa_f C_{H_2O_2} - \kappa_{13} C_{H_2O_2} C_{HO_2} \cdot - \kappa_{14} C_{H_2O_2} C_{HO_2} \cdot + \kappa_{15} C_{OH}^2 \cdot \\ \frac{dC_{O3}}{dt} &= -\kappa_1 C_a C_{O3} - \kappa_{103} IC_{O3} - \kappa_8 r_{CO_3} C_{OH} \cdot - \kappa_{12} r_{CO_3} C_{HO_2} \cdot \\ \frac{dC_{OH} \cdot c_{O3}}{dt} &= 2\kappa_f C_{H_2O_2} - \kappa_{13} C_{H_2O_2} C_{HO_2} \cdot + \kappa_{14} C_{H_2O_2} C_{HO_2} \cdot \\ &= 2\kappa_f C_{H_2O_2} - \kappa_{13} C_{H_2O_2} C_{HO_2} \cdot \kappa_{14} C_{A_2O_2} C_{HO_2} \cdot \\ &= \kappa_{15} C_{OH}^2 \cdot \kappa_{16} C_{OH} \cdot C_{HO_2} \cdot - \kappa_{42} C_{OH} \cdot - \kappa_{55} C_{a2} C_{OH} \cdot \\ &= \kappa_{13} C_{H_2O_2} C_{HO_2} \cdot \kappa_{14} C_{H_2O_2} C_{HO_2} \cdot \kappa_{16} C_{OH} \cdot C_{HO_2} \cdot \\ &= \kappa_{13} C_{H_2O_2} C_{HO_2} \cdot \kappa_{14} C_{H_2O_2} C_{HO_2} \cdot \kappa_{16} C_{OH} \cdot C_{HO_2} \cdot \\ &= \kappa_{5} C_a C_{HO_2} \cdot \kappa_{44} C_{a1} C_{HO_2} \cdot \kappa_{12} r_{CO_3} C_{HO_2} \cdot \\ &= \kappa_{13} C_{H_2O_2} C_{HO_2} \cdot \kappa_{12} r_{CO_3} C_{HO_2} \cdot \\ &= \kappa_{13} C_{H_2O_2} C_{HO_2} \cdot \kappa_{14} C_{H_2O_2} C_{HO_2} \cdot \\ &= \kappa_{13} C_{H_2O_2} C_{HO_2} \cdot \kappa_{14} C_{H_2O_2} C_{HO_2} \cdot \\ &= \kappa_{12} C_{HO_2} \cdot \kappa_{14} C_{A_1} C_{A_2O_2} C_{HO_2} \cdot \\ &= \kappa_{12} C_{HO_2} \cdot \kappa_{14} C_{A_1} C_{A_2O_2} C_{HO_2} \cdot \\ &= \kappa_{12} C_{HO_2} \cdot \kappa_{14} C_{A_1} C_{H_2O_2} C_{HO_2} \cdot \\ &= \kappa_{12} C_{HO_2} \cdot \kappa_{14} C_{A_1} C_{H_2O_2} C_{HO_2} \cdot \\ &= \kappa_{12} C_{HO_2} \cdot \kappa_{14} C_{A_1} C_{H_2O_2} \cdot \\ &= \kappa_{12} C_{HO_2} \cdot \kappa_{14} C_{A_1} C_{H_2O_2} \cdot \\ &= \kappa_{12} C_{HO_2} \cdot \kappa_{14} C_{A_1} C_{H_2O_2} \cdot \\ &= \kappa_{12} C_{HO_2} \cdot \kappa_{14} C_{A_1} C_{H_2O_2} \cdot \\ &= \kappa_{12} C_{H_2O_2} \cdot \kappa_{14} C_{H_2O_2} \cdot \\ &= \kappa_{12} C_{H_2O_2} \cdot \\ &= \kappa_{12} C_{H_2O_2} \cdot \\ &= \kappa_{12} C_{H_2O_2} \cdot \\ \\ &= \kappa_{12} C_{H_2O_2} \cdot \\ &= \kappa_{12} C_{H_2O_2} \cdot \\ \\ \\ \\ &= \kappa_{12} C_{H_2O_2} \cdot \\ \\ \\ \\ \\ \\ \\$$

$$\frac{dC_{O2}}{dt} = -K_{IO2I}C_{O2} + K_{LO2}a(C_{O2}s - C_{O2}) + K_{IO2}bC_{O2}*$$
$$\frac{dC_{O2}*}{dt} = K_{IO2I}C_{O2} - K_{6}C_{a}C_{O2}* - K_{IO2b}C_{O2}*$$

Initial conditions :

t = 0 Cao = Cain, Co2 = Co2o = 0.11,

$$C_{H_2O_2}$$
, Ca, Ca*, C_{OH}, C_{HO2}, C_{O3} = 0

The theoretical output concentration of the pollutant was compared to the experimental data to evaluate the proposed reaction kinetic models and the reaction rate constants.

