**The Hong Kong Polytechnic University**

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# LINURON DEGRADATION BY PHOTO-AIDED OXIDATION PROCESSES IN AQUEOUS PHASE - - KINETIC STUDY AND REACTION MECHANISMS

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# CERTIFICATE OF ORIGINALITY

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it reproduces no material previously published or written, nor material that has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text.

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# ABSTRACT

The widespread application of herbicides as a routine practice to control weed growth has led to increasing environmental concerns in the past decades because of their low biodegradability and long-term persistence in soil, which makes them ubiquitous. Most herbicides are diffused into aquatic environment via agricultural runoff or leaching. Linuron (N-(3, 4-dichlorophenyl)-N'-methoxy-N'-methylurea) (LNR), one of the most commercialized phenylurea herbicides, has received particular attention in recent years due to the toxicity, being frequently detected in the surface and underground waters, and possible endocrine disrupting properties of LNR and/or its metabolites. Till now, little is known about the degradability and reaction products of LNR by Vis (visible light)-induced photocatalysis. The knowledge regarding the LNR decomposition by UV, ozonation, and UV/ozone processes is far from complete although UV and ozonation has shown good performance in terms of LNR decay in some studies. In particular, the information about the intermediates and end products remains limited. Therefore, the aqueous degradation of LNR has been investigated by UV, ozonation, UV/ozone and $TiO_2/H_2O_2/Vis$ processes.

The investigation was conducted under idealized conditions and has taken into account both degradation kinetics and reaction mechanisms. It has been found that ozonation and $UV/O_3$ are pH-dependent while UV is pH-independent in terms of LNR decomposition. Experimental results also indicated overall rate constants increased exponentially with pH above 9.0 while the increase of rate constants with pH below 9 is insignificant in sole-$O_3$ system. In UV photolysis study, the LNR

decay rate constant is linearly increased with the intensity of light. Linear models were proposed on the basis of reaction kinetics of LNR decay by these three processes. All dominant parameters such as quantum yield ($\Phi_{LNR}$), $k_{OOH}$ (rate constant for the formation of free radical $HOO^{\bullet-}$ from ozone decomposition at high pH), rate constant of linuron with ozone ($k_{o_3,LNR}$), rate constant of linuron with hydroxyl radical ($k_{OH,LNR}$), and α (the ratio of the production rate of $HO^{\bullet}$ and the decay rate of ozone in UV/$O_3$ system), involved in the three processes were determined with the aid of proposed linear models. The effect of various anions on the performance of ozonation has also been examined.

Eight intermediates escaped from previous studies were detected in the sole-UV system in this study. $N$-terminus demethoxylation, photohydrolysis with dechlorination, hydroxylation on the benzene ring and $N$-terminus demethylation were found to be the major mechanisms in the linuron decay under the irradiation of UV at 254 nm while $N$-terminus demethoxylation, dechlorination and hydroxylation on the benzene ring were observed to be involved in the ozonation process. Different decay pathways were proposed based on the identified intermediates in the studied three processes. The release of chlorine and nitrogen as well as mineralization has also been quantified. UV/$O_3$ has demonstrated the best performance among these three processes in terms of LNR decay, mineralization, dechlorination and denitrogenation.

Furthermore, the degradation of LNR in $TiO_2$ suspension has been studied, with and without the aid of $H_2O_2$ under the irradiation of visible light. The removal of LNR in $TiO_2$-P25 suspension can be increased from 10% to nearly 100% after 3 hr of

reaction by simply adding $H_2O_2$ to the process. Various types of $TiO_2$ including anatase, rutile and $TiO_2$-P25 exhibited different photocatalytic activities on LNR decay, while their performances were strongly dependent on the presence and/or absence of $H_2O_2$. The $H_2O_2$-assisted $TiO_2$ photocatalysis using visible light could be optimized by adjusting $TiO_2$ dosage, initial concentration of $H_2O_2$ and the initial pH of the system. The LNR decay rate, generally, increased with the increase of $TiO_2$ dosage, but too high the $TiO_2$ dosage was not cost-effective due to the light attenuation. The initial $H_2O_2$ concentration in the tested range did not show a significant influence on the reaction rate. A neutral initial pH level was found to be favorable for the $H_2O_2$-assisted photocatalysis under visible light, which made the proposed process more attractive for real application.

The reaction mechanism of LNR degradation by the $TiO_2/H_2O_2/Vis$ process has been also examined through the investigation on the effects of various radical scavengers, monitoring the generation of photocurrent, examining the performance of other metal oxides in place of $TiO_2$ in this system, and comparing the intermediates and decay pathways of LNR by UV-$TiO_2$ and $TiO_2/H_2O_2/Vis$ processes with 16 and 17 intermediates identified, respectively. The generation of electrons was first confirmed by monitoring photocurrent with a $TiO_2$-coated ITO electrode immersed in $H_2O_2$ solution under the irradiation of visible light. It has been revealed that demethoxylation and demethylation through alkylic-oxidation is the major mechanism of LNR degradation while dechlorination (hydroxylation at the chlorine site) and direct hydroxylation on the benzene ring is minor in both processes. The mineralization and the release of chlorine and nitrogen have been also studied.

# Publications arising from the thesis

## *Journal Papers*

**1. Rao Y. F.**, Chu W., A New Approach to Quantify the Degradation Kinetics of Linuron with UV, Ozonation and UV/$O_3$ processes, *Chemosphere* 2009, 74(11), 1444-1449.

**2. Rao Y. F.**, Chu W., Reaction Mechanism of linuron degradation in $TiO_2$ suspension under visible light irradiation with the assistance of $H_2O_2$, *Environmental Science & Technology* 2009, 43, 6183-6189.

**3. Rao Y. F.**, Chu W. Linuron degradation in aqueous semiconductor suspension under visible light irradiation-with and without $H_2O_2$, *Chemical Engineering Journal*, 2010, 158 (2), 181-187.

**4. Rao Y. F.**, Chu W. Degradation of linuron by UV, Ozonation, and UV/$O_3$ processes---Effect of Anions and Reaction Mechanism *Journal of Hazardous Materials*, 2010, 180 (1-3), 514-523.

## *Conference Presentation*

1. **Rao Y. F.,** Chu W., Modeling the Reaction Kinetics and Product Identification of Linuron Decay by UV/$O_3$ Process, *The 5th IWA Specialist Conference/ 10th IOA-EA3G Berlin Conference on Oxidation Technologies for Water and Wastewater Treatment*, 30 March-02 April, Berlin, Germany, 2009.

# ACKNOWLEDGEMENTS

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at 254 nm.

concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0,
R denotes rutile, A represents anatase.).

for UV/TiO$_2$ system, six 350 nm UV lamps were used).

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# Chapter 1  Introduction

## 1.1 Background

Around one-fifth of the world's population has no access to safe water while two-fifths suffer the consequences of unacceptable sanitary conditions (United Nations Educational, 2003). More than one-third of the Earth's accessible renewable freshwater is used for agricultural, industrial, and domestic purposes, and the majority of these activities result in this precious water supply being polluted with numerous synthetic and geogenic compounds (Schwarzenbach et al., 2006). Therefore, it is not surprising that water-environment problems arising from chemical contamination have received increasing worldwide concerns in the past decade. Undoubtedly, micropollutants such as herbicides and pesticides coming from agricultural practice play an important role in water pollution. It has been reported that 140 million tons of fertilizers and several million tons of pesticides are applied every year (FAO, 2006). Unfortunately, less than 1% of total applied herbicides can reach their intended targets with the dominant majority being diffused into the aquatic environment via agricultural runoff or leaching (Pimentel, 1995). Herbicides have thus become some of the most frequently detected organic pollutants in natural waters.

