ABSTRACT

Title of Thesis: The Kinetics and Mechanism of Photo-Oxidation of

Acrylonitrile, Acetonitrile with Hydrogen Peroxide

and Ozone in Wastewater

Name: Jung-Yuan Yeh

Master of Science in Environmental Science.

Thesis directed by: Dr. C.R. Huang

The study presents three types of Advanced Oxidation Processes , Ozone with UV, Ozone with Hydrogen Peroxide in the presence of UV, Various Hydrogen peroxide dosages and PH levels in the presence of UV.

A reaction kinetic model was proposed. The reaction rate constants and mass transfer coefficients are determined by a series of experiments and the use of the Rosenbrock Hillclimb Optimization Algorithm in conjuction with the Fourth - Order Runge - Kutta method on a digital computer.

Experimental results indicated that the Hydrogen peroxide with UV at low PH level has been proven more effective for the treatment of acrylonitrile, acetoni- trile - containing wastewater, and Ozone with Hydrogen Peroxide in the presence of UV light has a significant accelerating effect on the rate of oxidation of acry- lonitrile, acetonitrile to enhance Ozone with UV process.

The Kinetics and Mechanism of Photo-Oxidation of Acrylonitrile, and Acetonitrile with Hydrogen Peroxide and Ozone in Wastewater

by

Jung-Yuan Yeh

Thesis submitted to the faculty of the graduate school of the New Jersey Institute of Technology in partial fullfillment of the requirements for the degree of Master of Science in Environmental Science.

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APPROVAL OF THESIS

Title of Thesis :   The Kinetics and Mechanism of Photo-Oxidation of
Acrylonitrile, Acetonitrile with Hydrogen Peroxide
Ozone in Wastewater.

Name of Candidate :   Jung-Yuan Yeh
Master of Science in Environmental Science

Thesis and Abstract approved by :

_____   7/18/90

Dr. C.R. Huang   Date
Professor of Chemical Engineering
Department of Chemical Engineering,
Chemistry & Environmental Science

_____   7/23/90

Dr. R. Trattner   Date
Professor of Environmental Science & Chemistry
Department of Chemical Engineering,
Chemistry & Environmental Science

_____   8/6/90

Dr. Su-Ling Cheng   Date
Professor of Civil and Environmental Engineering
Department of Civil and Environmental Engineering

VITA

Name : Jung-Yuan Yeh

Present address :

Degree & Date : Master of Science in Environmental Science
1991

Date of Birth :

Place of Birth :

Secondary education : Chu-Ee high school

Collegiate Institute	Date	Degree	Date Graduated
Chinese Culture University	1980-1984	B.S Ch.E	June, 1984
New Jersey Institute of Technology	1987-1991	M.S En.Sc	Jan, 1991

Major : Environmental Science

Position Held :

1988-1990 :   Research Assistant in NJIT,   NJ

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Contents

List of Figures

List of Tables

Chapter 1

Introduction

The removal of low levels of hazardous organic compounds from water can be a difficult and expensive task. Conventional treatment methods such as *packed bed aeration* and *granular activated carbon adsorption* can effectively remove some compounds but not others. Aeration is only useful for highly volatil pollutants and is not practical for small scale use such as by home owners with polluted wells. Carbon adsorption has the disadvantage that the carbon must be replaced or regenerated when its adsorptive capacity is reached.

An alternative to aeration and adsorption is the oxidation of organic pollutants in water by the combination of ultraviolet light *(UV)* and a chemical oxidant. *UV* light accelerates the rate of removal of a pollutant by activating the oxidant and in some cases by rendering the pollutant more susceptible to oxidation.

A process in which *UV light-catalyzed ozone* acts as the oxidant has received con-

siderable research attention. the process has been proven effective for the oxidation of numerous organic compounds in water.

While *Ozone/uv* treatment is undoubtedly effective on a wide range of compounds, it has a number of disadvanges. Ozone is an unstable gas and must be generated onsite and used immediately. An ozone contacting device must be provided which can achieve adequate mass transfer of ozone into the liquid phase. Ozone generators and contactors are probably too expensive for small industrial or domestic water treatment systems.

An oxidant which may be as effective as ozone or more effective than ozone for some compound but is better suited for use in small treatment system is *Hydrogen Peroxide.* Since hydrogen peroxide is a relatively stable liquide, it may be stored for later use. There is no problem of mass transfer between phases so elaborate contacting devices are unnecessary.

This study presents a mechanism and comparison of the destruction efficency of *Acrylonitrile , Acetonitrile* by *Ultraviolet Catalyzed Oxidation* using *Ozone, Hydogen Peroxide and Ozone plus Hydrogen Peroxide as the oxidizing agent.* Experimental results indicated that the Hydrogen Peroxide/UV process has been proven more effective for the treatment of acrylonitile, acetonitrile-containing wastewaters.

Chapter 2

Previous studies

2.1 Application of Ozone

Ozone is commonly used throughout Europe to disinfect and improve the quality of drinking water. The first commercial plant for this application began operation in 1906 in Nice, France. In 1980, There were nearly 1000 water treatment facilities using Ozone, with the largest installation being the Choisy Le Roi water treatment plant in Paris.

Ozone is a powerful oxidant and disinfectant, second only to elemental fluorine among the commercially available oxidants used in water and wastewater treatment plants. As such, it has the ability to oxidize a great number of organic and inorganic materials. Its natural applications include the purification and disinfection of process water, and treatment of industrial and municipal wastes.

2.2 Mechanism of Ozone Decomposition in Water

Ozone decomposition reaction has been the subject of numerous kinetic studies since 1913 (Rothmund and Burgstaller, 1913)(1). A number of different, sometimes contradictory, kinetic expressions for the reaction rate were derived both theoretically and experimentally. The radical-chain nature of the ozone decomposition is probably universally recognized by now. The effecs of radical scavengers, including certain buffers(Staehelin and Hoigne,1982)(2), as well as direct observations of radical species in the system(Forni et al. 1982)(3) have been reported in the past. Several kinetic schemes based on radical reactins were proposed, starting with the pioneering work of Weiss(1935)(4).

The first radical-chain reaction sequence suggested by Weiss(1935)(4), includes the ozone attack on the hydroxide ion as the initiation step, two chain propagation reactions involving $OH \cdot$ and HO_2^- radicals with ozone, and recombination reactions between the two radicals. Of couse, either the rates of elementary processes or relative thermodynamic stability of the radicals involved was practically not known at the time. Virtually the same scheme, supplemented by a second initiation reaction between ozone and water, was suggested by Sotelo et al (1987)(5) to explain an apparent independence of the rate on PH in the acidic region.

Sotelo et al taking into account their results and the reaction mechanism proposed by Weiss(1935) (4) proposed the following reaction mechanism for the ozone decomposition in an aqueous solution:

$$O_3 + H_2O \longrightarrow 2HO^{\cdot} + O_2$$

$$O_3 + OH^- \longrightarrow {}^{\cdot}O_2^- + HO_2^{\cdot}$$

$$O_3 + HO^{\cdot} \longrightarrow O_2 + HO_2^{\cdot}$$

$$O_3 + HO_2^{\cdot} \longrightarrow 2O_2 + HO^{\cdot}$$

$$2HO_2^{\cdot} \longrightarrow O_2 + H_2O2$$
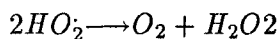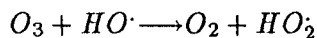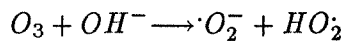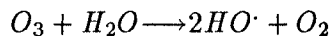
All of above mentioned investigators generally agreed that the decomposition of ozone in an aqueous solution can produce hydroxyl radical, hydroperoxyl radical and be catalyzed by these radicals.

2.3 Photochemistry

2.3.1 Ultraviolet Light

Ultraviolet light is electromagnetic radiation having wavelengths shorter than visible light but longer than *X-ray* radiation. The range of practical interest, however, covers the wavelengths between 180 nm(nanometers) and 380 nm. Visible violet light is about 400 nm. UV or any other light can be considered a stream of photons, indivisible packets of electromagnetic energy. The energy carried by a photon varies directly with its frequency and thus inversely with wavelength:

$E = h\nu = hc/\lambda$ where E is energy, h is Plank's constant, c is the speed of light, ν is frequency and λ is wavelength. If we consider a gram-mol(gmol) of photons(called

Table 2.1: Examples of Photochemical Reactions and their Effects

Reaction	Effective Wavelength, nm	Result
$H_2O + h\nu \longrightarrow H\cdot + HO\cdot$	184.9	Water broken into free radicals
$H_2O_2 + h\nu \longrightarrow 2HO\cdot$	253.7	Hydrogen peroxide broken into hydroxyl radicals
$O_2 + h\nu \longrightarrow O_3$	253.7	Oxygen molecules converted to ozone
$RH + h\nu \longrightarrow H\cdot + R\cdot$	184.9	Organic broken into free radicals
$NO + h\nu \longrightarrow N_2 + O_2$	184.9	Nitric oxide decomposed (smog avoided)
$NO_2 + h\nu \longrightarrow NO + O$	313.0	Nitric oxide formed
$NH_3 + h\nu \longrightarrow NH_2^- + H\cdot$	184.9	Ammonia broken into free radicals

an einstein), and convert energy to units of kcal, the energy associated with a given

wavelength(nm) is:

$E = 28,591/\lambda kcal/gmol$ The basic law of photochemistry is that only light that is

absorbed will cause a chemical or physical change. In fact, atoms and molecules absorb

only those wavelengths that provide just the right amount of energy to change their

state. In the case of microwaves, for example, this state change is a change in internal

spin. But UV light typically causes a transition of electrons from one orbital to another-

a much more energetic quantum step. If the electron belongs to a chemical bond, the

bond may be broken by this transition.

2.3.2 Examples of Photochemical Reactions and their Effects

2.3.3 UV light plus an oxidant

Many engineering applications of ultravioletlight involve the use of an oxidant such as ozone or hydrogen peroxide. When UV light splits the molecules of an oxidant, *the free radicals* that form are yet more powerful oxidizers. Compared with systems that use oxidant alone, UV plus oxidant systems are faster and capable of oxidizing more types of chemicals. In fact, it is possible to sterilize a stream and reduce its total organic carbon(TOC) to zero by using UV with an oxidant.

2.4 Advanced Oxidation

Oxidation processes offer the option, at least in principle, of completely destroying organic contaminants. Of the oxidants currently available, ozone is attracting the most attention because of its high thermodynamic oxidation potential(2.07 V) and the apparent lack of hazardous by-products. Neither ozone nor any other oxidant. However, has proved itself as a BAT process for removing synthetic organic compounds from wastewater. To overcome this deficiency and to enhance ozone's effectivness for oxidation of organics, modifications of traditional ozonation have been investigated in bench-scale laboratory tests.

Each of the processes studied, referred to as advanced oxidation processes, involves the generation of the hydroxyl radical($OH\cdot$), a very active internediate that generally has far greater oxidizing power than ozone. Rate constants for reaction of $OH\cdot$ with organic species are commoly in the range $10^9 - 10^{10} M^{-1} S^{-1}$ *(7)*. This work deals with

$O_3/UV, O_3/H_2O_2/UV, H_2O_2$-UV system.

2.4.1 Photolytic of Ozonation

Photolytic ozonation was developed in the early 1970s for the treatment of cyanide-containing wastes. It has been shown by several investigators *(8,9)* to be more effective for the destruction of some organic compounds than ozonation alone and has significant pontential as a water treatment process for the destruction of organic compounds. Many authors have proposed *(10-13)* that hydroxyl or other free radical are responsible for the ability of photolytic ozonation to destroy compounds which are refractory even to ozonation, but these hypotheses have not been supported directly by experimental data. Indeed, Leitus et al.(14) have given arguments against hydroxyl radical involvement and found photolytic ozonation to be only slightly more effective than ozonation alone in some cases.

The UV radiation is believed to play a dual role in the UV/Ozone treatment system : both as a reactant and as a catalyst *(5)*. As a reactant the UV radiation dissociates the C-CL bond *(15)*, and as a catalyst the UV radiation accelerates the destruction of organic compounds by O_3 *(16)*. The UV radiation also may activate the organic compound, making it more amenable to reaction with hydroxyl radicals.