4.12.2 For H₂O₂/UV Process

The reaction mechanism is same as the H_2O_2/UV process in the batch reactor. The material balance for each species becomes as follows :

$$\begin{aligned} \frac{dC_a}{dt} &= \frac{Q}{V} \times C_{a0} - \frac{Q}{V} \times C_a - r_a \\ r_a &= -\kappa_{IA} I C_a + \kappa_3 C_{a^*} - \kappa_6 C_a C O_2^* - \kappa_4 C_a C_{OH} - \kappa_5 C_a C_{HO_2} . \\ \frac{dC_{a^*}}{dt} &= -\kappa_2 C_{a^*} + \kappa_{IA} I C_a - \kappa_3 C_{a^*} \\ \frac{dC_{a1}}{dt} &= \kappa_4 C_a C_{OH} - \kappa_{44} C_{a1} C_{HO_2} . \\ \frac{dC_{a2}}{dt} &= \kappa_5 C_a C_{HO_2} - \kappa_{55} C_{a2} C_{OH} . \\ \frac{dC_{H2O_2}}{dt} &= -\kappa_f C_{H_2O_2} - \kappa_{13} C_{H_2O_2} C_{HO_2} - \kappa_{14} C_{H_2O_2} C_{HO_2} . + \kappa_{15} C_{OH}^2 . \end{aligned}$$

$$\begin{aligned} \frac{dC_{OH}}{dt} &= 2K_{f}C_{H_{2}O_{2}} - K_{13}C_{H_{2}O_{2}}C_{HO_{2}} + K_{14}C_{H_{2}O_{2}}C_{HO_{2}} - 2K_{15}C_{OH}^{2} - K_{16}C_{OH} + K_{14}C_{H_{2}O_{2}}C_{HO_{2}} - K_{15}C_{a2}C_{OH} - K_{55}C_{a2}C_{OH} - K_{55}C_{a2}C_{OH} - K_{55}C_{a2}C_{OH} - K_{15}C_{a2}C_{HO_{2}} - K_{14}C_{H_{2}O_{2}}C_{HO_{2}} - K_{16}C_{OH} + C_{HO_{2}} - K_{16}C_{OH} + C_{HO_{2}} - K_{5}C_{a}C_{HO_{2}} - K_{44}C_{a1}C_{HO_{2}} - K_{16}C_{OH} + C_{HO_{2}} - K_{5}C_{a}C_{HO_{2}} - K_{44}C_{a1}C_{HO_{2}} - K_{16}C_{OH} + C_{HO_{2}} - K_{5}C_{a}C_{HO_{2}} - K_{44}C_{a1}C_{HO_{2}} - K_{16}C_{OH} + K_{10}C_{O2} +$$

Initial conditions :

and the second second

...

t = 0 Cao = Cain,
$$C_{O2} = C_{O20} = 0.11$$
, $C_{H2O20} = C_{H2O2in}$
 C_{H2O2} , Ca, Ca*, C_{OH}, C_{HO2}, = 0

Again the computed output concentration of pollutant was compared to the experimental data to evaluate the accuracy of the reaction rate constants and the proposed kinetic model.

After demonstrating the validness of the proposed reaction mechanisms and the calculated reaction rate constants, we could control the effluent concentration of the pollutant from the reactor by changing the parameters. In the UV/H_2O_2 CSTR process the controlling parameters are the influent flow rate and the quantities of the hydrogen peroxide. In the O₃/UV CSTR process, it is the inlet flow rate.

CHAPTER 5 RESULTS AND DISCUSSIONS

5.1 Experimental Results

In order to study the photo-initiated oxidation of organic pollutants, different experiments had been run including : (1) hydrogen peroxide with UV radiation, (2) ozone with UV radiation, (3) air stripping effects on pollutants, (4) UV radiation effects on pollutants, (5) pollutants under UV radiation with oxygen, (6) pollutants with hydrogen peroxide, (7) pollutants under UV radiation with hydrogen peroxide, (8) pollutants with ozone, (9) pollutants under UV radiation with ozone, (10) CSTR experiments, including UV/O₃ process and UV/H₂O₂ process.