Linuron (N-(3, 4-dichlorophenyl)-N'-methoxy-N'-methylurea) (LNR), one of the most commercialized phenylurea herbicides, has been widely used to control annual and perennial broadleaf and grassy weeds by inhibiting photosynthesis upon absorption in the roots of a wide range of crops such as soybean, cotton, potato, corn,

winter wheat, asparagus, carrot and various fruit. LNR is moderately persistent in soil with a half-life ranging from 38 to 67 days (Katsumata et al., 2005). LNR is frequently detected in surface and ground waters near or below the areas with intensive use. In one particularly extreme case, LNR was detected in a drinking-water well in concentration of up to 2.8 mg $L^{-1}$ (Caux et al., 1998). LNR and some of its naturally decayed intermediates (such as chloroaniline) have been suspected as a possible human carcinogen and endocrine disruptor (Lintelmann et al., 2003, Orton et al., 2009). LNR is also highly toxic to non-target aquatic organisms such as fish and shellfish. The LC50 for linuron in trout and bluegill is 16 mg/l, and 40 mg/l in crawfish (Wagner, 1983), which entails the design of effective, cost-efficient, environmentally friendly treatment techniques to eliminate LNR and its intermediates in aqueous phase.

As a result, LNR has succumbed to the increasing investigation of its treatability by various processes. It has been reported that physical treatments such as adsorption (Rodriguez-Cruz et al., 2008) and membrane filtration (Benitez et al., 2009) can successfully remove LNR from wastewater and water. However, the adsorption capacity of sorbent and retention capacity of membrane both decline due to interference with natural organic matter. In addition, membranes may also suffer fouling problem. For their successful application, both the adsorption and filtration processes thus entail regeneration strategy, which results in high operation cost of these two processes. Biological methods (Dejonghe et al., 2003; Sorensen et al., 2005) have also demonstrated fair performance in terms of decomposing LNR. The bacteria harboring the potential to mineralize LNR have been successfully isolated. However, biological degradation of LNR generally requires a long time and the operation of

biological process is quite delicate and involves intricate techniques since it is well-known that the activity of bacteria is extremely condition-dependent. These may rationalize the growing attention that AOPs have received in the past decade. AOPs are based on the *in situ* production of the highly-reactive hydroxyl radicals that can efficiently oxidize organic compounds to $CO_2$ and $H_2O$ under mild experimental conditions. Due to the high reactivity of hydroxyl radicals (redox standard potential 2.8 eV *versus* NHE), their attack is non-selective, which is especially useful for the treatment of wastewater containing recalcitrant organic pollutants. It therefore comes as no surprise that LNR has also experienced varied AOPs such as photo-Fenton procedure (Benitez et al., 2007b; Farre et al., 2007), $O_3/H_2O_2$ (Benitez et al., 2007a; Chen et al., 2008), and photocatalysis (Lopez et al., 2005) under a wide range of experimental conditions. A major part of these studies, however, focuses on degradation kinetics of LNR. If the fate of the resulting products remains unanswered, the treatment process cannot be proposed as a trouble-free method since the decay of the parent compounds may result in the generation of more toxic organics than their parent compounds. Hence, the major objective of this study is to design new environmentally friendly treatment process for the degradation and mineralization of LNR.

## 1.2 Objectives of Study

In this study, the use of well-established treatment processes such as UV photolysis, ozonation and $UV/O_3$, as well as a newly-developed treatment technology---$TiO_2/H_2O_2$/vis (visible light) is studied to evaluate their potential to degrade and mineralize LNR, since detailed information is limited concerning the treatability of LNR by these methods, and the respective process design.

The primary aim of this study is to investigate the use of different treatment processes for removal of the herbicide before discharging to the publics. The specific objectives of this study are as following:

i)   To examine the degradation kinetics of LNR by UV photolysis, ozonation, and UV/$O_3$;

ii)  To establish a treatment model for each process by the application of a quantum yield model for the UV process, a direct and indirect-radical oxidation model for the ozonation or UV/$O_3$ process;

iii) To study the decay pathways of LNR by UV photolysis, ozonation, and UV combined with ozone;

iv)  To investigate the feasibility of degrading and mineralizing LNR by $TiO_2/H_2O_2/Vis$ process;

v)   To explore the degradation mechanism of LNR in $TiO_2$ suspension under the irradiation of visible light with the assistance of $H_2O_2$ via monitoring the generation of photocurrent and comparing the products and decay pathways of LNR by UV/$TiO_2$ and $TiO_2/H_2O_2/Vis$ processes;

vi)  To identify the parameters that affect the performance of these processes such as initial pH level, ozone dosage, light intensities, $TiO_2$ dosage, $H_2O_2$ dosage, and initial LNR concentration; and

vii) To evaluate the efficiency of mineralization and dechlorination of each process.

## 1.3 Scope of Study

This thesis consists of eight chapters. The present chapter covers the background, objectives and organization of this thesis.

Literature review is presented in Chapter 2 where background information concerning LNR is described in detail and ozone-based treatment processes are given in-depth discussion. In particular, the theory of heterogeneous photocatalysis using $TiO_2$ as photocatalyst is discussed. Furthermore, a brief review of the efforts involved with shifting the optical response of $TiO_2$ from UV to visible spectral range is also presented in this chapter. Finally, the studies on the system of $TiO_2/H_2O_2/Vis$ are summarized.

Chapter 3 involves the detailed description of methodology.

A new approach to quantify the degradation kinetics of LNR by UV photolysis, ozonation, and $UV/O_3$ processes will be presented in chapter 4 based on the investigation on the effect of varied parameters on the LNR decomposition.

In Chapter 5, the effects of pH values on the performance of UV photolysis, ozonation, and $UV/O_3$ processes and varied anions on the performance of ozonation are investigated in terms of LNR decay rate. Furthermore, main intermediates of LNR decay by these three processes are identified by LC/MS, and decay pathways are proposed accordingly in this chapter.

Chapter 6 discusses the feasibility of LNR decomposition in semiconductor suspension under the irradiation of visible light with and without $H_2O_2$. The

influences of varied parameters such as the type of $TiO_2$, initial pH level, $H_2O_2$ concentration, $TiO_2$ dosage, initial concentration of LNR on the performance of this process are given detailed description.

Chapter 7 presents in-depth investigation on the degradation mechanism of LNR by $TiO_2/H_2O_2/Vis$ process through examining the effects of various radical scavengers and the performance of other metal oxides in place of $TiO_2$ in this system, monitoring the generation of photocurrent, and comparing the intermediates and decay pathways of LNR by UV-$TiO_2$ and $TiO_2/H_2O_2/Vis$ processes.

In Chapter 8, conclusions are presented in company with the limitation of this work and the recommendations for future work.

# Chapter 2  Literature Review

## 2.1 Wastewater Treatment Processes

2.1.1 UV photolysis

There is a long-standing interest in the use of photochemical reactions as a tool in the degradation of organic compounds such as herbicides  (Crosby and Tang, 1969; Hayase and Takahashi, 1983; Funakoshi et al., 1988;  Jirkovsky et al., 1997; Chan and Chu, 2005), dye or dye derivatives (Chu and Tsui, 2002; Rezaee et al., 2008; Ma et al., 2009), antibiotics (Edhlund et al., 2006), aromatic amino acid (Jin et al., 1995) and other organic pollutants (Lau et al., 2005; Chu and Jia, 2009). In order to obtain a deep insight into the photolysis mechanism of organic compounds, this review sets out with the basic principles of photochemical reaction. It was reported that Alexander the Great was one of the first exploiters of a photochemical process when he equipped his troops with a treated cloth 'wristwatch' which changed color under the influence of the sun. However, it is during the $20^{th}$ century that a systematic understanding of photochemical processes has developed (Wayne, 1970).