Until recently, the enhanced effectiveness of O_3 and/or H_2O_2 to destroy organic compounds when used with UV radiation was believed to be due to hydroxyl or other free radicals, but the mechanism for this was not supported by laboratory data. It was suggested that the UV/O_3 treatment process produced the hydroxyl radical directly
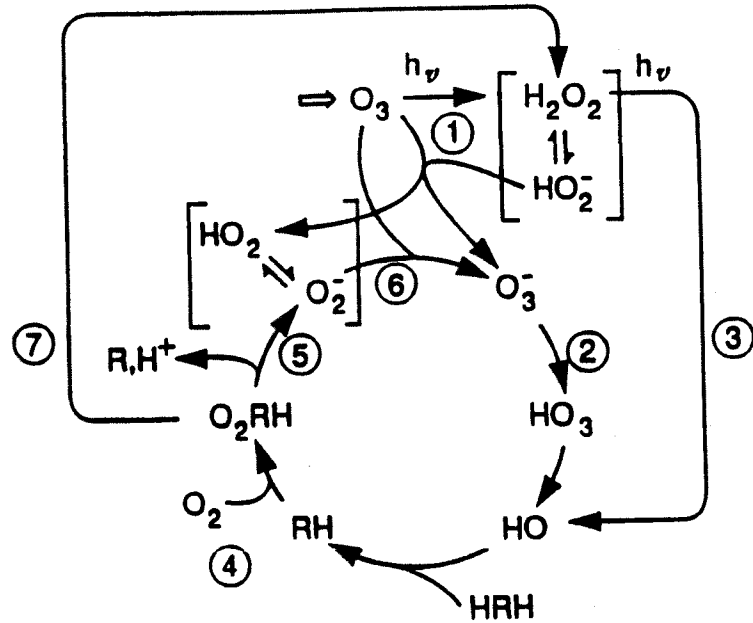
Figure 2.1: Reaction Cycles in Photolytic Ozonation

(17) or produced H_2O_2 *(18)*.

1. Prengle presented the overall reaction mechanisms of UV/O_3 treatment process produced the hydroxyl radical directly.

$$O_3 \longrightarrow O_2^* + O^{\cdot}$$

$$O^{\cdot} + H_2O \longrightarrow 2OH^{\cdot}$$

$$O_3 + OH^{\cdot} \longrightarrow HO_2^{\cdot} + O_2$$
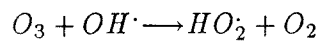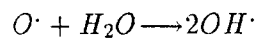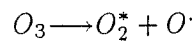
2. Gary R. Peyton and Willian H.Glaze proposed the mechanisms for the UV/O_3 process produced H_2O_2 shown in Fig. 1 .

Table 2.2: Principal reactions in the ozone-hydrogen peroxide process

Reaction	Constant
$H_2O_2 \longrightarrow HO_2^- + H^+$	$K_{per} = 1.6 \times 10^{-12}M$
$HO_2^- + O_3 \longrightarrow O_3^- + H_2O$	$K_1 = 2.8 \times 10^6 M^{-1}s^{-1}$
$HO_2 \longrightarrow H^+ + O_2^-$	$K_{HO2} = 1.6 \times 10^{-5}M$
$O_2^- + O_3 \longrightarrow HO_3$	$K_2 = 1.6 \times 10^9 M^{-1}s^{-1}$
$O_3^- + H^+ \longrightarrow HO_3$	$K_3 = 5.2 \times 10^{10}M^{-1}s^{-1}$
$HO_3 \longrightarrow HO \cdot + O_2$	$K_4 = 1.1 \times 10^5 s^{-1}$
$OH^- + O_3 \longrightarrow O_2^- + HO_2^{\cdot}$	$K_6 = 70M^{-1}s^{-1}$
$OH \cdot + HO_2^- \longrightarrow OH^- + HO_2^{\cdot}$	$K_7 = 7.5 \times 10^9 M^{-1}s^{-1}$
$OH \cdot + H_2O_2 \longrightarrow H_2O + HO_2^{\cdot}$	$K_8 = 2.7 \times 10^7$

2.4.2 Ozone plus H_2O_2 in the presence of UV

With an oxidation treatment, the only way to obtain high removal of ozone refractory compounds is to generate very highly reactive but poorly selective radical species like the hydroxyl radical (Hoigne, 1979). On means to produce those radicals in the aqueous phase is to combine two ozidants (Prengle, 1977; Nakayama, 1979; Hango, 1981).

According to the works of Hoigne et al (19-21) and Hart et al(25,26). Glaze and Kang proposed the following mechanism for the $Ozone/H_2O_2$ shown in Table 2.2 .

Glaze and Kang concluded that hydrogen peroxide accelerates the oxidation of TCE and PCE by ozone. At peroxide-to-ozone dosage ratios of 0.7(w/w), the process appears to be mass transfer limited. High levels of bicarbonate ion in the ground water significantly decreased the efficiency of TCE and TCE removal by the ozone-peroxide system, suggesting that softening prior to oxidation may improve the process.

2.4.3 H_2O_2 in the presence of UV light

The chemistry of the hydrogen peroxide plus UV rections involves generation of hydroxyl radicals and other reactive species by the photochemical action of *uv light* on hydrogen peroxide. The hydroxyl radicals attack organic species by abstracting a hydrogen atom or by adding to the double bonds of unsaturated molecules. Ultraviolet light may also activate certain organic species and make them more susceptible to hydroxyl radical attact. With suitable operating conditions, the final products are mainly CO_2, H_2O or other small molecules. For many toxic and refactory compounds, the reaction rates are slow for *uv* or H_2O_2 treatment alone, but the combination of H_2O_2 and *uv* provides free radicals and excited state species that can greatly enhance the rate of oxidation.

It is probable that H_2O_2 is photolyzed at first, forming radical $\cdot OH$, followed by further reaction such as formation of $HOO\cdot$ etc.

Hochanade *(22)* proposed the following simple mechanism for the H_2O_2/UV reaction.

$$H_2O_2 \xrightarrow{h\upsilon} 2\cdot OH$$

$$H_2O_2 + \cdot OH \longrightarrow H_2O + HO_2^{\cdot}$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2^{\cdot}$$
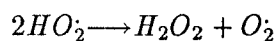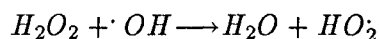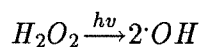
Yoshiro Ogata el etc.(1980)*(23)* summarized the various literature and proposed the following mechanism of the H_2O_2/UV reaction:

$$H_2O_2 \xrightarrow{h\nu} 2HO^{\cdot}$$

$$HO^{\cdot} + H_2O_2 \longrightarrow HOO^{\cdot} + H_2O$$

$$HOO^{\cdot} + H_2O_2 \longrightarrow HO^{\cdot} + H_2O + O_2$$

$$2HOO^{\cdot} \longrightarrow H_2O_2 + O_2$$
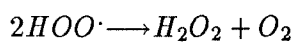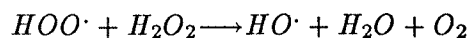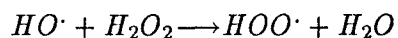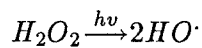
Weir and co-workers(1986) (24) investigated the destruction of halogenated aliphatics by ultrovilet catalyzed oxidation with hydrogen peroxide. They found that the rates of decomposition increased with increasing hydrogen peroxide concentration and temperature,and highly dependent on chemical structure.

Also, in next years(1987). They investigated the destruction of aromatic pollutant, Bengen, by ultraviolet catalyzed oxidation with hydrogen peroxide. They found that alkaline PH was detrimental to the reaction rate, probably because of the base-catalyzed decomposition of hydrogen peroxide.

Chapter 3

Reaction Mechanism and

Kinetic Models

The reaction kinetic models for each experimental model were initially developed by Dr. C.R. Huang in 1983 and revised in 1984 , 1988 and 1990. 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. ,bubbling with nitrogen; UV radiation only; nitrogen bubbling with UV radiation ; oxygen bubbling with UV radiation; ozone and oxygen bubbling only; ozone and oxygen bubbling with UV radiation; hydrogen peroxide only; hydrogen peroxide with UV radiation; CSTR for ozone/UV reaction; CSTR for hydrogen peroxide/UV reaction.

The reaction kinetoc models set up for each experiments are based upon the following three assumption :

1. The reaction in each of the mechanism is considered as first order reaction.

2. The intermediates which are produced during reaction will not consume the UV photons and their concentration will change with time.

3. Assume complet mixing by both bubbling and pumping circulation.

The detailed models for each experiments are discribed in following section.

3.1 Mass Transfer

3.1.1 Stripping of Pollutants by N_2 from Liquid Phase

The purpose of this experiment is to estimate the evaporation effect of the chemical by introduce nitrogen bubble.

Two film theory is used to produce the following material balance equation in the different phase. It is assumed that the resistance between the gas film and the gas bulk is negligible because a well mixing is poatulated, that is the concentration of species A in the gas film (C'_{ag}) is equal to the concentration in the bulk gas phase (C_{ag}) (Fig. 1). It is further assumed that the concentration of the liquid film at the gas-liquid interface (C_{as}) satisfies the Henry's law relationship with C'_{ag}, that is :

$$C_{ag} = C'_{ag} = MC_{as}$$

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

Figure 3.1: Concentration Profile in the Interface
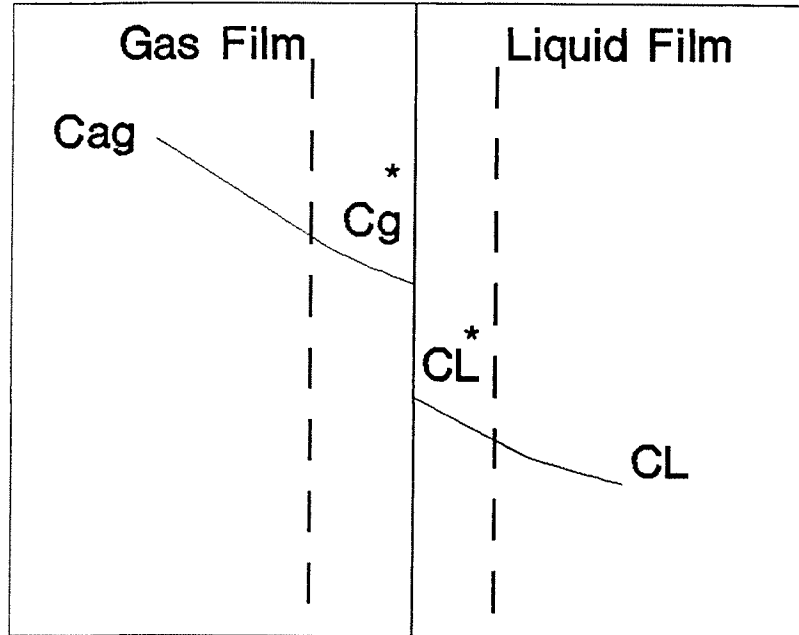
$Input - Output = Accumulation$

$$0 - V \times K_{LA}A \times (C_a - C_{as}) = V\frac{dC_{ag}}{dt}$$

here K_{LAa} 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

$$0 - (C_{ag}Q_g + K_{LA}A \times V \times (C_{as} - C_a)) = \frac{dC_{ag}}{dt}$$

Henry's law gives : $C_{ag} = M \times C_{as}$

The initial conditions are :

t=0 C_{ag}=0 $C_a = C_{a0}$

We can easily solve the simultaneous equations (1), (2), (3) with the initial conditions

:

$$C_a = \frac{K_{LAa} + M_2}{M_2 - M_1} \times e^{M_1 \times t} - \frac{K_{LAa} + M_1}{M_2 - M_1} \times e^{M_2 \times t}$$

where

$$M_1 = \frac{-C_1 + \sqrt[q]{C_1^2 - 4C_2}}{2}$$

$$M_2 = \frac{-C_1 - \sqrt{C_1^2 - 4C_2}}{2}$$

$$C_1 = K_{LA}A + \frac{K_{LA}A}{E \times M} + \frac{Q_g}{E \times V}$$

$$C_2 = \frac{K_{LA}A \times Q_g}{E \times V}$$

The values of K_{LAa} and M can be optimized with the aid of Rosenbrock Hillclimb

Optimization program, so as to give the best fit to the experimental data.