The above experimental results for three pollutants, nitrotoluene, naphthalene and 2,4,6-trichlorophenol are shown in Figure 1 through Figure 31. In these figures, the dot points represent the experimental data while the curves were drawn based on calculations from the reaction mechanism that was proposed in chapter 4. The comparison plots of different decomposition effects on the pollutants are shown in Figure 32 to Figure 49. The different design consideration of CSTR process are shown in Figure 50 to Figure 58. The GC/MS spectra of the pollutants and the intermediates which produced from the decomposition of the pollutants are shown in Figure 59 to Figure 65. The reaction rate constants which were calculated by the Rosenbrock Hillclimb Optimization Algorithm are listed in Table 1. A detailed description is as follows.

5.1.1 Decomposition of Hydrogen Peroxide with UV Radiation.

The experimental data and the theoretical prediction of the decomposition of hydrogen peroxide under UV radiation is shown in Figure 5.1 - 1. The pH value was controlled between 6.8 and 7.2 and the temperature maintained between 25 °C and 27 °C. The values of the optimal reaction rate constants are $K_f = 0.1169E-4 \text{ min}^{-1}$, $K_{13} =$

0.522E+5 1/mole-min, $K_{14} = 0.8461$ E+4 1/mole-min, $K_{15} = 0.5804E+5$ 1/molemin and $K_{16} = 0.4679E+4$ 1/mole-min. The same experiment was run with the different initial hydrogen peroxide concentration, the result is in Figure 5.1 - 2 which shows a good agreement between experimental data and theoretical prediction. From these two figures we can find that the decomposition of hydrogen peroxide under UV radiation is very slow. The calibration curve between ozone concentration and hydrogen peroxide concentration is in Figure 5.2. The calibration curve had the slope 0.3622, intercept 4.476E-3 with the correlation 0.999121. This relationship would be used in the convertion of ozone concentration to hydrogen concentration in the next experiments.

5.1.2 Saturation of Ozone in Water and the Effects of UV Radiation

The saturation curve of ozone dissolved into water is shown at the initial 62 minutes in the Figure 5.3. After the water was saturated with ozone, UV radiation was turned on and the ozone feed to the reactor was turned off. With the UV radiation, the dissolved ozone is decomposed to two hydroxyl radicals instantly and hydrogen peroxide is produced. Since there is no continuous ozone supply, the concentration of ozone should be zero. However, ozone is still detected in the reactor by using the ozone measurement method. It is believed that there is a interference of hydrogen peroxide when we used the ozone measurement method to measure the ozone concentration. Figure 5.2 is the calibration curve for ozone and hydrogen peroxide. By using this calibration curve we could convert the theoretical output of the hydrogen peroxide concentration to the ozone concentration. The result was the solid line in Figure 5.3 after 62 minutes. In other experiment, ozone was continuously sparged into water after UV radiation was turned on, as shown in Figure 5.4. In this experiment, most of the influent ozone would be decomposed to hydroxyl radicals and the left ozone would react with free radicals which were produced from the photo-decomposition of ozone. By this experiment we calculate the rate constants, $K_{IO3}I$, K_{8f} and K_{12f} .in the kinetic model. These valuess are listed in Table 5.1.

The ozone mass transfer coefficient and the saturated concentration of ozone also were also determined by the first part of this experiment. The mass transfer coefficient is 0.1817 1/min and the saturated concentration of ozone is 0.045 mg-mole/l at 25° C.

Table 5.1

	Co3s	K _{LO3} a	K _{IO3} I	K _{8f}	K _{12f}
value	0.048	0.1817	0.9800	0.1562E+5	0.3985E+4

5.1.3 Bubbling with Nitrogen

This experiment was designed to calculate the gas stripping effects on the pollutants. By this experiment we calculate the mass transfer coefficient of pollutant, K_{LAa} , which transferred from liquid phase to gas phase and the Henry constant, M, for the pollutant

The experimental results for three different pollutants are shown in Figure 5.5 to Figure 5.7, nitrotoluene in Figure 5.5, naphthalene in Figure 5.6 and 2,4,6-trichlorophenol in Figure 5.7. The flow rate of the nitrogen influent was 10 l/min. The results showed that almost no concentration change in 2,4,6 - trichlorophenol and

a small concentration changed in nitrotoluene. Thus, $K_{LA}a$ and M are both zero for 2,4,6 - trichlorophenol. The values for the other two pollutants are listed in table 5.2

	K _{LA} a 1/min	М
Nitrotoluene	0.8434E-2	0.465E-2
Naphthalene	0.2814E-1	0.2735E-1