(1)  The Laws of photochemistry

All photochemical processes obey four photochemical laws which can be applied generally in photochemistry (Calvert and Pitts, 1966; Rabek, 1982):

a.  Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule;

b.  The absorption of light by a molecule is a one-quantum process, so that the sum of the primary process quantum yields $\Phi$ must be unity;

c.  Each photon or quantum absorbed by a molecule has a certain probability of populating either the lowest excited singlet state ($S_1$) or the lowest triplet state ($T_1$); and

d.   The lowest excited signlet ($S_1$) and triplet ($T_1$) states are the starting levels (in solution) of most organic photochemical processes.

 (2) The fates of electronic excitation

Photochemical processes involving the absorption of light can be divided into the act of absorption, which falls within the domain of spectroscopy, and the subsequent fate of the electronically excited species formed. In this study, the latter is the major concern.

Figure 2-1 illustrates, in simplified form, the various paths by which an electronically excited species may lose its energy (Wayne, 1988).

Energy transfer, corresponding to paths (iv) and (v) in the Figure 2-1, leads to excited species, which can then join any of the general processes.

Photochemical change can come about either as a result of dissociation of the absorbing molecule into reactive fragments (process i), or as a result of direct reaction of the electronically excited species (process ii); electronically excited species may also undergo spontaneous isomerization or rearrangement, as indicated by path (iii). A special case of dissociation is that of ionization, shown as path (viii).

Physical quenching
AB

Luminescence
AB + hv   (vii) | +M        AB⁺+ e
          Ionization
(vi)        (viii)

AB⁺
Intramolecular      (v)    AB*    (i)     A + B
energy transfer                     Dissociation
(radiationless transition)
+CD              +E
(iv)        (ii)
(iii)

AB + CD‡                    AE + B or ABE
Intermolecular                    Direct reaction
energy transfer      BA
Isomerization or Rearrangement
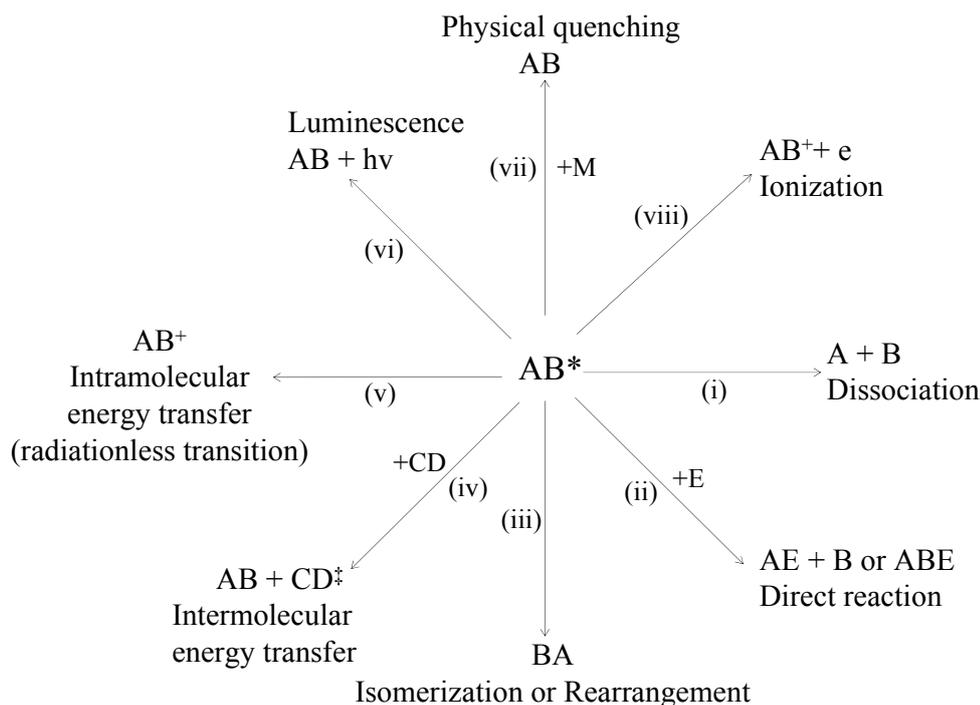
Figure 2-1: The possible routes to loss of photochemically excited molecule. The use of the symbols *, +, and ‡ is only intended to illustrate the presence of electronic excitation and not necessarilly differences in states

Radiative loss of excitation energy (path vi) generates the phenomenon of luminescence: the terms *fluorescence* or *phosphorescence* are used to describe particular aspects of the general phenomenon.

Path (vii) demonstrated in Figure 2-1 is physical quenching. In this process an atom or molecule M can relieve AB* of its excess energy. Physical quenching differs only formally from intermolecular energy transfer in that M, which must initially take up some excitation energy, does not make its increased energy felt in terms of its chemical behavior. The electronic excitation of AB* is, in fact, frequently converted to translational or vibrational excitation of M.

(3) Photochemical reactions

Electronically excited molecules are highly energetic and have the potential for internal isomerization or rearrangement or reaction with other molecular species in the system. The general types of photochemical reaction are summarized as following (Wells, 1972):

**a. Photoreduction**

The photoreduction occurs via the $T_1$ state of the photo-excited carbonyl compound in the great majority of cases. Molecules in this state react by abstracting hydrogen from a substrate species RH to give a hydroxylmethyl radical and a radical $R^{\bullet}$:

$$R_2{}'C{=}O\ (T_1) + RH \rightarrow R_2{}'C^{\bullet}OH + R^{\bullet} \tag{2-1}$$

The final reaction products are formed by self-combination and cross-combination reactions of the radicals produced in the hydrogen abstraction step. The efficiency of the hydrogen abstraction step is dependent upon factors such as the nature of the $T_1$ state of the carbonyl compound, the structure of the carbonyl compound, the dissociation energy of the R–H bond and the type of solvent used.

The hydrogen abstraction described above is an intermolecular process. Hydrogen abstraction is also one of the most important intramolecular reactions of excited species. The intramolecular abstraction of H is of particular importance in the photochemistry of most carbonyl compounds, since it is part of the sequence of events leading to the 'Norrish Type II' fragmentation. Equation 2-2 shows a six-membered transition state in the Type II fission of a ketone: this cyclic intermediate favors intramolecular H-abstraction over intermolecular abreaction from the solvent.

$$CH_3CH_2CH_2COCH_3 + h\nu \longrightarrow H_2C \overset{\overset{H \; \text{------} \; O}{\diagdown}}{\underset{CH_2 \text{------} CH_2}{\diagup}} C\text{---}CH_3 \longrightarrow CH_2\!=\!CH_2 + CH_2COHCH_3$$

(2-2)
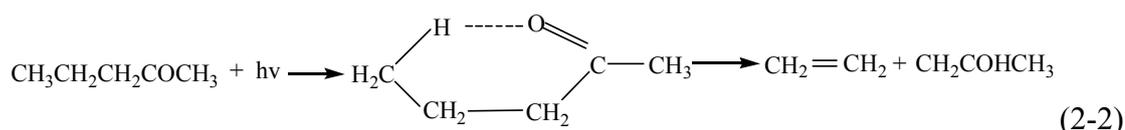
**b. Photodimerization**

Photodimerization involves the combination of an electronically excited molecule with a same ground state molecule to give a 1:1 photo-adduct. It has been reported that the dimerization pathway is the principal reaction during the photolysis process of butylated hydroxylanisole (BHA) at 254 nm, leading to the high yield of intermediate di-BHA (Lau et al., 2007).