3.1.2   Bubbling with Oxygen and Ozone

These experiments are used to determine the mass transfer coefficient of ozone and

oxygen from gas phase to liquid phase by bubbling pure oxygen or ozone into the un-

contaminated water. Science the concentration of oxygen or ozone in liquid phase can

be measured at different time period, the mass transfer coefficients can be found in

these experiments.

$$O_{2l} \xrightarrow{K_{LO2}A} O_{2g}$$

$$O_{3l} \xrightarrow{K_{LO3}A} O_{3g}$$
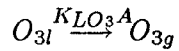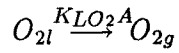
The marterial balance for oxygen and ozone can be expressed as following equations.

$$\frac{dC_{O2}}{dt} = K_{LO2}A(C_{O2S} - C_{O2})$$

$$\frac{dC_{O3}}{dt} = K_{LO3}A(C_{O3I} - C_{O3})$$

Initial condiations :

$$C_{O2} = C_{O20}$$

$$C_{O3} = C_{O30}$$

3.2 Reaction with UV light

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

The reaction mechanisms for these two types are as follows:

3.2.1 With Nitrogen

Evaporation and decomposition occur at the same time.

$$A + h\nu \underset{k_3}{\overset{k_{IA}I}{\rightleftharpoons}} A^* \xrightarrow{k_2} Decomposition product$$
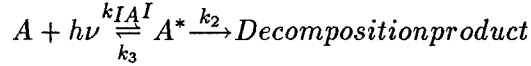
Substrate Mass Trasfer : $A_l \xrightarrow{K_{LA}A} A_g$ The material balance for each species is :

$$\frac{dC_a}{dt} = -k_{IA}IC_a + k_3C_a^* + K_{LA}A(C_{ag}/M - C_a)$$

$$\frac{dC_a^*}{dt} = -k_2C_a^* + k_{IA}IC_a - k_3C_a^*$$

$$\frac{dC_{ag}}{dt} = -\frac{C_{ag} \times Q_g}{V \times E} - \frac{K_{LA}A(C_{ag}/M - C_a)}{E}$$

Initial conditions : at t=0, $C_a = C_{a0}$

$C_{ag} = 0$ $C_a^* = 0$

3.2.2 Without Nitrogen

$$A + h\nu \underset{k_3}{\overset{k_{IA}I}{\rightleftharpoons}} A^* \xrightarrow{k_2} Decomposition product$$
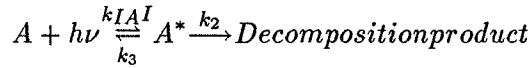
The material balance for species A and A* are

$$\frac{dC_a}{dt} = -k_{IA}IC_a + k_3C_a^*$$

$$\frac{dC_a^*}{dt} = -k_2C_a^* + k_{IA}IC_a - k_3C_a^*$$

Initial conditions : at t=0, $C_a = C_{a0}$ $C_a^* = 0$

These simultaneous differential equations are solved by the forth order Runge-Kutta method. The reaction rate constants, $k_{IA}I$, k_2 and k_3 can be determined also using the Resenbrock Hillclimb Optimization program.

3.2.3 Reaction with Oxygen Bubbling

This experiment is designed to determine the interaction between the pollutant species

A and activated oxygen (O_2^*).

The reaction mechanism is as follows:

$$O_2 + h\nu \underset{k_{IO_2}}{\overset{k_{IO_2}I}{\rightleftharpoons}} O_2^*$$

$$A + h\nu \underset{k_3}{\overset{k_{IA}I}{\rightleftharpoons}} A^* \xrightarrow{k_2} Decomposition Product$$

$$A + O_2^* \xrightarrow{k_6} Decomposition Product$$
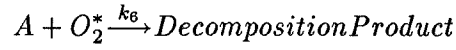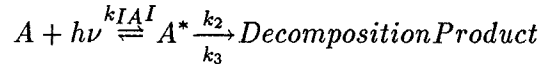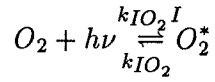
Oxygen mass transfer : $O_{2l} \xrightarrow{K_{LO_2}} O_{2g}$

Substrate mass transfer : $A_l \xrightarrow{K_{LA}A} A_g$

Mass balance for each species are :

$$\frac{dC_a}{dt} = -k_{IA}IC_a + k_3C_a^* + K_{LAa}(C_{ag}/M - C_a)$$

$$-k_6C_aC_{O_2}^*$$

$$\frac{dC_a^*}{dt} = -k_2C_a^* + k_{IA}IC_a - k_3C_a^*$$

$$\frac{dC_{O_2}}{dt} = -k_{IO_2}IC_{O_2} + K_{LO_2}A(C_{O_2} - C_{O_2}) + K_{IO_2b}C_{O_2}^*$$

$$\frac{dC_{O_2}^*}{dt} = k_{IO_2}IC_{O_2} - k_6C_aC_{O_2}^*$$

$$\frac{dC_{ag}}{dt} = -C_{ag}Q_g/V' - K_{LA}A(C_{ag}/M - C_a)/E$$

Initial condictions : t=0, $C_a = C_{a0}$, $C_{O_2} = C_{O_{20}} = 0.11, C_a^*, C_{O_2}^* = 0$

$C_{OH^-}, C_{ag} = 0$

The rate constants $k_{IO_2}I$, $k_{IO_2}b$, k_5, k_6 and $K_{LO_2}A$ are determined in this experiment.

3.3   Reaction with ozone alone

Ozone may decompose the pollutants. From this experiment, the effect of ozone on decomposition of the polutants can be determined. The ozone is generated from pure oxygen by use of an ozonator is at least 2 % by weight.

The mechanism of ozonation of chemicals can be expressed as :

$$A + O_3 \xrightarrow{K_1} Decomposition Product$$
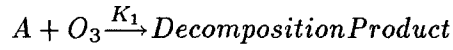
Ozone mass transfer : $O_{3l} \xrightarrow{K_{LO_3}} O_{3g}$

Substrate mass transfer : $A_l \xrightarrow{K_{LA}A} A_g$

The mass balance for each species are as following :

$$\frac{dC_a}{dt} = -k_1 C_a C_{O_3}$$

$$\frac{dC_{O_3}}{dt} = -k_1 C_a C_{O_3} + K_{LO_3}A(C_{O_{3s}} - C_{O_3})$$

Initial conditions :

t=0 $C_a = C_{a0}$ $C_{O_3} = 0$ k_1 is determined using the same optimization method.

3.4 Reaction with ozone ,oxygen and UV light

In this experiment the combined effect of all the relative radicals created by the ozone and the oxygen under UV radiation is determined. This reaction mode is faster and more effective than previous experiments.

The mechanism is described as follows:

$$O_3 + H_2O \xrightarrow[h\nu]{k_{IO_3}} O_2 + 2OH\cdot$$

$$O_3 + OH \xrightarrow{k_8} O_2 + HO_2\cdot$$

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

$$OH\cdot + OH\cdot \xrightarrow{k_{14}} H_2O_2$$

$$HO_2\cdot + HO_2\cdot \xrightarrow{k_{15}} H_2O_2 + O_2$$

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

$$H_2O_2 + h\nu \xrightarrow{k_{IH_{22}}{}^I} 2OH\cdot$$

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

$$H_2O_2 + HO_2 \xrightarrow{k_{11}} OH\cdot + O_2 + H_2O$$

$$O_2 + h\nu \underset{k_{IO_2}b}{\overset{k_{IO_2}{}^I}{\rightleftharpoons}} O_2^*$$

$$A + h\nu \underset{k_3}{\overset{k_{IA}{}^I}{\rightleftharpoons}} A^* \xrightarrow{k_2} Decomposition Product$$

$$A + O_2^* \xrightarrow{k_6} Decomposition Product$$

$$A + O_3 \xrightarrow{k_1} Decomposition Product$$

$$A + OH \cdot \xrightarrow{k_4} Decomposition Product$$

$$A + HO_2 \cdot \xrightarrow{k_5} Decomposition Product$$
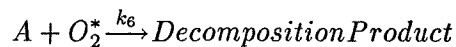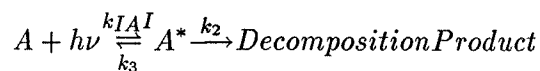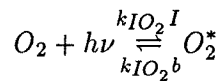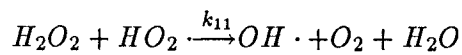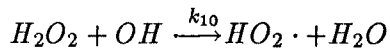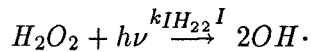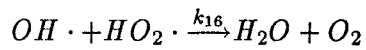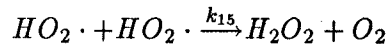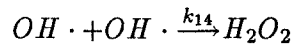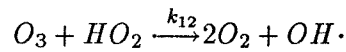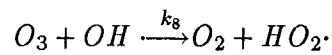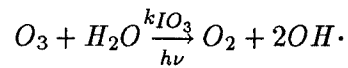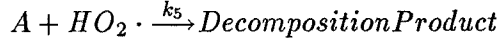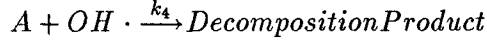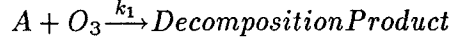
Oxygen mass transfer : $O_{2l} \xrightarrow{K_{LO_2}} O_{2g}$

Ozone mass transfer : $O_{3l} \xrightarrow{K_{LO_3}} O_{3g}$

The mass balance for each species are as following :

$$\frac{dC_a}{dt} = -k_1 C_a C_{O_3} - k_4 C_a C_{OH\cdot} - k_5 C_a C_{HO_2\cdot} - k_6 C_a C_{O_2^*}$$

$$+ k_3 C_a^* - k_{IA} I C_a$$

$$\frac{dC_a^*}{dt} = -k_2 C_a^* - k_3 C_a^* + k_{IA} I C_a$$

$$\frac{dC_{O_3}}{dt} = -k_1 C_a C_{O_3} - k_{IO_3} I C_{O_3} - k_{8f} C_{O_3} C_{OH\cdot} - k_{12f} C_{O_3} C_{HO_2\cdot}$$

$$+ K_{LO_3} A (C_{O_{3s}} - C_{O_3})$$

$$\frac{dC_{O_2}}{dt} = K_{LO_2} A (C_{O_{2s}} - C_{O_2}) + k_{IO_3} I C_{O_3} + k_{8f} C_{O_3} C_{OH\cdot} + 2k_{12f} C_{O_3} C_{HO_2\cdot}$$

$$- k_{IO_2} I C_{O_2} + k_{IO_2 b} C_{O_2}^*$$

$$\frac{dC_{O_2^*}}{dt} = k_{IO_2} I C_{O_2} - k_6 C_a C_{O_2}^* - k_{IO_2 b} C_{O_2}^*$$

$$\frac{dC_{OH\cdot}}{dt} = -k_4 C_a C_{OH\cdot} + 2k_{IO_3} I C_{O_3} - k_{8f} C_{O_3} C_{OH\cdot} + k_{12f} C_{O_3} C_{HO_2\cdot}$$

$$- 2k_{14} C_{OH\cdot}^2 - k_{16} C_{OH\cdot} C_{HO_2\cdot} + k_{11f} C_{H_2O_2} C_{HO_2\cdot} - k_{10f} C_{H_2O_2} C_{OH\cdot}$$

$$\frac{dC_{HO_2\cdot}}{dt} = -k_5 C_a C_{HO_2\cdot} + k_{8f} C_{O_3} C_{OH\cdot} - k_{12f} C_{O_3} C_{HO_2\cdot} - 2k_{15} C_{HO_2\cdot}^2$$

$$-k_{16}C_{OH}.C_{HO_2}. - k_{11f}C_{H_2O_2}C_{HO_2}. + k_{10f}C_{H_2O_2}C_{OH}.$$

$$\frac{dC_{H_2O_2}}{dt} = k_{14}C_{OH}^2. + k_{15}C_{HO_2}^2. - k_{IH_2O_2}C_{H_2O_2}$$

$$-k_{11f}C_{H_2O_2}C_{HO_2}. - k_{10f}C_{H_2O_2}C_{OH}. \quad \text{Initial conditions :}$$

at t=0, $\qquad C_a = C_{a0} \qquad C_{O_2} = C_{O_2} = 0.11 \qquad C_{O_3}, C_a^*, C_{O_2}^*, C_{OH}., C_{HO_2}.=0$

The rate constants, $k_{IO_3I}, k_4, k_5, k_{IH_2O_2I}$ are determined in this experiment.

3.5 Reaction with hydrogen peroxide only

In this experiment, the acrylonitrile and acetonitrile would not directly react with hydrogen peroxide.

3.6 Reaction with hydrogen peroxide and UV light

Hydrogen peroxide can serve as a source of hydroxyl radical in aqueous solution under UV radiation. Hydroxyl radical has a high oxidation potential, with reference to hydrogen and can facilate the degradation of pollutants.

there are two types of processes in this reaction. one is with nitrogen bubbling, the other one is without nitrogen bubbling.