Table 5.2

5.1.4 Reaction with UV Radiation

The experimental results of the effects of UV radiation on the pollutants are shown in Figure 5.8 to Figure 5.10. In this experiment, nitrogen was sparged into the reactor with the flow rate of 10 l/min. Since there were no oxidants present in the aqueous solution, the decomposition of pollutant was caused by the UV proton which broke down the chemical bond of the pollutant. The effects of uv radiation on nitrotoluene is very small, after running for 130 minutes at 10 % treatment efficiency. However, the effects on 2,4,6 - trichlorophenol was significant, with nearly 70 % decomposed in 70 minutes. Figure 5.9 shows the result of naphthalene, which was decomposed 60 % in 2 hours.

The reaction rate constants calculated in this experiment were $K_{IA}I$, $K_{IA}Ib$ and K_2 . These values are listed in Table 5.3
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	C _{ao} ppm	K _{IA} I 1/1-min	K _{IA} Ib 1/i-min	K ₂ 1/min
Nitrotoluene	91.64	0.4646E-2	0.1141	0.2281E-2
Naphthalene	19.86	0.4315E-2	0.9956E+1	0.5561E-1
2,4,6 - TCP	60.5	0.1715E-1	0.5375E-1	0.9961E+1

5.1.5 Reaction with Oxygen and UV Radiation

This experiment was designed to calculate the effects of activated oxygen on the pollutant. Oxygen under the uv radiation would produce activated oxygen which is also a strong oxidant. The experimental results for these three pollutants are shown in Figure 5.11 to Figure 5.13. These results indicated that some of the nitrotoluene would be decomposed by the activated oxygen. But, it is not so important in the decomposition of naphthalene and 2,4,6 - trichlorophenol which are shown in Figure 5.12 and Figure 5.13.

In this experiment the rate constants of $K_{IO_2}I$, $K_{IO_2}b$ and K_6 are determined which are listed in the Table 5.4.

Table 3.4	1
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	Cao ppm	K _{IO2} I	K _{IO2} b	K ₆
Nitrotoluene	110.56	0.7985E-2	0.3459E+2	0.1973E-1
Naphthalene	18.057	0.7985E-2	0.3459E+2	0.559E-1
2,4,6-TCP	70.448	0.7985E-2	0.3459E+2	0.5595E-1

5.1.6 Reaction with Hydrogen Peroxide

Figure 5.14 to Figure 5.16 show that hydrogen peroxide would not decompose the pollutants, although hydrogen peroxide is also an oxidant. At higher temperatures the oxidizing ability of hydrogen peroxide may increase, however, we run this experiment at room temperature. From these results we could neglect the effects of hydrogen peroxide on the pollutants.

5.1.7 Photolytic Hydrogen Peroxide Oxidation

Hydrogen peroxide under the uv radiation can produce two hydroxyl radicals and hydroperoxide is also produced from the consequent chain reaction of hydroxyl radicals with hydrogen peroxide. These two radicals play a major roles in the decomposition of the pollutant and its intermediates.

The experimental result of the decomposition of nitrotoluene on this experiment is shown in Figure 5.7. Two intermediates were found during the decomposition of nitrotoluene. These intermediates were identified by the GC/MS were oxime cyclobutanone and 2-methyl cyclobutanone. The spectrum of these two intermediates were shown in Figure 5.59 and Figure 5. 65. It is also believed that the 2-methyl cyclobutanone was from the oxidizing of nitrotoluene by hydroxyl radicals and the oxime cyclobutanone was from the hydroperoxide radicals attack on nitrotoluene. The reaction schematic diagram is as follows :



Since the decomposition rate of nitrotoluene is not fast by this process, the concentration of intermediates was very small. For the kinetic model, the rate constants that were calculated by this experiment are K_4 , K_5 , K_{44} , K_{55} . These values are listed in Table 5.5.

The experimental result for the naphthalene is shown in Figure 5.18. After running 40 minutes the naphthalene in the aqueous solution was nearly decomposed totally. During the reaction, there was only one intermediate present. Figure 5.61 shows the GC/MS spectrum of this intermediate, 4-methyl 2-pentanone. This intermediate was produced from the destruction of naphthalene by hydroxyl radicals. The concentration of another intermediate which was produced from the attack of hydroperoxide radicals was very low and could not be detected by the GC/MS. The concentration of 4-methyl 2-pentanone was quite high, thus, it became a competitive reaction between naphthalene and 4-methyl 2-pentanone. The reaction schematic diagram is as follows :



The reaction rate constants K_4 , K_5 , K_{44} are listed in Table 5.5.