**c. Photo-addition**

Photo-addition may be defined as the combination of an electronically excited molecule with a different ground state molecule to give a 1:1 photo-adduct.

**d. Photo-oxidation**

Irradiation of organic compounds in the presence of a sensitizer and oxygen can lead to the involvement of oxygen in the photoreaction and the formation of oxygenated products. The presence of a sensitizer is believed to be necessary to the reaction and normally the photosensitized oxidations proceed via the $T_1$ state of the sensitizer. The sensitizer acts in one of the two ways --- either by abstracting hydrogen from the substrate to form radicals which subsequently react with the oxygen ( Type I process) or by activating the oxygen so that a direct reaction can happen between oxygen and the substrate (Type II process).

The generalized mechanism for the Type I process is as follows:

$$\text{sens} + h\nu \rightarrow \text{sens (S}_1) \rightarrow \text{sens (T}_1) \tag{2-3}$$

$$\text{sens (T}_1) + \text{RH} \rightarrow {}^\bullet\text{sens-H} + \text{R}^\bullet \tag{2-4}$$

$$\text{R}^\bullet + \text{O}_2 \rightarrow \text{RO}_2{}^\bullet \tag{2-5}$$

$$\text{RO}_2{}^\bullet + \text{RH} \rightarrow \text{ROOH} + \text{R}^\bullet \tag{2-6}$$

$$\text{RO}_2{}^\bullet + {}^\bullet\text{sens-H} \rightarrow \text{ROOH} + \text{sens} \tag{2-7}$$

In Type II photo-oxidations the reaction between oxygen and the organic substrate may occur either when (1) the oxygen is complexed with the sensitizer or when (2) the oxygen is in the $S_1$ state formed by energy transfer from the sensitizer. The two possible mechanisms for the Type II photo-oxidation are given below:

*Type II (1)* $\quad \text{sens} + h\nu \rightarrow \text{sens (S}_1) \rightarrow \text{sens (T}_1)$ $\hfill$ (2-8)

$$\text{sens (T}_1) + \text{O}_2 \rightarrow {}^\bullet\text{sens-O-O}^\bullet \tag{2-9}$$

$$^\bullet\text{sens-O-O}^\bullet + \text{M} \rightarrow \text{sens} + \text{MO}_2 \tag{2-10}$$

*Type II (2)* $\quad \text{sens} + h\nu \rightarrow \text{sens (S}_1) \rightarrow \text{sens (T}_1)$ $\hfill$ (2-11)

$$\text{sens (T}_1) + \text{O}_2 \rightarrow \text{sens} + \text{O}_2 \text{ (S}_1) \tag{2-12}$$

$$\text{O}_2 \text{ (S}_1) + \text{M} \rightarrow \text{MO}_2 \tag{2-13}$$
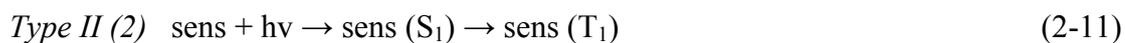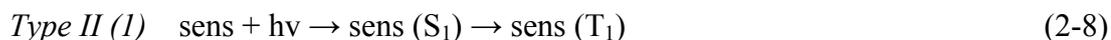
However, it has been reported photo-oxidation of organic compounds can also proceed in the absence of any sensitizer under the UV irradiation of 254 nm (Jin et al., 1995). In their study, the tyrosine triplet state ($^3$TYROH) is quenched by $O_2$, leading to the generation of $^1O_2$ which reacts with TYROH by H abstraction. The

resulting intermediates TYRO$^\bullet$ and HO$_2$$^\bullet$ are believed to be the precursors of photo-oxidation products. In addition, another mechanism involving the generation of intermediate 'endoperoxide' has also been proposed in their study.

**e. Photoisomerization and photorearrangement**

Electronically excited molecules have considerable excess energy over ground state molecules and so it comes as no surprise that changes in the bonding system and of the positions of atoms in the molecular framework can happen in these energy rich species. Such rearrangement can give rise to ground state products which are isomeric with the original reactant. The reactant and products can be either *structural* isomers where groups or atoms in the isomers are located entirely differently or *valence-bond* isomers where the bonding system in the isomers differs.

(4) Quantum yields

To quantify the photodegradation of organic compounds, the decay rate and the quantum yield of their photodecomposition should be acquired. A pseudo first-order decay is expected at constant temperature, light intensity, and illumination wavelength (Chu and Tsui, 1999). The quantum yield for pollutant decay using a monochromic light source, therefore, can be calculated from experimental first order decay rate as described by Choudhry and Webster (Choudhry and Webster, 1987):

$$\phi = \frac{k}{2.303 I_{\lambda,0} \varepsilon_{p,\lambda} l} \qquad (2\text{-}14)$$

where $\phi$ = quantum yield for the disappearance of LNR

$I_{\lambda,0}$ = intensity of the incident light at wavelength $\lambda$, Einstein L$^{-1}$s$^{-1}$

$\varepsilon_{p,\lambda}$ = molar absorptivity of LNR at wavelength $\lambda$, $M^{-1}cm^{-1}$

l = cell path length within the reactor, cm

k = the first order decay rate constant, $s^{-1}$

$\varepsilon_{p,\lambda}$ = molar absorptivity of LNR at wavelength $\lambda$, $M^{-1}cm^{-1}$

2.1.2 Ozone-based Advanced Oxidation Processes

Ozone has been widely applied in the treatment of municipal and industrial wastewaters and the disinfection of drinking water due to its high oxidation potential (2.08eV) (Chu and Ma, 2000; Graham et al., 2003; Hoigne and Bader, 1983). However, ozonation process is highly selective since high electrophilicity and selectivity of the reaction between $O_3$ and organic compound lead to organics with electron-donating substituent group (e.g. OH and $CH_3$) showing higher reactivity toward ozone and organics with electron-withdrawing substituents (e.g. Cl and $NO_2$) having lower ozone reactivity (Adewuyi, 2005). The coupling of ozonation with other processes such as ultrasound, UV, electrocoagulation and photocatalysis or chemical oxidation utilizing $H_2O_2$ or ferrous ion presents interesting and attractive approaches which can produce nonselective strong oxidants---hydroxyl radicals. Therefore, many recent efforts have been devoted to improving the efficiency of ozonation by exploiting the advantages of combinative or hybrid processes involving the simultaneous or sequential use of ozonation and other AOPs.

(1) US/$O_3$

Chemical effects of ultrasound are believed to be due to the phenomenon of acoustic cavitation, which involves the formation and subsequent collapse of microbubbles from acoustical wave-induced compression/rarefaction (Weavers and Hoffmann, 1998). In a collapsing cavitation bubble, the thermolytic decomposition of ozone and subsequent hydroxyl radicals formation occurs as follows:

$$O_3 \xrightarrow{\text{US}} O_2 + O(^3P)$$

(2-15)

$$O(^3P) + H_2O \longrightarrow 2HO^\bullet \qquad\qquad (2\text{-}16)$$

These decomposition reactions occur in the gas phase. The reaction products migrate to the interfacial sheath of the bubble where they subsequently react in the aqueous phase. As we can see from eq. 2-15. and eq. 2-16., the combination of $O_3$ and ultrasound may be more effective since two $HO^\bullet$ are formed per $O_3$ molecule consumed.