3.6.1 with nitrogen bubbling

The proposed reaction models are :

$$H_2O_2 \underset{h\nu}{\overset{k_{IH_{22}}I}{\longrightarrow}} 2OH.$$

$$H_2O_2 + OH \cdot \xrightarrow{K_{10}} HO_2 \cdot + H_2O$$

$$H_2O_2 + HO_2 \cdot \xrightarrow{k_{11}} OH \cdot + O_2 + H_2O$$

$$OH \cdot + OH \cdot \xrightarrow{k_{14}} H_2O_2$$

$$HO_2 \cdot + HO_2 \cdot \xrightarrow{k_{15}} H_2O_2 + O_2$$

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

$$O_2 + h\nu \underset{k_{IO_2}}{\overset{k_{IO_2}}{\rightleftharpoons}} O_2^*$$

$$A + h\nu \underset{k_3}{\overset{k_{IA}I}{\rightleftharpoons}} A^* \xrightarrow{k_2} Decomposition\,product$$

$$A + O_2^* \xrightarrow{k_6} Decomposition\,Product$$

$$A + OH \cdot \xrightarrow{k_4} Decomp.product$$

$$A + HO_2 \cdot \xrightarrow{k_5} Decomp.Product$$
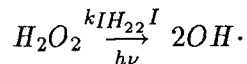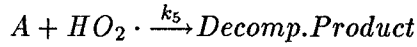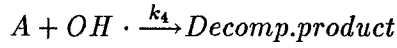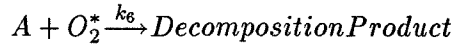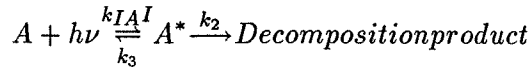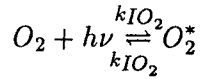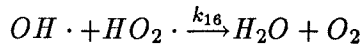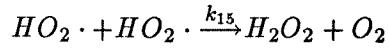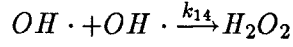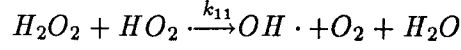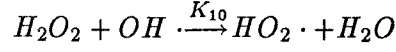
The mass balance for each species are as following :

$$\frac{dC_a}{dt} = -k_4 C_a C_{OH\cdot} - k_5 C_a C_{HO_2\cdot} - k_6 C_a C_{O_2^*} + k_3 C_a^* - k_{IA} I C_a$$

$$\frac{dC_a^*}{dt} = -k_2 C_a^* - k_3 C_a^* + k_{IA} I C_a$$

$$\frac{dC_{H_2O_2}}{dt} = -k_{IH_2O_2} I C_{H_2O_2} - k_{10f} C_{H_2O_2} C_{OH\cdot} - k_{11f} C_{H_2O_2} C_{HO_2\cdot}$$

$$+ k_{14} C_{OH\cdot}^2 + k_{15} C_{HO_2\cdot}^2$$

$$\frac{dC_{O_2}}{dt} = k_{11f} C_{H_2O_2} C_{HO_2\cdot} - k_{IO_2} I C_{O_2} + k_{IO_2b} C_{O_2}^*$$

$$+k_{14}C_{OH\cdot}^2 + k_{16}C_{OH\cdot}C_{HO_2\cdot} + K_{LO2}A(C_{O2S} - C_{O2})$$

$$\frac{dC_{O_2^*}}{dt} = k_{IO_2}IC_{O2} - k_6C_aC_{O_2}^* - k_{IO_2b}C_{O_2}^*$$

$$\frac{dC_{OH\cdot}}{dt} = -k_4C_aC_{OH\cdot} - 2k_{14}C_{OH\cdot}^2 - k_{16}C_{OH\cdot}C_{HO_2\cdot}$$

$$+k_{11f}C_{H_2O_2}C_{HO_2\cdot} - k_{10f}C_{H_2O_2}C_{OH\cdot}$$

$$\frac{dC_{HO_2\cdot}}{dt} = -k_5C_aC_{HO_2\cdot} - 2k_{12}C_{HO_2\cdot}^2 - k_{11f}C_{H_2O_2}C_{HO_2\cdot} + k_{10f}C_{H_2O_2}C_{OH\cdot}$$

$$-k_{13}C_{OH\cdot}C_{HO_2\cdot}$$

Initial conditions :

at t=0, $\quad C_a = C_{a0}$ $\quad C_{O_2} = C_{O_2} = 0.11$ $\quad C_a^*, C_{O_2}^*, C_{OH\cdot}, C_{HO_2\cdot} = 0$

$C_{H_2O_2} = C_{H_2O_2 0}$

3.6.2 without nitrogen

By neglecting the substrate mass transfer in the reaction kinetic model, the rate constants, $k_{IH_2O_2}I$, k_{10f}, k_{11f}, and are optimized to give the best fit to the experimental results in this process.

3.7 CSTR process

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

A mass balance can be given as follows:

accumulation of A = input - output - decomposition by reaction

3.7.1 for $O_3/O_2/$UV process:

The reaction mechanism is same as the $O_3/O_2/$UV experiment in the semi batch reaction. The reaction rates for each species are :

$$\frac{dC_a}{dt} = \frac{Q}{V} \times C_{a0} - \frac{Q}{V} \times C_a - r_a$$

$$r_a = -k_1 C_a C_{O_3} - k_4 C_a C_{OH\cdot} - k_5 C_a C_{HO_2\cdot} - k_6 C_a C_{O_2^*} + k_3 C_{a^*} - k_{IA} I C_a$$

$$\frac{dC_{a^*}}{dt} = -k_2 C_{a^*} - k_3 C_{a^*} + k_{IA} I C_a$$

$$\frac{dC_{O_3}}{dt} = -k_1 C_a C_{O_3} - k_{IO_3} I C_{O_3} - k_{8f} C_{O_3} C_{OH\cdot} - k_{12f} C_{O_3} C_{HO_2\cdot}$$

$$+ K_{LO_3} A (C_{O_3 s} - C_{O_3})$$

$$\frac{dC_{O_2}}{dt} = K_{LO_2} A (C_{O_2 s} - C_{O_2}) + k_{IO_3} I C_{O_3} + k_{8f} C_{O_3} C_{OH\cdot} + k_{12f} C_{O_3} C_{HO_2\cdot}$$

$$- k_{IO_2} I C_{O_2} + k_{IO_2 b} C_{O_2^*}$$

$$\frac{dC_{O_2^*}}{dt} = k_{IO_2} I C_{O_2} - k_6 C_a C_{O_2^*} - k_{IO_2} b C_{O_2^*}$$

$$\frac{dC_{OH\cdot}}{dt} = 2 k_{IO_3} I C_{O_3} + 2 k_{IH_2O_2} I C_{H_2O_2} - k_4 C_a C_{OH\cdot} - k_{8f} C_{O_3} C_{OH\cdot}$$

$$+ k_{12f} C_{O_3} C_{HO_2\cdot} - 2 k_{14} C_{OH\cdot}^2 - k_{16} C_{OH\cdot} C_{HO_2\cdot}$$

$$+ k_{11f} C_{H_2O_2} C_{HO_2\cdot} - k_{10f} C_{H_2O_2} C_{OH\cdot}$$

$$\frac{dC_{HO_2\cdot}}{dt} = -k_5 C_a C_{HO_2\cdot} + k_{8f} C_{O_3} C_{OH\cdot} - k_{12f} C_{O_3} C_{HO_2\cdot} - 2 k_{15} C_{HO_2\cdot}^2$$

$$-k_{16}C_{OH.}C_{HO2.} - k_{11f}C_{H_2O_2}C_{HO2.} + k_{10f}C_{H_2O_2}C_{OH.}$$

$$\frac{dC_{H_2O_2}}{dt} = k_{14}C_{OH.}{}^2 + k_{15}C_{HO2.}{}^2 - k_{IH_2O_2}IC_{H_2O_2} - k_{11f}C_{H_2O_2}C_{HO2.}$$

$$-k_{10f}C_{H_2O_2}C_{OH.}$$

Initial conditions : t=0, $C_{a0} = C_a$, $C_{O_2} = C_{O_{20}} = 0.11$,

$$C_a, C_{O_3}, C_{a*}, C_{O_2^*}, C_{OH.}, C_{HO2.} = 0 ,$$

The computed output concentration is compared to the experimental data to evaluated

the proposed reaction kinetic models and the reaction rate constants.

3.7.2 for $H_2O_2/N_2/\text{UV}$ process

The reaction mechanism is same as the $H_2O_2/N_2/\text{UV}$ process in the batch reactor.

The reaction rates of each components are as follows :

$$\frac{dC_a}{dt} = \frac{Q}{V} \times C_{a0} - \frac{Q}{V} \times C_a - r_a$$

$$r_a = -k_4C_aC_{OH.} - k_5C_aC_{HO2.} - k_6C_aC_{O_2^*} + k_3C_{a*} - k_{IA}IC_a$$

$$\frac{dC_{a*}}{dt} = -k_2C_{a*} - k_3C_{a*} + k_{IA}IC_a$$

$$\frac{dC_{O_2}}{dt} = k_{11f}C_{H_2O_2}C_{HO2.} + k_{10f}C_{H_2O_2}C_{OH.} - k_{IO_2}IC_{O_2} + k_{IO_2b}C_{O_2^*}$$

$$\frac{dC_{O_2^*}}{dt} = k_{IO_2}IC_{O_2} - k_6C_aC_{O_2^*} - k_{IO_2b}C_{O_2^*}$$

$$\frac{dC_{OH.}}{dt} = 2k_{IH_2O_2}IC_{H_2O_2} - k_4C_aC_{OH.} - 2k_{14}C_{OH.}{}^2 - k_{16}C_{OH.}C_{HO2.}$$

$$+k_{11f}C_{H_2O_2}C_{HO2.} - k_{10f}C_{H_2O_2}C_{OH.}$$

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

$$+k_{10f} C_{H_2O_2} C_{OH\cdot}$$

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

$$-k_{10f} C_{H_2O_2} C_{OH\cdot}$$

Initial conditions : t=0, $\quad C_{a0} = C_a$, $\quad C_{O_2} = C_{O_{20}} = 0.11$,

$$C_{H_2O_2}, C_a, C_{a^*}, C_{O_2^*}, C_{OH\cdot}, C_{HO_2\cdot} = 0 \ , \quad C_{H_2O_{20}} = C_{H_2O_2}$$

The computed output concentration of pollutants is used to evaluated the kinetic models and rate constants for the continuous wastewater treatment process.

Chapter 4

Material and Experimental

Techiques

4.1   Experimental Installation

Figure 4.1: The Experimental Installation

The experiments were carried out in a continuously sparged tank photochemical reactor operated in the batch and semi-batch mode with respect to liquid. *Figure–1* shows a detailed diagram of the experimental installation. There are there three distinguishable parts: the reactor, the source of radiation and the ozone generator.

4.2 Apparatus

4.2.1 The photochemical Reactor

The photochemical reactor is a vertical cylinder contained nine vertical sample ports evenly spaced in three rows. It was mode of #304 stainless steel. The Reaction chamber gives it approximately 104 liters of hold-up volume in the following dimensions : 13 inches in outside diameter and 55 inches high. The *UV* lamp resids in the reactor with an annular space of about 3.5 inches between the lamp and the reactor wall.

4.2.2 Mixing

The system is also provided with two pumps to achieve a good mixing and to feed the pollutant sollution to the reactor from a reservoir tank. Ozone, oxygen or nitrogen is introduced into the bottom of the reactor through a four-head sparger of medium porosity. The exhaust gas is vented from the top of the reactor through absorption bottle into the laboratory hood. Complete mixing of solution is achieved by recycling the solution and bubbling nitrogen gas into the reactor.

4.2.3 Ozone generator

Ozone is produced by a T-816 Ozone Generator, 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 flowrate is adjustable by a ball valve. The power was set at 110W and 99.6% pure, dry oxygen was used for ozone generation in this experiment.

4.2.4 Ultraviolet light source

The ultraviolet light source is a high pressure mercury vapor fused quartz lamp with an arc length of 25 inches and has a power rate of 5 kils watts. The power supplied to the lamp was set to 200 watts/inch level. Output wavelength of the lamp is around 245nm.

4.3 Analysis

4.3.1 Pollutants characteristics

Acrylonitrile(AN)(CH_2CHCN)

- Carcinogen(EPA-CAG)(Probable, IARC)(9)(A-62)(A-64)

- Hazardous substance(EPA)

- Hazardous waste(EPA)

Figure 4.2: UV lamp
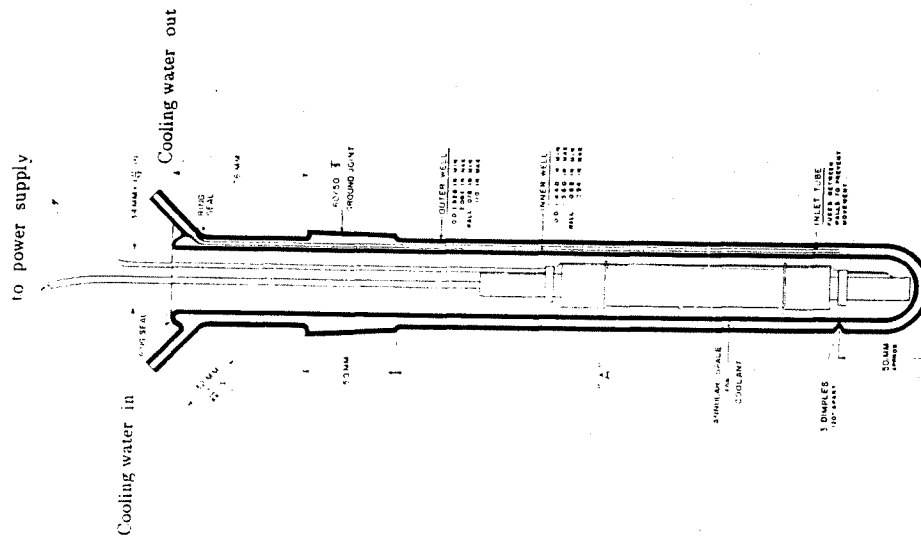
- Priority toxic pollutant(EPA)

Code Numbers : CAS 107-13-1 RTECS AT 5250000 UN 1093

DOT Designation : Flammable liquid and poison

Potential Exposure : Acrylonitrile is used in the manufacture of synthetic fibers, acrylostyrene plastics, acrylonitrile-butadiene-styrene plastics , nitrile rubbers, chemicals, and adhensives. It is also used as a pesticide. NIOSH estimates that approximately 125,000 persons are potentially exposed to acrylonitrile in the workplace.