The experimental result for 2,4,6 - trichlorophenol is shown in Figure 5.19. From this figure we could see that the decomposition rate is slow, compared to the O₃/UV process. During the reaction we could not detect any intermediates. Two reasons may explain this phenomena (1) The decomposition rate of 2,4,6 - trichlorophenol by this process was slow. The intermediate was produced and suddenly destroyed by the oxidants. Thus the concentration of the intermediate was very small.

(2) The effects of UV proton on the pollutant was significant. The result of the UV/N_2 experiment, Figure 5.10, gives us the information that the chemical structure of 2,4,6 - trichlorophenol is easily destroyed by UV proton.

The reaction rate constants K4, K5 are listed in Table 5.5

	Cao ppm	K ₄	K5	K ₄₄	K ₅₅
Nitrotoluene	116.66	0.963E+3	0.25E+4	0.832E+4	0.76E+5
Naphthalene	18.5	0.137E+4	0.5262E+3	0.35E+3	
2,4,6-TCP	59.52	0.8525E+4	0.1915E+5		

Table 5.5

5.1.8 Reaction with ozone alone

The purposes of this experiment is to evaluate the effect of ozone on the pollutant. Ozone dissolved in water would produce hydroxyl radicals and further reaction would produce hydroperoxide radicals, although the quantities of this radical was small. Basically, ozone mass transfer reaction and hydroxyl radical attack predominate the reaction of decomposition of pollutant. The experimental results for these three pollutants are shown in Figure 5.20 to Figure 5.22. In Figure 5.20, the results shows that the attack of ozone to the nitrotoluene is significant. The decomposition rate is a little slower than the decomposition rate of H_2O_2/UV process. It took about 9 minutes to decompose 90 % of naphthalene which shows in Figure 5.21. The

experimental result for 2,4,6 - trichlorophenol is shown in Figure 5.22. Within 25 minutes, 2,4,6 - trichlorophenol was decomposed 90 % of its initial concentration. From these three figures conclude that the effect of ozone is very important.

The reaction rate constants which were calculated by this experiment are K_{7f} , K_{8f} , K_{12f} and K_1 . These values are listed in Table 5.6. For the initial guess values of K_{8f} and K_{12f} , we could use the values which were calculated in section 5.1.2.

5.1.9 Photolytic Ozonation

The reaction involved three strong oxidants : hydroxyl radicals, hydroperoxide radicals and ozone. Since ozone was continuously introduced into the aqueous solution, the decomposition rate of pollutant would be very fast. The experimental result of the reaction for three pollutants is shown in Figure 5.23 to Figure 5.25.

Nitrotoluene was decomposed about 90 % within 1 hour by this process and the result is shown in Figure 5.23. During the decomposition of nitrotoluene two intermediates, 2-methyl,cyclobutanone and oxime,cyclobutanone were detected. These two intermediates are the same intermediates which were produced in the H_2O_2/UV process. However, the concentration of intermediates in the O_3/UV process was much higher than in the H_2O_2/UV process.

Naphthalene was decomposed completely within 5 minutes and the experimental result is shown in Figure 5.24. There was only one intermediate, 4-methyl 2 pentanone, detected by GC/MS. Although naphthalene was decomposed instantly, the concentration of intermediate was quite high and was decomposed slowly. 2,4,6-trichlorophenol was also decomposed by this process quickly. The result is shown in Figure 5.25. It was like decomposition of 2,4,6-trichlorophenol by UV/H_2O_2 process, there was no intermediates detected by GC/MS in this process.

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The reaction rate constant that was calculated from the experimental data is $K_{IO3}I$. The other rate constants which were used in this kinetic model had already been calculated in the previous experiments. The optimal value of the $K_{IO3}I$ is 0.9008 1/min.

	Nitrotoluene	Naphthalene	2,4,6 - TCP
Cao ppm	112.6	16.05	73.03
K _{7f} 1/min	0.1004E+2	0.1008E+2	0.1008E+2
K _{8f} 1/mg-mole min	0.1018E+5	0.1562E+5	0.1562E+5
K _{12f} 1/mg-mole min	0.3803E+4	0.3985E+4	0.3985E+4
K ₁ 1/mg-mole.min	0.8787E-2	0.6969E+1	0.3097E+3

Table 5.6

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CSTR Process

The purpose of the CSTR experiments is to test the validity of the proposed kinetic models and the calculated rate constants. The CSTR processes includes H_2O_2/UV process and O_3/UV process were run for three pollutants.