Weavers and Hoffmann (Weavers and Hoffmann, 1998) conducted cyclohexene degradation experiments using sonication (in the presence of $O_2$), ozonation, and sonolytic ozonation to determine the effect that ultrasound had on an $O_3$ gas bubble diffusing into a solution. The degradation experiments indicated that rates were the fastest when sonication was combined with ozonation, followed by sonication with $O_2$, and then ozonation alone in that order. Lall et al. investigated the decolorization of the dye Reactive Blue 19 by ozonation, ultrasound, and ultrasound-enhanced ozonation using a semibatch reactor. At dye concentration of 0.1 g/L and $O_3$ concentration of 9.4 mg/L with the presence of ultrasonic irradiations (20 kHz) at powers of 40, 80, and 120 W/L, rate constant increases 35.7, 75, and 139.9% for the respective ultrasonic powers as compared with ozone alone. They also studied the effect of ultrasonic power input on the overall mass transfer coefficient of ozone in solution. Using 5.4 mg/L $O_3$ and 0.03 g/L dye concentration at the maximum ultrasonic power input of 120 W/L, the ratio of mass transfer coefficient with ultrasound ($k_L a^*$) to that without ultrasound ($k_L a$) increased by 90%. The increase in overall rate was attributed to the combined effects of an increase in mass transfer and intrinsic kinetics resulting from cavitation (Lall et al., 2003). He et al. found the pseudo-forst-order degradation rate constants of TOC reduction were $9.0 \times 10^{-4}$,

$7.3 \times 10^{-3}$ and $1.8 \times 10^{-2}$ min$^{-1}$ for US, O$_3$ and a combination of US and O$_3$, respectively (He et al., 2007b).

(2) UV/O$_3$

The combined UV/O$_3$ system has been widely studied (Winarno and Getoff, 2002; Lau et al., 2007; Gong et al., 2008; Kim et al., 2008), and its overall oxidation reaction has been shown to be due to a synergistic effect of several individual reactions, such as direct (molecular) ozonation, direct photolysis, and indirect radical oxidation. Peyton and Glaze confirmed the formation of hydrogen peroxide as the first reaction intermediate of ozone photolysis. It was also proposed that the secondary reactions lead to the production of hydroxyl radical (HO$^\bullet$), the major oxidant in the UV/O$_3$ process (Peyton and Glaze, 1988). Hydroxyl radical (HO$^\bullet$) may then react with ozone to produce other radicals such as singlet oxygen and peroxyl radicals, which is also believed to be involved in the overall oxidation reaction (Winarno and Getoff, 2002).

Lau et al. investigated the degradation of butylated hydroxyanisole (BHA) in UV, ozonation, and UV/O$_3$ processes. Their experimental results indicated that the degradation of BHA increases in order: UV photolysis, ozone, and UV/O$_3$. The TOC removal was insignificant in both the UV photolysis and ozonation processes, while 90% mineralization was achieved by using the UV/O$_3$ process after 180 min (Lau et al., 2007). Song et al. observed the total mineralization of CI Reactive Yellow 145 after 150 min in the UV, O$_3$, and UV/O$_3$ schemes was 4%, 63%, and 80%, respectively (Song et al., 2008).

(3) Catalytic Ozonation

Catalytic ozonation can be considered firstly as homogeneous catalytic ozonation, which is based on ozone activation by metal ions present in aqueous solution, and secondly as heterogeneous catalytic ozonation in the presence of metal oxides, metals/metal oxides on supports or other solid particles. Catalytic ozonation has been found to be effective for the removal of several organic compounds from drinking water and wastewater (Canton et al., 2003; Giraldez et al., 2007; Kastner et al., 2008; Zhang and Ma, 2008).

*Homogeneous catalytic ozonation*

Generally, two main processes can be considered when attempting to hypothesize the mechanism of homogeneous catalytic ozonation: ozone decomposition by means of active metal species, followed by the generation of free radicals, and complexes formation between the catalyst and organics followed by a final oxidation reaction.

The catalysts proposed for the process of homogeneous catalytic ozonation are transition metals such as Fe(II), Mn(II), Ni(II), Co(II), Cd(II), Cu(II), Ag(I), Cr(III), Zn(II). The nature of transition metal applied determines not only the reaction rate but also selectivity and ozone consumption (Kasprzyk-Hordern et al., 2003).

Legube and Leitner observed that, during the ozonation of wastewaters, Fe (II), Mn (II), Ni (II) and Co (II) sulphate induce an increase of total organic carbon (TOC) removal when compared with ozonation alone (Legube and Leitner, 1999). Trace amounts of cobalt (II) ($2 \times 10^{-6}$ M) were also found to be capable of accelerating the decay rate of organic compounds such as oxalic acid, which does not readily react with molecular ozone ($k_{O_3} = 0.0\ 4\ M^{-1}\ s^{-1}$) (Pines and Reckhow, 2002). In their study, the degradation mechanism of oxalic acid was proposed in Co (II)/ozone

system: the first step in the catalytic ozonation reaction pathway is the formation of a cobalt (II) oxalate complex. Cobalt (II) oxalate is then oxidized by ozone to form cobalt (III) oxalate. The catalytic cycle is completed with decomposition of the cobalt (III) complex to form cobalt (II) and an oxalate radical. Xiao et al. have examined the effect of $Mn^{2+}$ on the mineralization of 2, 4- dichlorophenol (DCP) by ozone. The results of their study show that trace amount of $Mn^{2+}$ accelerates the mineralization of DCP. It was also observed that $Mn^{2+}$ could induce the generation of more hydroxyl radicals via initiating the decomposition of ozone in catalytic ozonation system than those in sole-ozone system (Xiao et al., 2008).

*Heterogeneous catalytic ozonation*

The degradation mechanism of organic compounds by heterogeneous catalytic ozonation has not been well-understood till now. In the work of Beltrán et al., the decay mechanism of oxalic acid in $TiO_2/O_3$ system was proposed as following (Beltran et al., 2002):

$$O_3 + S \leftrightarrow O=O–O–S \tag{2-17}$$

$$O=O–O–S \rightarrow O–S + O_2 \tag{2-18}$$

$$B + S \leftrightarrow B – S \tag{2-19}$$

$$O–S + B – S \leftrightarrow 2CO_2 + H_2O + 2S \tag{2-20}$$

Where S represents the free active centers on the surface of catalyst and B denotes oxalic acid. Based on this mechanism, it is believed that the adsorption of both ozone and oxalic acid on the surface of catalyst is critical to guarantee the catalytic effect.

Some authors, however, believe that an interaction between ozone and hydroxyl groups on the surface of catalysts leads to the generation of hydroxyl radicals (Ernst et al., 2004; Zhao et al., 2009). Zhao et al. examined the enhancement mechanism of heterogeneous catalytic ozonation by cordierite-supported copper for the degradation of nitrobenzene in aqueous solution. In their work, the production of hydroxyl radicals was confirmed by means of the spin trapping/EPR technique and a good correlation between density of surface hydroxyl groups and relative intensity of DMPO-OH adduct signal at the different loading percentage of Cu was found, indicating the formation of hydroxyl radicals is subjective to the density of the surface hydroxyl groups. In addition, Ernst et al. reported that the adsorption of organics on the catalyst's surface would not be necessary to provide the catalytic effect, and DOC (dissolved organic compounds) adsorption would probably inhibit the effect due to an overlaying of hydroxyl groups.

In some papers, the involvement of hydroxyl radicals into the heterogeneous catalytic ozonation is disagreed because the performance of ozonation is not influenced by the presence of radical scavengers like bicarbonates (Kaptijn, 1997; Logemann and Annee, 1997).

Other authors consider it possible that the improvement of direct ozonation results in the enhancement of heterogeneous catalytic ozonation. The pre-coating of γ-alumina by perflurooctanoic acid stablizes ozone, thus boosting its oxidation efficiency towards organic compounds in aqueous solution (Kasprzyk and Nawrocki, 2002).