Permissible Exposure Limits in Air : An emergency temporary standard set the TWA at 2ppm, down from 20 ppm in a previous determination. The economic

impact of these standards has been assessed and the ETS was later made perma-

nent. The ACGIH as of 1983/84 has set a TLV of 2ppm with the notation *skin*

is added by ACGIH indicating the possibility of cutaneous absorption.

Permissible Concentration in Water To protect freshwater aquatic life on an acute

basis, 7,550 *ug/l* and on a chronic basis, 2,600 *ug/l* over 30 days. To protect

saltwater aquatic life- insufficient data to yield a value. To protec human health-

perferably zero. Water concentration should be below 0.58 *ug/l* to keep lifetime

cancer risk below 10^5.

Systemic Acrylonitrile exposure may produce nausea, vomiting, headache ,sneezing,

weakness, and light-headedness. Exposure to high concentrations may produce

profound weakness, asphyxia, and death.

Points of Attack : Cardiovascular system, liver, kidneys, central nervous system ,

skin.

Acetonitrile(CH_3CN)

- Hazardous waste (EPA)

Code Numbers: CAS 75-05-8 RTECS AL7700000 UN 1648

DOT Designation : Flammable liquid.

Pontential Exposures : Acetonitrile is used as an extractant for animal and veg-

etable oils, as a solvent, particularly in the pharmaceutical industry , and as a

chemical intermediate in pesticide manufacture, e.g.. It is present in cigarette smoke.

Permissible Exposure Limits in Air : The Federal standard is 40 ppm. This is the 1983/84 ACGIH TWA value with the notation that skin absorption may be significant. The STEL value proposed is 60 ppm. The IDLH level is 4,000 ppm.

Permissible Concentration in Water : Acetonitrile is infinitely soluble and stable in water. No criteria have been set, but EPA has proposed an ambient environmental goal of 970 μg/l based on health effects.

Systemic : Acetonitrile has a relatively low acute toxicity, but there have been reports of severe and fatal poisonings in man after inhalation of high concentrations. Acetonitrile is metabolized to HCN which can be found in high levels in the brain, heart, kidney and spleen. Signs and symptoms may include nausea, vomiting, respiratory despression, weakness, chest or abdominal pain, hematemesis, convulsions, shock, unconsciousness, and death. In most cases there is several hours between exposure and onset of symptoms, It has been thought that acetonitrile itself has relatively little toxic effect and that the delayed response is due to the slow release of cyanide. No chronic disease has been reported.

Points of Attack : Kidneys, liver, lungs, skin, central nervous system, cardiovascular system.

4.3.2 Method

The pollutant solutions were analysed at $100^{o}C$ on a Hewlett- packard Model 5730A gas chromatograph filled with a $25 meters \times 0.31 mm$ Chrompack fused silica column packed with a film thickness of 1.2um and a Flame Ionization Detector. Degradation products were identified by comparison of their rentention times with those of authentic standards. Calibration of flame ionization detector to obtain appropriate molar response factors was done by injecting a known quantity of the relevant compound, into the injection port then measuring the corresponding response area. The relative response factor has been determined for compounds. Base on the experimentally verified relative response factors, the specific component peak area from each set of samples was converted to the equivalent of moles of each compound.

4.4 Experiment:

4.4.1 Batch Experiments

Two experimental trials are 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 recycling is 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, is activated. Before switching the uv light source power on, cooling water and nitrogen flow for the uv lamp are started at a safe level. Setting the power rate at 125 W/inch first, after 30 seconds later, turn the power rate to 200 W/inch. Tim-

ing of the experiment begins about 20 seconds later.   The N_2 alone and the N_2/UV

processes belong to above mode batch experiment.   Another batch mode experiments

are the H_2O_2 and the N_2/H_2O_2/UV processes. The pollutants solution are 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. After 1 minute mixing of the H_2O_2 with solution,

we begin to do the following procedure as the N_2 or the N_2/UV process.   Sample col-

lection was as frequent as possible and all the samples are subjected to analysis as soon

as possible after collection in order to avoid of any possibility of chemical evaporation.

4.4.2   Semi-batch experiments:

In the semi-batch reactor, one reactant (pollutant species) is added batch-wise initially.

The experimental running is then conducted with a constant flow of the second reac-

tant.   Three experiments are 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 experi-

ment, cooling water and oxygen flow to the ozone generator before the ozone generator

power on.   Oxygen flow rate is regulated at 9 psig for a flow rate of about 10 l/min.

In the O_3/UV experiment, the uv light source power turns on after introducing the O_3

into the reactor.

4.4.3   CSTR experiments:

The O_3/UV and the H_2O_2/UV experiments are introduced in the CSTR experiments. The pollutant solution is dissolved in a reservoir tank before feeding to the reactor.   In the O_3/UV experiment, the feed, uv light and O_3 flow turn on simultaneously.   In the H_2O_2/UV process, hydrogen peroxide is dissolved the solution to the reactor.   Then the feed and uv light turn on at the same time.   The experiment is teriminated when the feed solution is exhausted.

Chapter 5

Results and Discussion

5.1 Results

The experimental results and rate constants computed from them are discussed below.

Details of mass transfer and kinetic models are given in the Chapter 3.

5.1.1 Mass Transfer of Nitrogen from Gas to Liquid Phase

Stripping effects of chemicals are not significant. The low stripping effects of chemicals may be caused by the high solubility of chemical(Acrylonitrile (257 g/l), Acetonitrile(infinitely soluble)). The mass transfer coefficient (k_{LAa}) between the bulk liquid stream and the liquid film is 0.2613 min^{-1}. The Henry's law: Cag=MCas, $M = 0.1322 \times 10^{-1}$.

Figure 5.1: Bubbling with Nitrogen

Ca / CaO Acrylonitrile decomposition
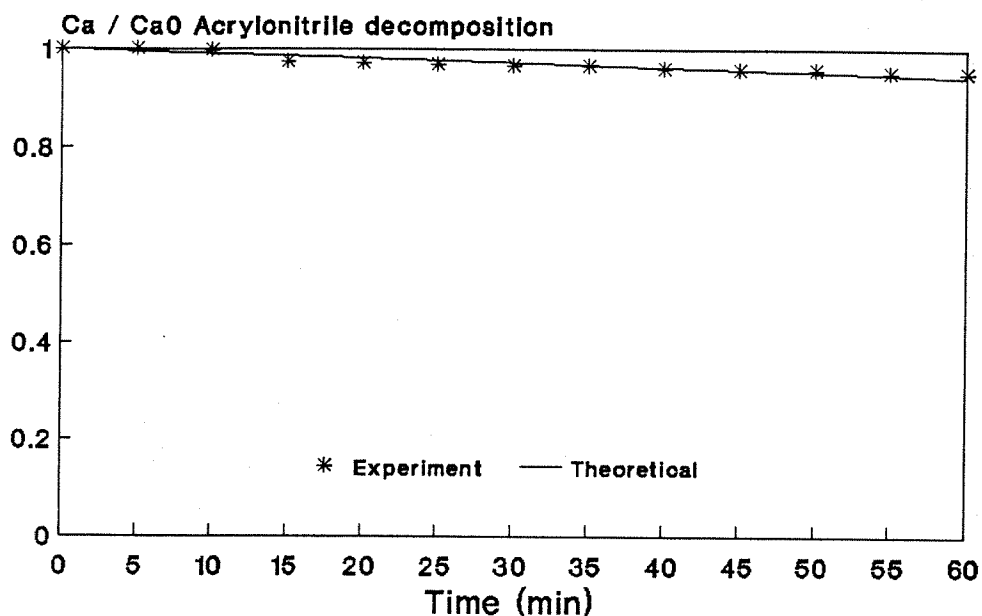
5.1.2 Ozone Concentration

Ozone concentration in the reactor, was monitored as a function of time, and was plotted in Fig 5.2 for ozonation and ozonation + u.v. irradiation in pure water. Steady-state was reached within 7 min under the experimental conditions. Steady-state ozone concentration values of 0.08 and 0.008 $(mg - mole/l)^{-1}(min)^{-1}$ were reached for ozone and ozone + u.v., respectively. The difference in these ozone concentration values can be explained by an increase in the rate of mass transfer of ozone. When the u.v. light was turned on, $[O_3]$ dropped instantaneously to an undetectable level , as also reported by other researchers(Peyton et al., 1982). Hence, the increase in the rate of mass transfer in the presence of u.v. light is completely due to the photolytic effect of U.V.

Figure 5.2: The change in $[O_3]$ with time during ozonation of pure water, ozonation and u.v. irradiation of pure water
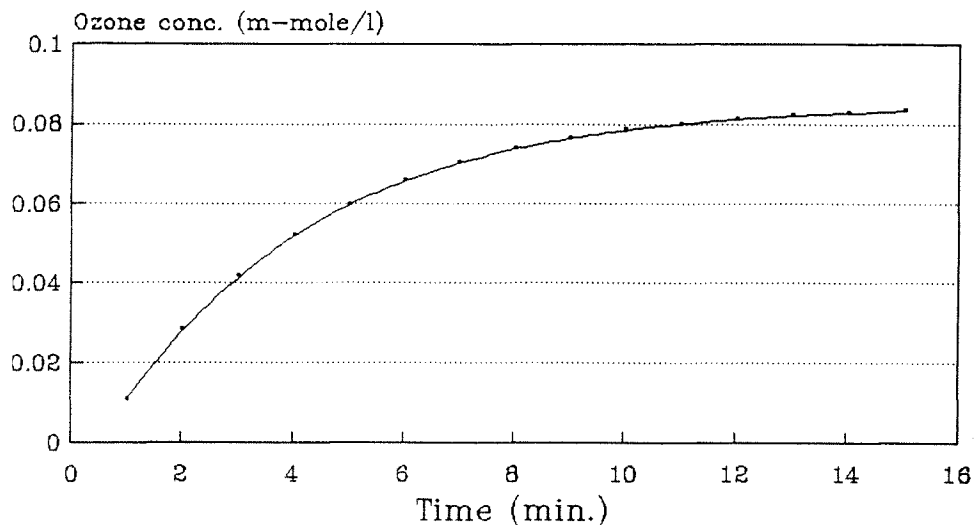
on$[O_3]$, and there is no enhancement in the mass transfer coefficient.

5.1.3   Oxidation of Acrylonitrile with Ozone

The oxidation of Acrylonitrile with ozone alone was carried out at operating conditions and ozone flow rate identical to those of mass transfer experiments. The two differential equations resulting from mass balance of ozone and acrylonitrile (Equations in Chapter 3) were solved by a Runge-Kutta fourth-order numerical method on a computer. The optimized value of the reaction rate constant k_1 was calculated by using Rosenbrock's "Hill-Climb" optimization [15]. The optimum value of k_1 is 3.5 $(mg - mol/liter)^{-1}(min)^{-1}$. A comparison of this rate is constant to the experimental

Figure 5.3: Oxidation of Acrylonitrile witth Ozone

Ca / CaO AN decomposition
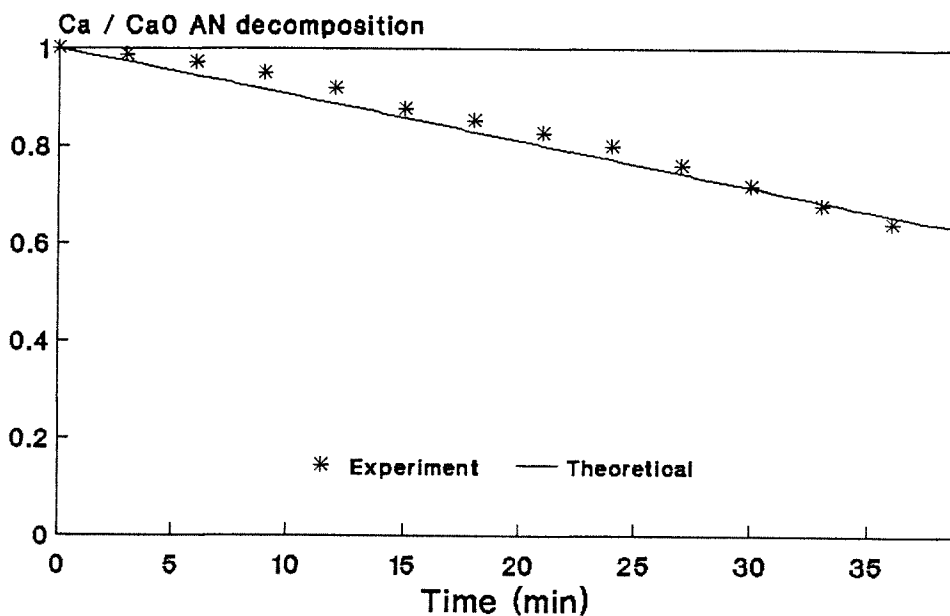
data is shown in Figure 5.3.