5.1.10 Photolytic Hydrogen Peroxide Oxidation Process

The experimental results for these three pollutants are shown in Figure 5.26 to Figure 5.28. The flow rate of the influent was controlled at a certain value. The pH value was also controlled between 6.8 - 7.2. Since the reaction rate constants which are required in the kinetic model of CSTR process had already been calculated in the

batch or semi-batch experiments, a theoretical output of the decomposition of the pollutant by this process can be plotted. The comparison between the theoretical prediction and the experimental result for nitrotoluene is shown in Figure 5.26. From this figure we can see that the deviation of theoretical prediction is very small, especially at the steady state. The comparison plot for naphthalene is shown in Figure 5.27. The result shows that the prediction was also quite match to the experimental data, except at the first 10 minutes of experiment. The comparison plot for 2,4,6 - trichlorophenol is in Figure 5.28. The theoretical prediction is a little smaller than the experimental data, however it is still in the permissible range, 3% deviation from the experimental result. There is a common phenomena in these figures : we had a larger prediction error at the beginning of the experiment. This is because of the UV lamp did not warm enough at the beginning of the experiment. From these comparison plots, it proves that the kinetic model of decomposition of pollutants by H_2O_2/UV process and the rate constants we calculated can be practical used in the waste water treatment.

The operation conditions of this experiment for three chemicals are listed in the Table 5.7.

Table 5.7

	nitrotoluene	nephthalene	2,4,6 TCP	
Cao ppm	107.6	14.07	60.594	
Flow rate GPM	0.4	1.2	0.7	
C _{H2O20} mg-mole/l	57.19	5.72	3.43	

5.1.11 Photolytic Ozonation Process

The experimental results and the theoretical prediction of this process for the three chemicals are shown in Figure 5.29 to Figure 5.31. From these figures we found that the prediction values are higher than the experimental data at the beginning of experiment which is opposite to the CSTR H_2O_2/UV process. This is because of the fact ozone can suddenly be decomposed and produce free radicals even at the lower UV radiation. The theoretical prediction of nitrotoluene output fits the experimental data well which shows in Figure 5.29.

The theoretical prediction of output concentration of naphthalene which shows in Figure 5.30 is higher than the experimental data. This difference is from the high flow rate of the effluent. Because the feeding pump we used was small, it caused the fluctuation of influent at the higher feeding flow rate. This phenomena also happened in the experiment for 2,4,6 - trichlorophenol. Although there is a small deviation in the theoretical prediction for naphthalene and 2,4,6-trichlorophenol, it believed that the rate constants still can be used in the design purpose.

The operation conditions are listed in the Table 5.8

Table 5.8

	Nitrotoluene	Naphthalene	2,4,6 - TCP
Cao (ppm)	107.55	18.31	51.37
Flow rate (GPM)	0.7	2.0	1.6

5.2 Discussions

5.2.1 Analysis of the Decomposition Effects

By the comparison of the decomposition curves of pollutants in the different experiments, we can know the individual effect on the decomposition of pollutants. The comparison analysis is as follows :

(1) Effect of UV radiation : UV/N_2 versus N_2 .

- (2) Effect of activated oxygen : UV/O_2 versus UV/N_2 .
- (3) Effect of ozone : O_3 versus N_2 .
- (4) Effect of photolytic ozonation : UV/O_3 versus UV/N_2 and O_3 .
- (5) Effect of photolytic hydrogen peroxide : UV/H_2O_2 versus UV/N_2 .

(1) Effect of UV Radiation

The effect of UV radiation on nitrotoluene and naphthalene is very small. In Figure 5.33 shows that about 10% of nitrotoluene is decomposed by UV radiation after 2 hours reaction. It is about 25 % of naphthalene decomposed by UV protons within 2 hours which shows in Figure 5.34. However, the effect on the 2,4,6 - trichlorophenol is significant. From Figure 5.35 we can see that there is about 70% of 2,4,6 - trichlorophenol decomposed by UV radiation within 70 minutes. Since it is so easy to be destroyed by UV proton, this may be able to explain the phenomena that there is no intermediates found by the GC/MS analysis in the O₃/UV and H₂O₂/UV process.

(2) Effect of Activated Oxygen

Oxygen under UV radiation would produce activated oxygen which is also a strong oxidant. However, from Figure 5.35 to Figure 5.37 we could see that the effect of activated oxygen on the decomposition of these three pollutants are very small. There

is even no contribution to the decomposition of naphthalene. Thus we may eliminate the decomposition reaction between the pollutant and the activated oxygen.