In summary,  there are generally three possible mechanisms of catalytic ozonation in heterogeneous systems (Kasprzyk-Hordern et al., 2003):

- chemisorption of ozone on the catalyst surface leading to the formation of active

  species which react with non-chemisorbed organic molecule;

- chemisorption of organic molecule (associative or dissociative) on the catalytic

  surface and its further reaction with gaseous or aqueous ozone; and

- chemisorption of both ozone and organic molecules and the subsequent interaction

  between chemisorbed species.

The main catalysts proposed for the process of heterogeneous catalytic ozonation are metal oxides ($MnO_2$, $TiO_2$, $Al_2O_3$), metals or metal oxides on metal oxide supports (e.g. $Cu-Al_2O_3$, $Cu-TiO_2$, $Ru-CeO_2$, $V-O/TiO_2$, V-O/silica gel and $TiO_2/Al_2O_3$, $Fe_2O_3/Al_2O_3$) and activated carbon (Faria et al., 2008; Faria et al., 2009; Li et al., 2009) as well as some other material such as wood fly ash (Kastner et al., 2008), ceramic honeycomb (Zhao et al., 2008) and cordierite-supported copper (Zhao et al., 2009).

The efficiency of the catalytic ozonation process depends to a great extent on the catalyst and its surface properties as well as the pH of the solution that influences the properties of the surface active sites and ozone decomposition reactions in aqueous solutions.

The $O_3/TiO_2$ system was found to be efficient for oxalic acid degradation in water at acidic pH (Beltran et al., 2002). In the absence of catalyst, oxidation of oxalic acid was negligible at 20℃ while around 70% removal of oxalic acid was achieved after 3 hr of reaction in the presence of $TiO_2$. Alumina was also shown to be an effective catalyst for the ozonation of 2-chlorophenol. The highest efficiency (more than twice

as high) of catalytic ozonation when compared to ozonation alone was observed at neutral pH. At an acidic pH value, the usage of the $Al_2O_3/O_3$ system resulted in an increase of 83.7% of TOC degradation when compared to ozonation alone. Only a 17% increase of the efficiency of catalytic ozonation was obtained at a basic pH value, mainly because, under an alkaline environment, oxidation with hydroxyl radical from ozone decomposition initiated by $OH^-$ is already strong (Ni and Chen, 2001). It was also reported that the catalytic ozonation with goethite (FeOOH) can substantially enhance nitrobenzene degradation compared with ozonation alone (Zhang and Ma, 2008).

Activated carbon is believed to act not only as the absorbent but also as a catalyst in promoting ozone oxidation. It was evidenced that the presence of activated carbon during ozonation increased the degradation rate of both oxamic and oxalic acid leading to mineralization (Faria et al., 2008). Giráldez et al. reported that AC (activated carbon) ozonation process significantly improved both polyphenol conversion and mineralization (Giraldez et al., 2007).

*Photocatalytic ozonation*

The photocatalytic oxidation, one of AOPs methods, has been widely investigated (Sanchez et al., 1998; Wang et al., 2002; Farre et al., 2005; Gimeno et al., 2007; Beltran et al., 2009). The process is based on the production of electron–hole pairs by semiconductor illuminated by light of suitable energy in an aqueous medium, which subsequently react with adsorbed species of suitable redox potential. In the presence of air, adsorbed molecular oxygen accepts photogenerated electrons, while water molecules can react with photogenerated holes to produce hydroxyl radicals (Sanchez et al., 1998; de Moraes et al., 2000):

$$O_2 + e^- \rightarrow O_2^{\bullet-} \qquad\qquad (2\text{-}21)$$

$$H_2O + h^+ \rightarrow HO^\bullet + H^+ \qquad\qquad (2\text{-}22)$$

Oxygen is usually introduced into the system as an oxidizing agent. The disadvantage of oxygen is the slow electron transfer from $TiO_2$ to oxygen. Ozone with its unique properties is a potential oxidant for the photocatalytic oxidation process (Gilbert, 2002).

In photocatalytic ozonation process, both direct and indirect reactions of ozone occur. With the presence of $TiO_2$ under illumination, ozone can generate $HO^\bullet$ radicals through the formation of an ozonide radical ($O_3^{\bullet-}$) in the adsorption layer (Tanaka et al., 1996; Sanchez et al., 1998; Klare et al., 1999):

$$TiO_2 + hv \rightarrow e^- + h^+ \qquad\qquad (2\text{-}23)$$

$$O_3 + e^- \rightarrow O_3^{\bullet-} \qquad\qquad (2\text{-}24)$$

The generated $O_3^{\bullet-}$ species rapidly reacts with $H^+$ in the solution to give $HO_3^\bullet$ and subsequently $HO^\bullet$ (Sanchez et al., 1998; Klare et al., 1999):

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet \qquad\qquad (2\text{-}25)$$

$$HO_3^\bullet \rightarrow O_2 + HO^\bullet \qquad\qquad (2\text{-}26)$$

The photocatalytic process in the presence of oxygen requires a total of three electrons for the generation of a single $HO^\bullet$ species, which is a less favorable situation if compared with the one electron needed through the $O_3^{\bullet-}$ reaction pathway.

That is the reason why the presence of ozone is more effective in terms of the production of $HO^\bullet$.

Generally, the presence of dissolved ozone in the irradiated $TiO_2$ suspension significantly increases the OH radical production by means of two processes--- inhibiting the recombination of electrons and holes and self-decompostion initiated by photogenerated electrons on the surface of $TiO_2$.

(4) Ozone-based other AOPs

Ozone combined with other oxidizing agents such as $H_2O_2$ has been proved effective treatment for the elimination of persistent and recalcitrant organic compounds (Chen et al., 2006; Al Momani et al., 2008). Al Momani et al. investigated the degradation of cyanobacteria toxin by ozone alone and $O_3/H_2O_2$ processes. It was found that at a fixed initial ozone concentration of 0.1 mg/L and different initial $H_2O_2$ concentrations, MC-LR degradation was enhanced from 65 to 95% as $H_2O_2$ initial concentrations increased from 0.001 to 0.005 mg/L. Complete MC-LR degradation was achieved in 80s with an initial $H_2O_2$ concentration of 0.01 mg/L (Al Momani et al., 2008). Kim et al. examined the degradability of 30 pharmaceuticals in water with $O_3/H_2O_2$ process. They observed $k_{O3/H2O2}$ values were 1.64 to 2.18 times higher than $k_{O3}$ values, and 1.37 to 1.77 times higher than $k_{O3/UV}$ values for acetaminophen, ifenprodil and theophyline (Kim et al., 2008).

Furthermore, coupling ozonation and electrocoagulation (He et al., 2007a) or electrolysis (Kishimoto et al., 2005; Kishimoto et al., 2007; Kishimoto et al., 2008) has received growing attention recently. Ozonation combined with electrolysis

(ozone–electrolysis) is a new AOP. The advanced oxidation mechanism for ozone–electrolysis was estimated to be as follows (Kishimoto et al., 2008):

$$O_3 + e \rightarrow O_3^- \text{ at cathodes,} \tag{2-27}$$

$$O_3^- + H_2O \rightarrow HO^\bullet + O_2 + OH^- \tag{2-28}$$

It was reported by Kishimoto et al. that the ozone consumption linearly increases with the electrolytic current in the hybrid system. They also observed that the rate constant $k$ was directly proportional to the electrolytic current, which indicated hydroxyl radicals concentration is proportional to the electrolytic current (Kishimoto et al., 2008).