5.1.4   Decomposition of Acrylonitrile with UV Light Alone

The UV oxidation of Acrylonitrile was carried out by pouring nitrogen gas instead of ozone into the reactor to bring about the same mixing effect as in the case of the ozone/O_2. Decomposition of Acrylonitrile with UV light was a relatively slow reaction. Only about 8% conversions was achieved in 30 min. Equations(in Chapter 3) were solved numerically by the RK-4 method used above. Three reaction rate constants, $k_{IA}I$, k_2, and k_3 were optimized by Rosenbrock's "Hill-Climb" optimization program on the computer. The values of the rate constants which gave the best fit to the experimental data are:

Figure 5.4: Decomposition of Acrylonirile with UV Light Alone
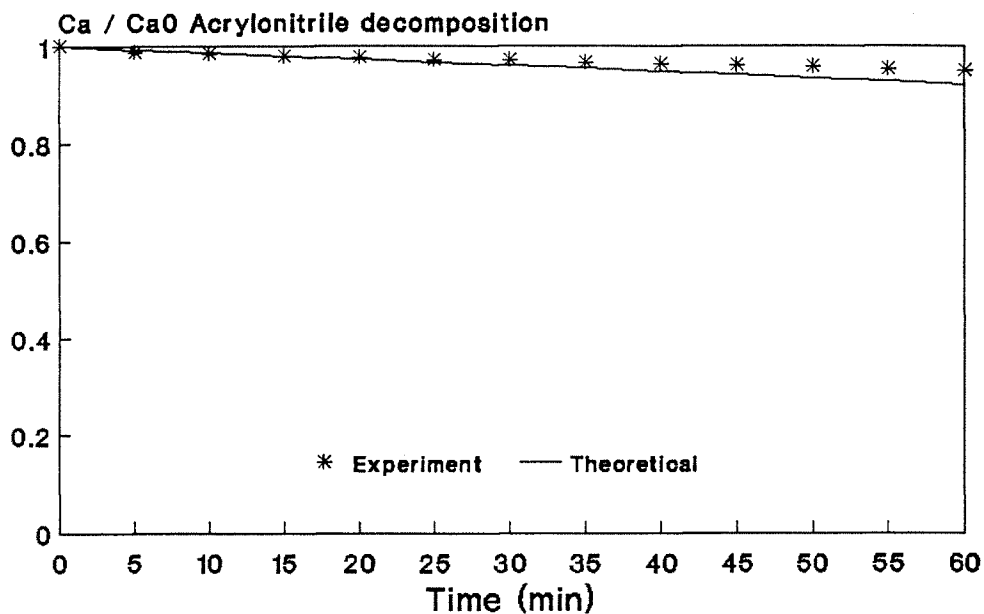
$k_{IA}I = 0.3128 \times 10^{-2}(min)^{-1}$

$k_2 = 0.5647 \times 10^{-1}(min)^{-1}$

$k_3 = 0.3699(min)^{-1}$

The theoretical curve based upon these values and its fit to the experimental data is shown in Figure 5.4.

5.1.5   Decomposition of Acrylonitrile with Oxygen and UV Light

The theoretical curve resulting from solving equation set (in Chapter 4) . is shown in Figure 5.5. The optimized values of rate constants used in this curve are given below:

$k_{IO_2}I = 0.555 \times 10^{-1}(min)^{-1}$

$k_6 = 0.2699 \times 10^{-5}(mg - mol/liter)^{-1}(min)^{-1}$

Figure 5.5: Decomposition of Acrylonitrile with Oxygen and UV Light
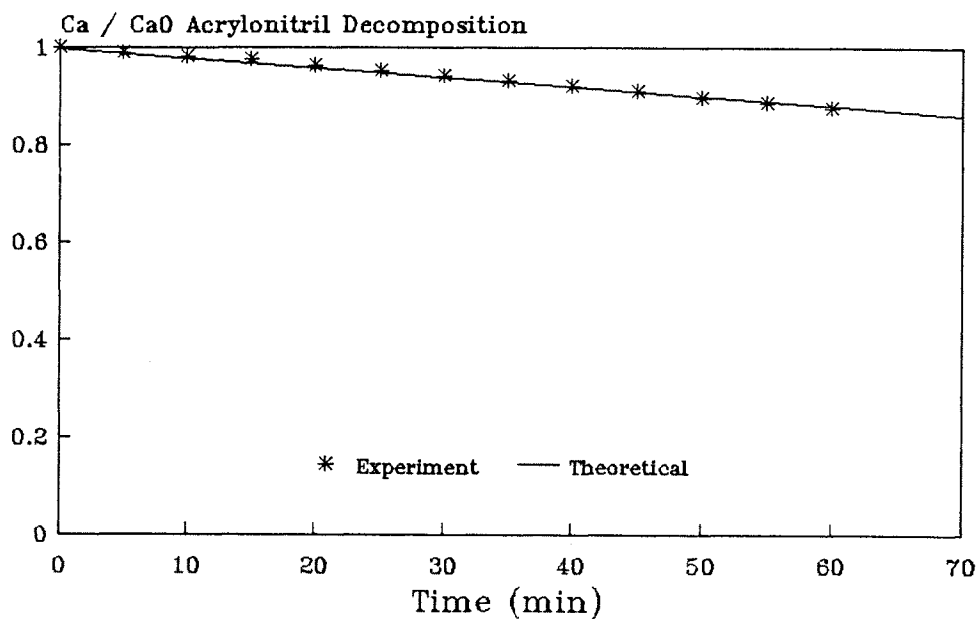
5.1.6 Decomposition of Acrylonitrile with Ozone/UV

The experimental results of this reaction are shown in Figure 5.6. A mechanism for the ozone/UV reaction with the specific organic pollutant, Acrylonitrile, is proposed and shown in the Chapter 3.

The eight differential equations (in Chapter 3) resulting from a material balance on this reaction scheme were solved by the Runge-Kutta fourth order numerical method using the data from each of the above-mentioned experimental studies. The optimized values of the reaction rate constants which gave the best fit to the experimental data are:

$$k_{8f} = 0.1894 \times 10^6 (mg - mol/liter)^{-1}(min)^{-1}$$

Figure 5.6: Decomposition of Acrylonitrile with Ozone/UV
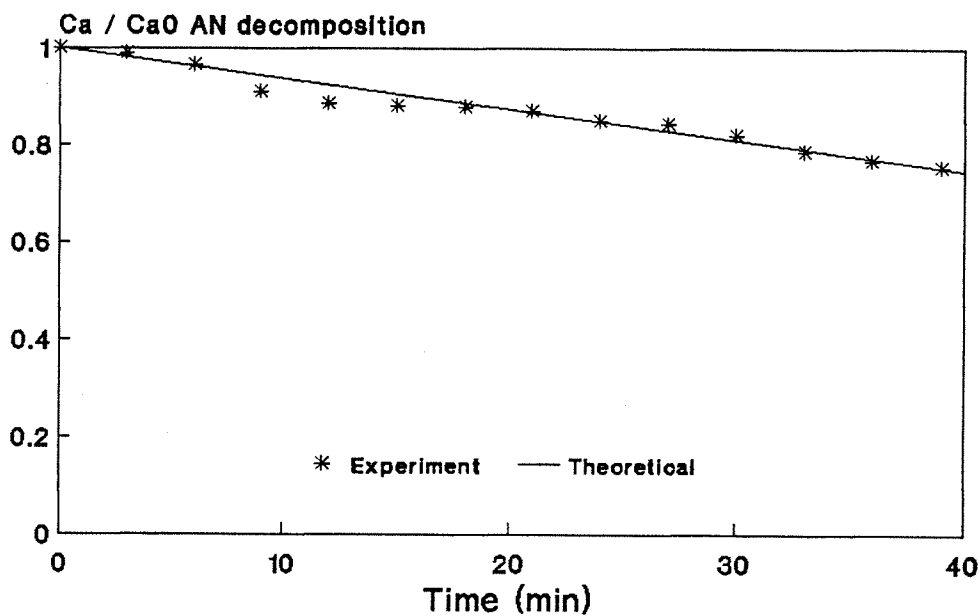
$$k_{12f} = 0.17 \times 10^6 (mg - mol/liter)^{-1}(min)^{-1}$$

$$k_{IO_3I} = 0.046(min)^{-1}$$

5.1.7 Decomposition of Acrylonitrile with H_2O_2/UV

The decomposition of Acrylonitrile with hydrogen peroxide in the presence of ultraviolet radiation is a faster reaction than any of the conversion reactions discussed above. The experimental results of this reaction are shown in Figure 5.7. The values of the rate constants which gave the best fit to the experimental data are:

$$k_{IH_2O_2I} = 0.9 \times 10^{-3}(min)^{-1}$$

$$k_4 = 0.588 \times 10^6 (mg - mol/liter)^{-1}(min)^{-1}$$

$$k_5 = 0.112 \times 10^2 (mg - mol/liter)^{-1}(min)^{-1}$$

Figure 5.7: Decomposition of Acrylonitrile with H_2O_2/UV
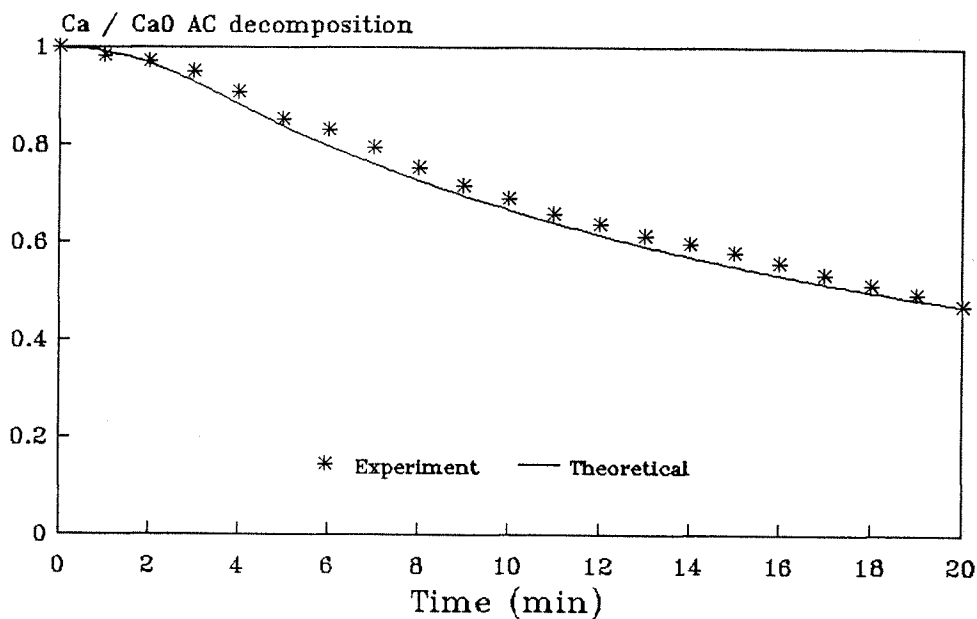
5.1.8 CSTR Process

The experimental data and the theoretical results of the CSTR O_3/UV and CSTR H_2O_2/UV process shown in Figure 5.8 ,Figure 5.9. The theoretical curves are dependent on the kinetic models proposed in the Chapter 3 with the rate constants which were calculated for the batch reactor. The deviation of the experimental data and the theoretical output is limited. Therefore one can be very confident concerning the reaction mechanism and rate constants.