(3) Effect of Ozone

The ability of ozone decomposition of these three chemicals is strong. From Figure 5.38 we can see that 90 % of nitrotoluene is decomposed by the ozone oxidation within 90 minutes. Naphthalene is totally decomposed within 10 minutes which shows in the Figure 5.39 and 95 % of 2,4,6 - trichlorophenol is decomposed within 25 minuteswhich shows in the Figure 5.40. When the pH value is at neutral, ozone mass transfer reaction and hydroxyl radicals predominate the oxidation of pollutants. Thus, most of the pollutants are decomposed by these two oxidants. Also this can be identified by the output of computer calculation which shows that the contribution of decomposition of pollutants by these two oxidants is about 95 %. Following conclusions are made from the experimental result and the kinetic model.

- 1. The mass transfer of ozone from gas phase to liquid phase performs a very important role in ozonation, specially for the pollutants like naphthalene which is easily decomposed by ozonation.
- The saturated concentration of ozone is increased with the decreasing of temperature. Thus, by decreasing the temperature we could improve the ozonation ability.
- 3. The quantity of hydroperoxide radicals which produced from the decomposition of dissolved ozone is small.

(4). Photolytic Ozonation

A comparison of ozonation and photolytic ozonation, from Figure 5.41 to Figure 5.43, show that there is an enhancement in the decomposition of pollutant by UV

radiation with ozone process. Photolytic ozonation reaction basically involved three oxidants hydroxyl radical, hydroperoxide radical and ozone. Although the concentration of ozone in this process is small, we still should not neglect its strong oxidation ability. From the comparison figures and the calculation of kinetic reaction the following conclusions are proposed :

- 1. The role of hydroperoxide radical in this process was very important. Because hydroxyl radicals would continuously react with dissolved ozone to produce hydroperoxide radicals.
- 2. It will produce less intermediates in this process for those chemicals which is easily decomposed by uv radiation.
- 3. Most of the decomposed products were acid chemicals, because the pH value of the solution during the reaction was going down very fast.

(5). Photolytic Hydrogen Peroxide

In the photolytic hydrogen peroxide, there are only hydroxyl radicals and hydroperoxide radicals present in this process. These radicals also existed in the photolytic ozonation process, however its ability of decomposition of pollutant is much higher than the photolytic hydrogen peroxide process, The comparison result for three pollutants shows in Figure 5.44 to Figure 5.46. There are four reasons which can explain this result

- 1 In photolytic hydrogen peroxide process, there is not ozone able to improve the decomposition of pollutant.
- 2 The decomposition of hydrogen peroxide under UV radiation to produce hydroxyl radicals is slow, but the dissolved ozone is very easily decomposed to hydroxyl radicals.

- 3. The commercial product of hydrogen peroxide was added some inhibitor in it. It would protect hydrogen peroxide to be decomposed by UV radiation.
- 4. Photolytic hydrogen peroxide is a acid catalyst reaction. That means we could increase the decomposition of pollutants by reduce the pH value in this process.

5.2.2 Comparison of the Experiments

The comparison of all experimental results for the three pollutants are shown in Figure 5.47 to Figure 5.4. From these figures we could see the sequence of decomposition rate of pollutants by the different processes as follow

For nitrotoluene : $UV/O_3 > O_3 > H_2O_2/UV > UV/O_2 > UV/N_2 > N_2$ For naphthalene : $UV/O_3 > O_3 > H_2O_2/UV > UV/O_2$, $UV/N_2 > N_2$ For 2.4.6-TCP : UV/O_3 , $O_3 > H_2O_2/UV > UV/O_2 > UV/N_2 > N_2$

5.2.3 CSTR Design Consideration.

Since we had already known the rate constants in the proposed kinetic model, by changing the operation conditions we could achieve the desired effluent concentration of pollutants from the CSTR process.

A CSTR Photolytic Hydrogen Peroxide Process

Two operation conditions could change the outlet concentration of pollutants from the CSTR process, inlet flow rate of solution from the reservoir and the quantities of hydrogen peroxide added into the reservoir. The computation results of the different inlet flow rate of pollutants from reservoir are shown in Figure 5.50 to Figure 5.52. The following conclusions can be obtained from these figures :

1. The decomposition of nitrotoluene and 2,4,6 - trichlorophenol by this process are not very fast, so we should operate at a low inlet flow rate.