He et al. also observed synergistic effect achieved by coupling electrocoagulation with ozone for the decolorization of RY 84 and decolorization rate increased with the increase of current density (He et al., 2007a).

2.1.3 Photocatalysis

$TiO_2$ has received considerable attention as a photocatalyst since Fujishima and Honda discovered the photocatalytic splitting of water on $TiO_2$ electrode (Fujishima and Honda, 1972). In recent years, applications of $TiO_2$ to the cleanup of groundwater and wastewater have been one of the most active research areas in heterogeneous photocatalysis, which is inspired by the potential of $TiO_2$-based photocatalysis to destroy a wide range of organic compounds.

(1) Theory of $TiO_2$-based photocatalysis

TiO$_2$ can exist in one of three bulk crystalline forms: rutile, anatase, and brookite. Only rutile and anatase are stable enough and can be used as photocatalyst, with anatase showing a higher photocatalytic activity. The initial process for the photocatalytic degradation of organic and inorganic compounds in semiconductor heterogeneous system is the generation of electron-hole pairs. In general, a photon with energy equal to or higher than the bandgap energy of semiconductor can initiate the excitation of electron, $e_{cb}^-$ from the valence band (VB) to the conduction band (CB), leaving a hole, $h_{vb}^+$ behind (Hoffmann et al., 1995b). Excited-state conduction-band electrons and the valence-band holes may suffer varied de-excitation pathways as shown in Figure 2-2.
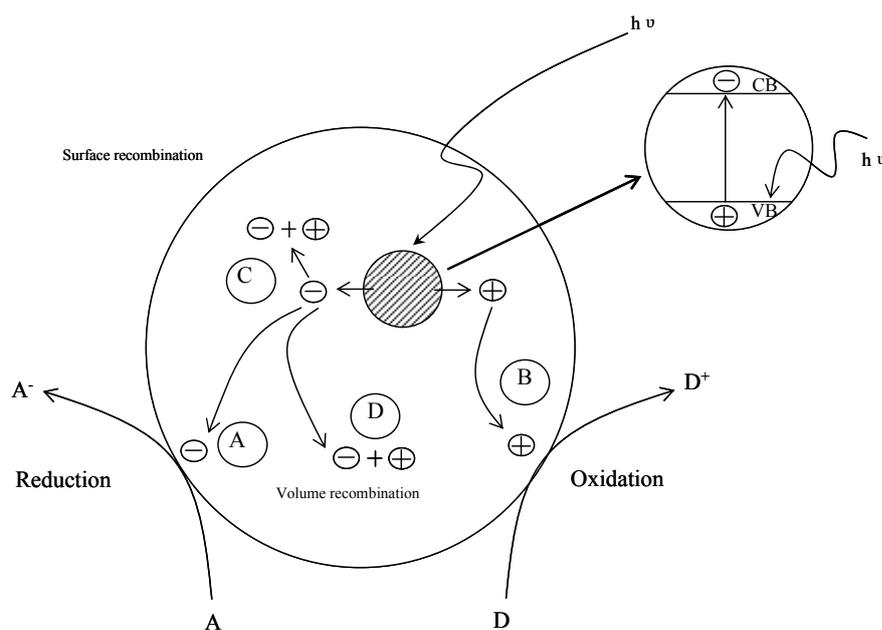


Figure 2-2: Schematic photoexcitation in a solid semiconductor followed by de-excitation events (Linsebigler et al., 1995)

The photoinduced electron transfer to adsorbed organic or inorganic species or the solvent stems from the migration of electrons and holes to the semiconductor surface. With the species adsorbed on the surface, the semiconductor can donate electrons to

reduce an electron acceptor (pathway C); in turn, a hole can migrate to the surface where an electron from a donor species can combine with the surface hole oxidizing the donor species (pathway D). The probability and rate of the charge transfer processes for electrons and holes depends on the respective positions of the band edges for the conduction and valence bands and the redox potential levels of the absorbate species (Linsebigler et al., 1995).

In competition with charge transfer to adsorbed species is electron and hole recombination. Recombination of the separated electron and hole can occur in the volume of the semiconductor particle (pathway B) or on the surface (pathway A) with the release of heat.

(2) Modification of $TiO_2$

Among all semiconductors, Titanium dioxide ($TiO_2$) is believed to be one of the most appropriate photocatalysts in terms of environmental application owing to its particularly optical properties, innocuity, low cost and enduring stability regarding photo- and chemical corrosion (Augugliaro et al., 1995; Hoffmann et al., 1995b). The widespread use of $TiO_2$ as an effective photocatalyst in practical application, however, has been curbed by its optical property that $TiO_2$ is only sensitive to UV light due to its large band gap ($Eg = 3.2$ eV and 3.0 eV for anatase and rutile phases, respectively). The sun can furnish an abundance of photons; however, UV light only accounts for a small portion ($\sim 5\%$) of the sun spectrum in comparison to the visible region ($\sim 45\%$). Driven by the need to utilize solar energy more efficiently, therefore, significant efforts have been dedicated to improve the utility of $TiO_2$ by shifting its optical response from the UV to the visible spectral range:

a. Combining $TiO_2$ with another semiconductor oxide

$TiO_2$ coupled with other semiconductor oxides such as CdS (Bessekhouad et al., 2006; Srinivasan et al., 2006), $Cu_2O$ (Bessekhouad et al., 2005; Han et al., 2009), $Fe_2O_3$ (Pal et al., 1999; Liu and Gao, 2006), $WO_3$ (Chai et al., 2006; Lin et al., 2008) and $Bi_2O_3$ (Bian et al., 2008) has demonstrated photocatalytic activity under the irradiation of visible light. It is believed that the electrons on the valence band of a smaller band gap semiconductor such as CdS (2.4-2.6 eV), $Cu_2O$ (2.0 eV), $Fe_2O_3$ (2.2 eV) and $Bi_2O_3$ (2.8 eV) excited by visible light to the conduction band can be transferred to the conduction band of a larger band gap semiconductor ($TiO_2$). This not only helps for charge separation by isolating electrons and holes in two distinct particles but at the same time, allows the extension of photoresponse of the composite photocatalyst to visible light range. The interparticle electron transfer theory was proposed by Serpone et al. for the first time (Serpone et al., 1995). Their work provides chemical evidence for electron and hole transfer between CdS and $TiO_2$.

b. Transition Metal Doping

The influence of transition metal dopants on the photocatalytic properties of $TiO_2$ has become another interesting area of semiconductor modification. Doping with transition metal ions such as Fe (Piera et al., 2003), Cr (Fan et al., 2008), V (Klosek and Raftery, 2001), Zr (Huang et al., 2006) and Co (Dvoranov et al., 2002), however, has shown both positive and negative effects on the photocatalytic activity of $TiO_2$; a number of authors claim that although metal ion doping could narrow the band gap of $TiO_2$, the metal ion may also serve as a

recombination center for electrons and holes, thus diminishing the overall activity of the photocatalyst (Thompson and Yates, 2006) .

c.  Non-metal Doping

Asahi et al. (2001) reported doping $TiO_2$ with nitrogen allowed it being sensitive to the irradiation of visible light (less than 500 nm) (Asahi et al., 2001), which initiates extensive research interest in doping $TiO_2$ with anionic species (Yu et al., 2003; Tachikawa et al., 2004; Zaleska et al., 2008). It has been proposed that band gap narrowing may result from the mixing of the p states of the dopants with O 2p states forming the valence band of $TiO_2$ in the work of Asahi et al. A similar conclusion has also been reached by Lin et al. for the spectral changes observed for P-doped $TiO_2$ (Lin et al., 2005).

d.  Surface Sensitization

Surface sensitization of $TiO_2$ via chemisorbed or physisorbed dyes also offers a way to extend the optical response of $TiO_2$ to the visible light range. The operating mechanism is the electrons from photoexcited dye molecules being injected into the conduction band of the semiconductor substrates, where the electrons can react with the electron acceptor such as oxygen or hydrogen peroxide to generate varied radicals or radical anions. Some common dyes used as sensitizers include phthalocyanine (Cao et al., 2003), thionine (Patrick and Kamat, 1992), and $Ru(bpy)_3^{2+}$ (Khan et al., 1987; Zang and Rodgers, 2000). Such dye sensitizers, however, are not sufficiently stable in the aquatic environment and need to be prepared only in the acidic pH range. Therefore,

challenges still confront the researchers to find a way to apply dye-sensitized TiO$_2$ in environmental cleanup.