Figure 5.8: CSTR H_2O_2/UV
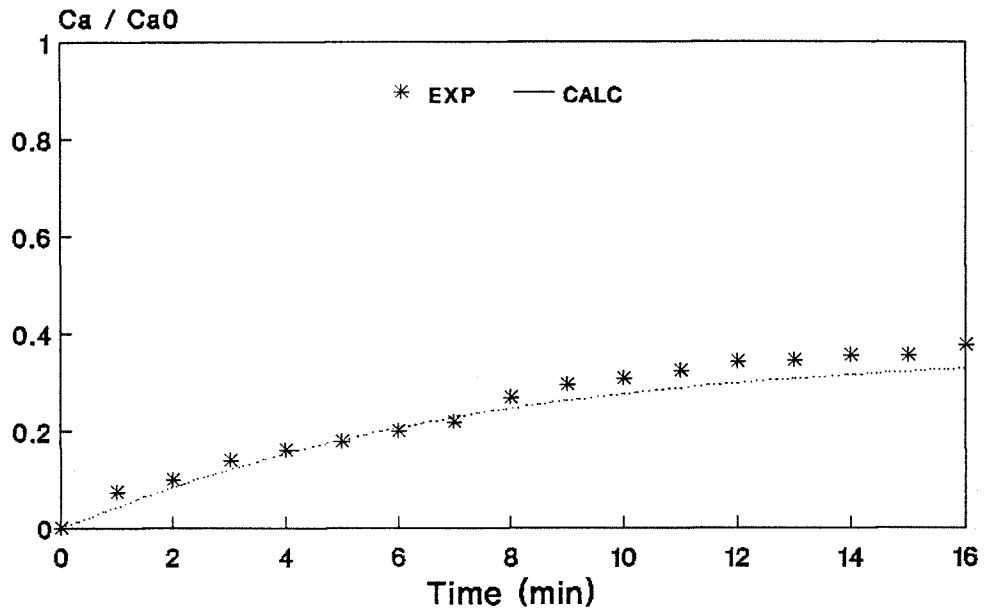
Figure 5.9: CSTR O_3/UV
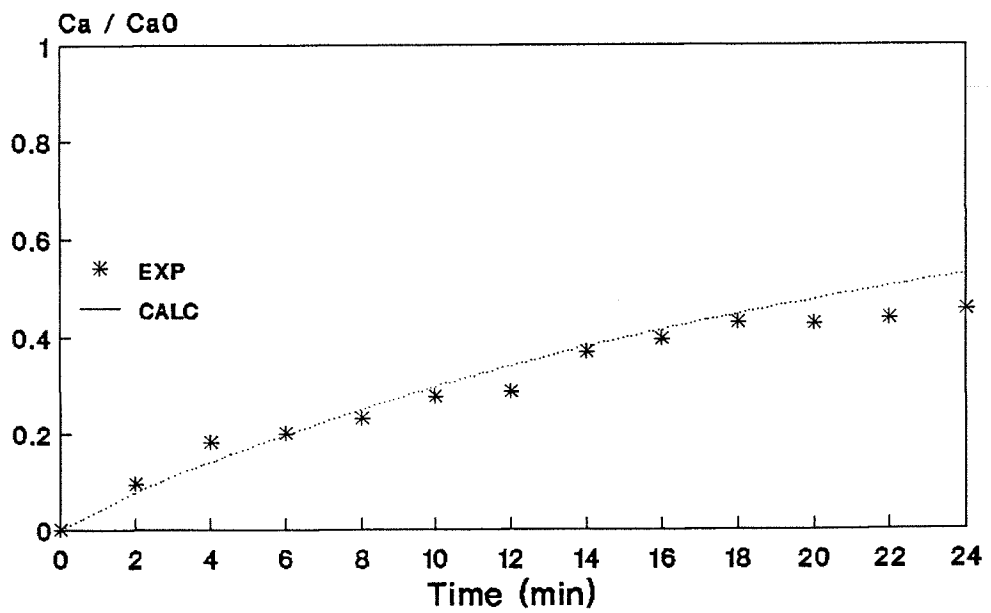
5.2 Discussions

5.2.1 Comparison of Ozone + UV with Ozonation and irradiation

The overall removal of acrylonitrile as a function of time is ploted for u.v. irradiation, ozonation and ozonation + u.v. in Figure 5.3, 5.4, 5.6. The removal is higher for ozone only than ozone/uv, that seems to be due to at low PH value have a direct electrophilic reaction between molecular O_3 and the organic.

According to our mechanism, when O_3 reacts with substances in water, the reaction is a combination of direct reaction with O_3 as well as with the hydroxyl radical. Therefore, the UV/O_3 treatment system employs both oxidation and photolysis and includes direct ozonation, decomposition of O_3 to the hydroxyl radical, direct photolysis of the organic compound. From Figure 5.4 and the mechanism, The results show that the direct reaction of ozone with acrylonitrile is more effective than the O_3/UV(combined O_3 and free radical). It mean ozone is dominant in ozone only and ozone/uv system for treatment of acrylinitrile and acetonitrile.

5.2.2 $H_2O_2/O_3/UV$

Oxidation of AN by O_3/UV in wastewater is a relatively slow process. Adding H_2O_2 up to an H_2O_2 to Acrylonitrile ration of about 5 (mol/mol) to Ozone/UV process ,compared with O_3/UV and H_2O_2/UV shown in Figure 5.6, 5.7, accelerates the oxidation rate and enhance the efficiency of pollutant decomposition shown in Fig 5.11.

Figure 5.10: Decomposition of Acrylonitrile with $H_2O_2/O_3/UV$
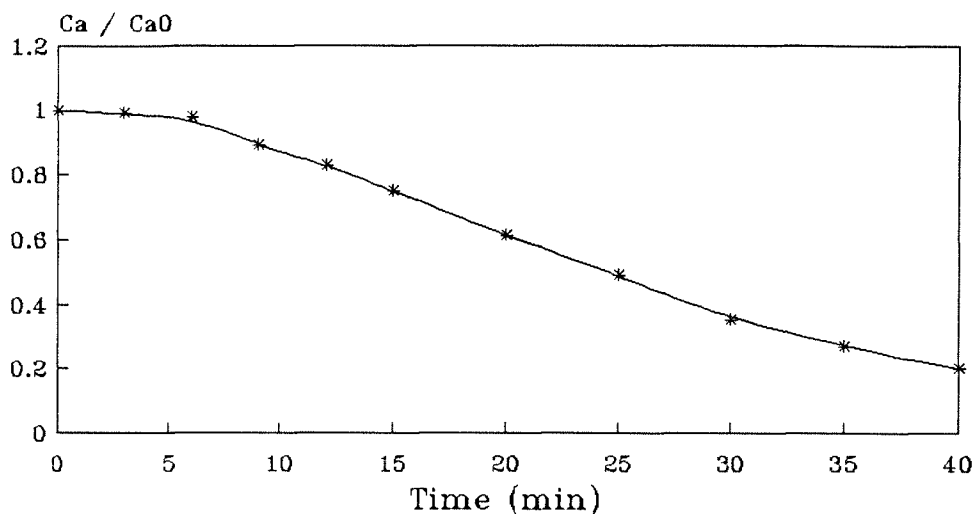
5.2.3 Effect of $H_2O_2/$UV

Experiments with a $H_2O_2/$UV system for the removal of acrylonitrile were performed to determine what factors affect the process. The synergistic effect of H_2O_2 plus UV on the reactionof AN is shown in Figure 5.7 . With H_2O_2 and no UV light, the rate of reaction was negligible. When exposed to UV light with no H_2O_2 present shown in Figure 5.4, a slightly rate of reaction was observed, indicating that UV light can generate free radicals from the organic species. In the presence of both H_2O_2 and uv light, the rate of reaction was increased substantically. The concentration of AN decreased from the initial 200 ppm to 20 ppm. According to our mechanism for this, the result show that the removal is the highest for H_2O_2/UV , that seems to due to

generate reactive free radical (HO_2^-, $OH\cdot$).

5.2.4 Effect of PH for H_2O_2/UV process

The reaction rate of AN was considerably slowed by an alkaline PH shown in Fig 5.12, probably because the hydrogen peroxide decomposed so rapidly under thebasic condition. Hydrogen peroxide is known to undogo base-catalyzed decomposition. One proposed mechanism for the decomposition involves the perhydroxyl(HO_2^-) ion.

$$H_2O_2 + HO_2^- \longrightarrow H_2O + O_2 + OH^-$$
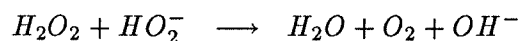
This type of decompositiom is undesirable because it consumes hydrogen peroxid without generating reactive free radical species. For PH values between 3 and 9, reaction rates increased as PH values was decreased.

5.2.5 Effect of Varying Amount of Hydrogen peroxide

In order to completely decompose the pollutants in wastewater, a minimum amout of hydrogen peroxide is necessary tö hasten the oxidation of the organic pollutants to carbon dioxide. This amount was determined by varying the hydrogen peroxide molecular(mol/mol) from 10 to 2.5. Figure 5.13 shows the comparison of efficiency of varying amount of H_2O_2. Table 1 shows that a 90 % reduction of AN was observed at the 5 (mol/mol)H_2O_2. Howere, in all later experiments, 5 (mol/mol) hydrogent peroxide was used to make sure an excess of reagent was present.

Figure 5.11: Effect of PH on decomposition of AN
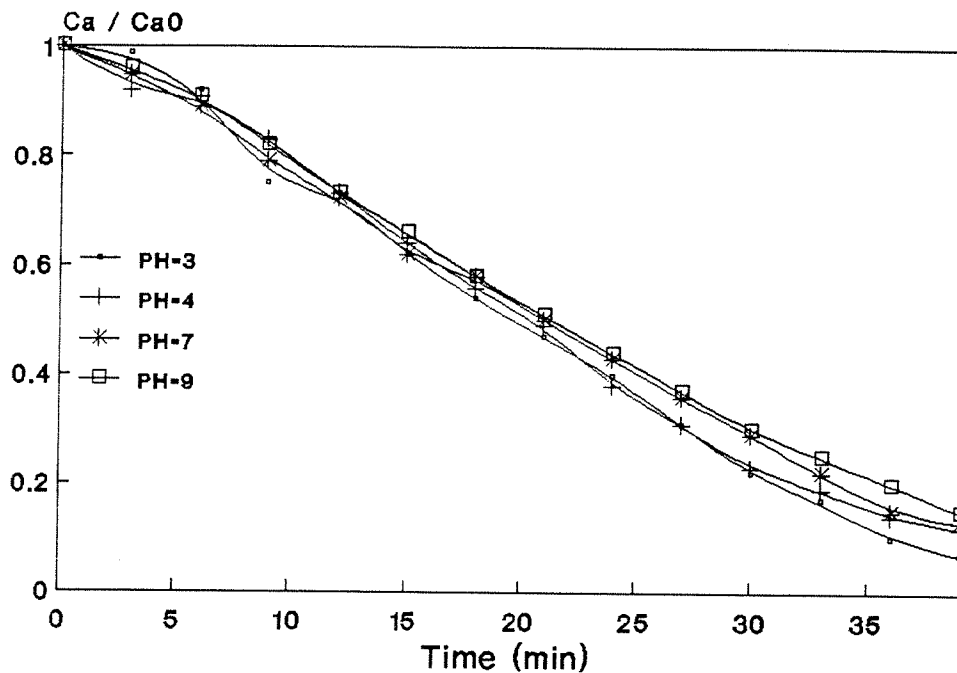
Figure 5.12: Comparison of varying amount of hydrogen peroxide
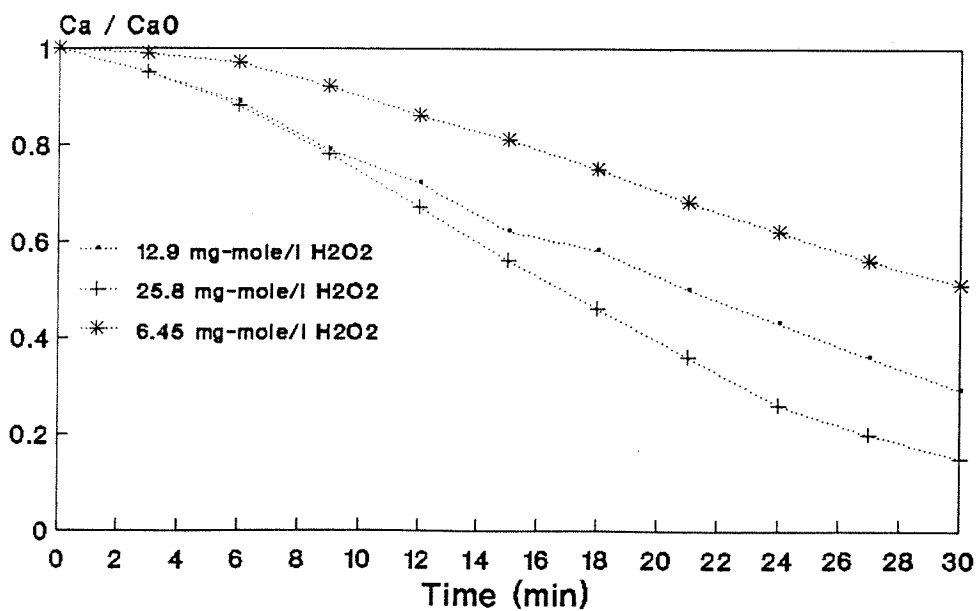
5.3 Conclusions

Destruction of Acrylonitrile, Acetonnitrile in water at several hundred concentrations by reaction with hydrogen peroxide and ultraviolet light has been shown to be significantly faster than reaction with either ozone or ozone/uv. Table 2, Table 3 show a mechanism which was proposed and detailed rate constants which were obtained. The experimental data indicate that a H_2O_2/UV radiation system, an O_3/UV radiation system, or a H_2O_2/O_3/UV radiation system can reduce the Acrylonitrile, Acetonitrile in the wastewater. A selection of the proper one should be based on economics, process flexibility, process effectiveness, and ease of operation.