2. The decomposition of pollutants is very sensitive to the inlet flow rate, specially for the low inlet flow rate.

The computation results of changing the amount of hydrogen peroxide added into the reservoir at a constant inlet flow rate are shown in Figure 5.53 to Figure 5.55. From these figures we have the following conclusion

- 1. The decomposition rate of pollutants is not proportion to the amount of hydrogen added.
- 2. The decomposition of nitrotoluene and 2,4,6-trichlorophenol is not seneitive to the change of the quantity of hydrogen peroxide added into the reservoir. However the change is significant for naphthalene.

B CSTR Photolytic Ozonztion Process

In this process we can change the inlet flow rate of solution from the reservoir to achieve the desired output concentration of pollutant from reactor. The computation results for the three pollutants are shown in Figure 5.56 to Figure 5.58. The following conclusions can be obtained from these three figures

- 1 Nitrotoluene is very seneitive to the change of inlet flow rate.
- 2. The effect of changing inlet flow rate of naphthalene is not significant. For 2,4,6,-trichlorophenol, the effect is important at low inlet flow rate.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

From the experimental results and the proposed kinetic models the conclusions are as follows:

- 1. Advance oxidation processes, ozonation, photolytic ozonation and photolytic hydrogen peroxide have been shown to be effective treatment methods for the three pollutants, nitrotoluene, naphthalene and 2,4,6-trichlorophenol.
- 2. The decomposition of hydrogen peroxide to produce hydroxyl radicals under UV radiation is slow. However, the dissolved ozone is instantly decomposed totally to hydroxyl radicals.
- 3. Air stripping effect on the three pollutants is very small.
- 4. 2,4,6 trichlorophenol can be destructed by UV radiation easily. This phenomena maybe because of the fact that there is no intermediate found in the advance photolytic oxidation processes. The effect of UV radiation on nitrotoluene is insignificant and it has a medium effect on naphthalene.
- 5. The effects of activated oxygen is negligible on the three pollutants .
- 6. Mass transfer of ozone from gas phase to liquid phase is the key factor in the ozonation process.
- 7. The intermediates produced from the photolytic ozonation and the photolytic hydrogen peroxide are same. Oxime cyclobutanone and 2-methyl cyclobutanone are the intermediates which have been identified from the photolytic oxidation of nitrotoluene. For naphthalene, there is only one intermediate, 4-methyl 2-pentanone, whereas no intermediates were detected for 2,4,6,- trichlorophenol during photolytic oxidation treatments.

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- 8. The production and decomposition of intermediates should be considered in the kinetic model, as there is a competitive reaction between the intermediates and the pollutants.
- 9. The free radicals, hydroxyl radical and hydroperoxide radical, have important contributions to the decomposition of pollutants in the photolytic oxidation processes.
- 10. The proposed kinetic models, in chapter 4, and the calculated rate constants have been used correctly in the CSTR processes and also can also be used for the practical design purpose.

6.2 Recommendations

In order to have a still better understanding of the photolytic oxidation processes, the following are the recommendations for the further study.

- 1. The intensity of UV radiation should be considered in the photolytic oxidation processes.
- 2. It is important to keep the solution at a constant pH value and as well as study the system at different pH values.
- 3. Hydrogen peroxide concentration should be observed during the photolytic hydrogen peroxide process.
- 4.Ozone concentration should be measured during ozonation process and photolytic ozonation.
- 5. The effects of temperature on the ozone mass transfer from gas phase to liquid phase should be studied.
- 6. A more basic study on the production and decomposition of intermediates should be investigated.

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facing 73



facing 74





decomposition of O3 under UV radiation













by UV radiation



facing 83

















Figure 5.17 Decomposition of nitrotoluene and intermediates by photolytic H2O2






by ozone alone



Figure 5.21 Decomposition of naphthalene by ozone alone













































































fIGURE 5.53 CSTR photolytic H2O2 Different H2O2 conc. for nitrotoluene


Different H2O2 conc. for naphthalene





Different inlet flow rate of nitrotoluen



Different inlet flow rate of naphthalene Figure 5.57 CSTR photolytic ozonation





Figure 5.59

GC/MS spectra of nitrotoluene and intermediates in photolytic ozonation process



GC/MS spectra of nitrotoluene and intermediates in photolytic hydrogen peroxide process



GC/MS spectra of naphthalene and intermediate in photolytic ozonation process



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GC/MS spectra of naphthalene and intermediate in photolytic hydrogen peroxide process



GC/MS spectrum of 2,4,6 - trichlorophenol in photolytic ozonation process



GC/MS spectrum of 2,4,6 - trichlorophenol in photolytic hydrogen peroxide process