Table - 5.1 Rate constants of acrylonitrile solved by computer

Reactions	Rate Constants	Units
$O_{2l} \xrightarrow{K_{LO_2}A} O_{2g}$	$K_{LO_2}A = 7.98$	$(min)^{-1}$
$O_{3l} \xrightarrow{K_{LO_3}A} O_{3g}$	$K_{LO_3}A = 0.39$	$(min)^{-1}$
$O_2 + h\nu \underset{k_{IO_2b}}{\overset{k_{IO_2}I}{\rightleftharpoons}} O_2^*$	$k_{IO_2}I = 5.55 \times 10^{-2}$	$(min)^{-1}$
	$k_{IO_2b} = 8.03 \times 10^3$	$(min)^{-1}$
$A + h\nu \underset{k_3}{\overset{k_{IA}I}{\rightleftharpoons}} A^* \xrightarrow{k_2} $Decomposition product	$k_{IA}I = 3.13 \times 10^{-3}$	$(min)^{-1}$
	$k_2 = 5.65 \times 10^{-2}$	$(min)^{-1}$
	$k_3 = 3.7 \times 10$	$(min)^{-1}$
$A + O_2^* \xrightarrow{k_6}$Decomposition product	$k_6 = 2.69 \times 10^{-6}$	$(mg - mole/l)^{-1}(min)^{-1}$
$A + O_3 \xrightarrow{k_1}$Decomposition product	$k_1 = 3.5$	$(mg - mole/l)^{-1}(min)^{-1}$
$H_2O_2 \xrightarrow[h\nu]{k_{IH_2O_2}I} 2OH\cdot$	$k_{IH_2O_2}I = 5.4 \times 10^{-3}$	$(min)^{-1}$
$H_2O_2 + OH\cdot \xrightarrow{k_{10f}} HO_2\cdot + H_2O$	$k_{10f} = 1.62 \times 10^6$	$(mg - mole/l)^{-1}(min)^{-1}$
$H_2O_2 + HO_2\cdot \xrightarrow{k_{11f}} OH\cdot + O_2 + H_2O$	$k_{11f} = 0.222$	$(mg - mole/l)^{-1}(min)^{-1}$
$OH\cdot + OH\cdot \xrightarrow{k_{14}} H_2O_2$	$k_{14} = 2.4 \times 10^8$	$(mg - mole/l)^{-1}(min)^{-1}$
$HO_2\cdot + HO_2\cdot \xrightarrow{k_{15}} H_2O_2 + O_2$	$k_{15} = 4.98 \times 10^4$	$(mg - mole/l)^{-1}(min)^{-1}$
$OH\cdot + HO_2\cdot \xrightarrow{k_{16}} H_2O + O_2$	$k_{16} = 9.22 \times 10^8$	$(mg - mole/l)^{-1}(min)^{-1}$
$A + OH\cdot \xrightarrow{k_4}$Decomposition product	$k_4 = 9.8 \times 10^3$	$(mg - mole/l)^{-1}(min)^{-1}$
$A + HO_2\cdot \xrightarrow{k_5}$Decomposition product	$k_5 = 0.1864$	$(mg - mole/l)^{-1}(min)^{-1}$
$O_3 + H_2O \xrightarrow[h\nu]{k_{IO_3}I} O_2 + 2OH\cdot$	$k_{IO_3}I = 4.6 \times 10^{-2}$	$(min)^{-1}$
$O_3 + OH\cdot \xrightarrow{k_{8f}} O_2 + HO_2\cdot$	$k_{8f} = 1.89 \times 10^5$	$(mg - mole/l)^{-1}(min)^{-1}$
$O_3 + HO_2\cdot \xrightarrow{k_{12f}} 2O_2 + OH\cdot$	$k_{12f} = 2.4 \times 10^8$	$(mg - mole/l)^{-1}(min)^{-1}$

Table - 5.2 Rate constants of acetonitrile solved by computer

Reactions	Rate Constants	Units
$O_{2l} \xrightarrow{K_{LO_2}A} O_{2g}$	$K_{LO_2}A = 6.4$	$(min)^{-1}$
$O_{3l} \xrightarrow{K_{LO_3}A} O_{3g}$	$K_{LO_3}A = 0.39$	$(min)^{-1}$
$O_2 + h\nu \underset{k_{IO_2b}}{\overset{k_{IO_2}I}{\rightleftharpoons}} O_2^*$	$k_{IO_2}I = 3.3 \times 10^{-2}$ $k_{IO_2b} = 8.6 \times 10^3$	$(min)^{-1}$ $(min)^{-1}$
$A + h\nu \underset{k_3}{\overset{k_{IA}I}{\rightleftharpoons}} A^* \xrightarrow{k_2}$ Decomposition product	$k_{IA}I = 3.1 \times 10^{-3}$ $k_2 = 5.65 \times 10^{-2}$ $k_3 = 3.7 \times 10$	$(min)^{-1}$ $(min)^{-1}$ $(min)^{-1}$
$A + O_2^* \xrightarrow{k_6}$ Decomposition product	$k_6 = 8.0 \times 10^{-3}$	$(mg - mole/l)^{-1}(min)^{-1}$
$A + O_3 \xrightarrow{k_1}$ Decomposition product	$k_1 = 3.37$	$(mg - mole/l)^{-1}(min)^{-1}$
$H_2O_2 \underset{h\nu}{\overset{k_{IH_2O_2}I}{\longrightarrow}} 2OH \cdot$	$k_{IH_2O_2}I = 5.4 \times 10^{-3}$	$(min)^{-1}$
$H_2O_2 + OH \cdot \xrightarrow{k_{10f}} HO_2 \cdot + H_2O$	$k_{10f} = 1.62 \times 10^6$	$(mg - mole/l)^{-1}(min)^{-1}$
$H_2O_2 + HO_2 \cdot \xrightarrow{k_{11f}} OH \cdot + O_2 + H_2O$	$k_{11f} = 0.222$	$(mg - mole/l)^{-1}(min)^{-1}$
$OH \cdot + OH \cdot \xrightarrow{k_{14}} H_2O_2$	$k_{14} = 2.4 \times 10^8$	$(mg - mole/l)^{-1}(min)^{-1}$
$HO_2 \cdot + HO_2 \cdot \xrightarrow{k_{15}} H_2O_2 + O_2$	$k_{15} = 4.98 \times 10^4$	$(mg - mole/l)^{-1}(min)^{-1}$
$OH \cdot + HO_2 \cdot \xrightarrow{k_{16}} H_2O + O_2$	$k_{16} = 9.22 \times 10^8$	$(mg - mole/l)^{-1}(min)^{-1}$
$A + OH \cdot \xrightarrow{k_4}$ Decomposition product	$k_4 = 5.4 \times 10^2$	$(mg - mole/l)^{-1}(min)^{-1}$
$A + HO_2 \cdot \xrightarrow{k_5}$ Decomposition product	$k_5 = 6.0 \times 10^{-3}$	$(mg - mole/l)^{-1}(min)^{-1}$
$O_3 + H_2O \underset{h\nu}{\overset{k_{IO_3}I}{\longrightarrow}} O_2 + 2OH \cdot$	$k_{IO_3}I = 3.9 \times 10^{-3}$	$(min)^{-1}$
$O_3 + OH \cdot \xrightarrow{k_{8f}} O_2 + HO_2 \cdot$	$k_{8f} = 1.6 \times 10^6$	$(mg - mole/l)^{-1}(min)^{-1}$
$O_3 + HO_2 \cdot \xrightarrow{k_{12f}} 2O_2 + OH \cdot$	$k_{12f} = 5.1 \times 10^5$	$(mg - mole/l)^{-1}(min)^{-1}$

Appendix A

Literature Cited

A.1 Literature Cited

1 Rothmund, V.; Burgstaller, A. Monatsh. Chem. 1913, 34, 665.

2 Staehelin, J.; Hoigne, J. Environ. Sci. Technol. 1982, 16, 676.

3 Forni, L.; Bahnemann, D.; Hart, E. J. J. Phys. Chem. 1982, 86,255.

4 Weiss, J. Trans. Faraday Soc. 1935, 668.

5 Sotelo, J.L.;Beltran, F.J.;Benitez, F.J.;Beltran-Heredia,J. Ind. Eng. Chem. Res. 1987, 26, 39.

6 Robert W.Legan, *Ultraviolet light taken on CPI role* , J. Chem. Engineering, January 25, 1982.

7 N.H. Glaze & J.W.Kang, Journal AWWA, May 1988.

8 Sterns, A.A.; Symons, J.M.,J.Am. Water Works Assoc. 1977, 69, 546.

9 Symons, J.M. *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*, U.S. Environmental Protection Agency, EPA-600/2-81-156, 1981.

10 Lee, M.K. See, G.G.;Wynveen, R.A.,*Reaction Kinetics of UV/Ozone with Organic Compounds in Hospital Wastewater*; Presented at the Symposium on Advanced Ozone Technology; International Ozone Institute; Cleveland, OH, 1977.

11 McCarthy, J. J.; Cowen, W.F.; Chian,E.S.K., Proc. Ind. Waste Conf.1977, 32nd, 310-324.

12 Prengle, H.W., J. Environ. Sci. Technol. 1983, 17, 743-747.

13 Lee, M.K.,*Chemistry of Water Reuse; Ann Arbor Science: Stoneham, MA,1981;445-464.*

14 *Leitus, E.;Zeff, J.D.; Smith, M.M.;Crosby, D.G.,* An Investigation into the Chemistry of the UV/Ozone Purification Process; *final report to the National Science Foundation on Grant ENV 76-24652; U.S. Government Printing Office: Washington, DC. Feb. 1980.*

15 *Eriks Leitis, Jack D. Ieff, and Matthen M. Smith, Chemistry and Application of Ozone and Ozone/UV light for Water Reuse 2, OWR/RU-83/5, U.S. Dept. of Interior, 1983.*

16 *Mirat D. Gurol and Robert Vatistas,* Oxidation of Phenolic Compounds by Ozone and Ozone/UV Radiation: A Comparative Study, *Water res. 21, 895-900, 1987.*

17 *H.W. Prengle, Jr. Environ. Sci. Technol., 17, 74-747, 1983.*

18 *Gary R.,peyton & William H.Glaze,* Destruction of Pollutions in Water with Ozone in Combination with Ultraviolet Radiation. 3. Photolysis of Aqueous Ozone, *Environ. Sci Technol., Vol. 22, No. 7, 1988.*

19 *Staehelin J. & Hoigne, J.* Decomposition of Ozone in water: Rate of Initiation by Hydroxide Ion and Hydrogen Peroxide. *Envir. Sci & Technol.,16:676, 1982.*

20 *Buhler, R. E.; Staehelin J.; & Hoigne, J.* Ozone Decomposition in Water Studiede

by Pulse radiolysis 1. HO_2/O_2 and HO_3/O_3 as Intermediates, *Jr. Phys. Chem., 88:2560, 1984.*

21 *Staehelin, J.; Buhler, R.E.; & Hoigne, J.* Ozone decomposition in Water Studied by Pulse Radiolysis. 2. OH and HO_4 as Chain Intermediates. Jour. Phys. Chem., 88:5999, 1984.

22 Hochanadel, *Photolysis of Hydrogen Peroxide*, Radiation Research Vol.17, 286-301.

23 Yoshiro Ogato, Kohtaro Tomizawa, and Kaoru Takagi, *Photo-Oxidation of formic, acetic, and propionic acides with aqueous hydrogen peroxide*, Can. J. Chem. Vol. 59, 1981.

24 B.A.Weir, D.W. Sundstrom, and H. E. Klei, *Destruction of Benzene by Ultra-violet Light-Catalyzed Oxidation with Hydrogen Peroxide*, Hazardous Waste & Hazardous Materials Vol.4, Number 2, 1987, Mary Ann Liebert Inc., Publishers.

25 Yocum, F.H. Presented at 86th National Meeting of American Institute of Chemical Engineers, April 1-5, 1979.

26 Horak, J.; Pasek, J.Design of Industrial Chemical Reactors from Laboratory Data; Heyden: Philadelphia, 1978; p358.