Whereas coupling, doping and photosensitization have demonstrated successful performance in either narrowing the band gap of TiO$_2$ or sensitizing photocatalytic properties of TiO$_2$ towards visible light irradiation, the preparation process of photocatalyst is time-consuming, technique-demanding and expensive and their photocatalytic activity under visible light irradiation is not high enough for the practical applications. Therefore, it still remains a big challenge to develop a cost-efficient and less technique-demanding TiO$_2$-based photocatalysis process which can work under the irradiation of visible light in the field of water treatment.

(3) H$_2$O$_2$-assisted Photocatalysis under Visible Light

It has also been reported that TiO$_2$ nanoparticles can work under the irradiation of visible light with the addition of H$_2$O$_2$ (Ohno et al., 2001; Li et al., 2001; Ogino et al., 2008). There are valence-unfilled Ti (IV) ion centers and O (II) centers which form basic $\equiv$ TiOH and acidic $\equiv$ OH on the surface of TiO$_2$ particle in aqueous solution, respectively (Regazzoni et al., 1998). In the presence of H$_2$O$_2$, the $-$ OOH groups of H$_2$O$_2$ substitute the $-$ OH groups of the basic $\equiv$ TiOH generating yellow surface complexes--Titanium peroxide. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy of H$_2$O$_2$-treated TiO$_2$ suggested the formation of the surface complexes and the diffuse reflectance absorption spectra of H$_2$O$_2$-treated TiO$_2$ demonstrated marked red shift to the visible region (up to 550 nm) (Boonstra

and Mutsaers, 1975; Ohno et al., 2001). It was proposed that the epoxidation reaction of 1-decene could be initiated by a photochemical reaction of Ti-$\eta^2$-peroxide with 1-decene (Ohno et al., 2001). On the other hand, the formation of active hydroxyl radicals was proven in $TiO_2/H_2O_2$ suspension under visible light irradiation in the work of Li et al (Li et al., 2001). A possible mechanism of the generation of hydroxyl radicals in this system was proposed. Titanium peroxide complex formed on the $TiO_2$ surface could extend the photoresponse to the visible region and can be excited by visible light. The excited surface complex injects an electron to the conduction band of $TiO_2$ where the electrons on the conduction band of $TiO_2$, then, initiate the decomposition of $H_2O_2$ to produce hydroxyl radicals. In addition, it was also reported that the water-oxide interface can lower the energy barrier for the $H_2O_2$ decomposition (the presence of oxides leads to the activation energy of the cleavage of the $O - O$ bond in $H_2O_2$ being decreased from 210 kJ/mol to 40 kJ/mol) ( Hiroki and LaVerne, 2005). As a result, hydroxyl radicals might be produced by the breakdown of $H_2O_2$ on the surface of $TiO_2$ under the irradiation of visible light ($H_2O_2$ + $TiO_2$ + vis$\rightarrow$ 2HO$^\bullet$) since the approximate energies of the visible radiation (from 400 nm to 700 nm) range from 293 kJ/mol to 167 kJ/mol (Wayne, 1970).

Although the interaction between $H_2O_2$ and $TiO_2$ is well-documented, the operating mechanism of $TiO_2/H_2O_2$ system under visible light irradiation is not well-understood.

## 2.2 Description of Linuron

2.2.1 Background

Linuron (LNR) is a substituted urea herbicide used to control annual and perennial broadleaf and grassy weeds on crop and non-crop sites. It is used as a pre and a postemergent herbicide. It works by inhibiting photosynthesis in target weed plants. It is labeled for use in soybean, cotton, potato, corn, bean, pea, winter wheat, asparagus, carrot, and fruit crops. It is also used on crops stored in warehouses and storerooms.
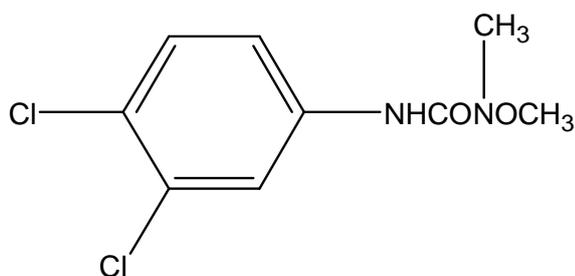


Figure 2-3: Chemical Structure of LNR

LNR is a Restricted Use Pesticide (RUP). Restricted Use Pesticides may be purchased and used only by certified applicators.

2.2.2 Toxicological Effects

LNR is classified by the EPA as a possible human carcinogen (EPA, 1984). LNR has been reported to be a weak competitive androgen receptor antagonist in vitro, inducing a positive response in the immature and adult rat Hershberger assay and suppresses androgen-dependent gene expression (Lambright et al., 2000; McIntyre et

al., 2000); it has been reported to inhibit the activity of 5α-reductase which is one of the key enzymes of human androgen metabolism (Lo et al., 2007); Wilson et al. have observed that LNR reduces testosterone production from the fetal rat testis (Wilson et al., 2009); Orton et al. have found out the yeast exposed to LNR at a low concentration suffers a reduction of antiestrogenic and antiandrogenic activity, inhibition of ovulation in vitro and the decrease of testosterone production (Orton et al., 2009). Furthermore, some of its naturally decayed intermediates (such as chloroaniline) have also been suspected as endocrine disruptors (Lintelmann et al., 2003). LNR is highly toxic to non-target aquatic organisms such as fish and shellfish. The LC50 for LNR in trout and bluegill is 16 mg/l, and 40 mg/l in crawfish. It is moderately toxic to wild birds. Its LC50 in mallard ducks is 3,000 mg/kg, 3,500 mg/kg in pheasants, and 5,000 mg/kg in quail (EPA, 1984).

2.2.3 Environmental Fate

LNR is moderately persistent in soils. The rates of dissipation in agricultural soils determined by laboratory and field experiments are highly variable, with values ranging from days to several years (Fryer and Kirkland, 1970; Smith and Emmond, 1975; Kempsonjones and Hance, 1979; Caux et al., 1998). This compound is bound to soil (especially clay) and organic matter and does not move freely. The movement of the compound decreases as the organic content of the soil increases (Sorensen et al., 2005).

LNR is slightly to moderately soluble in water, and is not readily broken down in water. It is frequently detected in surface and ground waters near or below areas with

intensive use, and in one extreme case, LNR was detected in a drinking-water well in concentration up to 2,800 µg/L (Caux et al., 1998).

2.2.4 Previous degradation studies of LNR

The toxicological effects and persistence of LNR in the environment promotes the need of developing effective treatment techniques to eliminate and mineralize this contaminant. There have been a few number of previous studies referred to the general degradation of LNR, such as biological methods (Dejonghe et al., 2003; Sorensen et al., 2005), $O_3/H_2O_2$ (Tahmasseb et al., 2002; Chen et al., 2008), direct photolysis (Faure and Boule, 1997), photo-Fenton procedure (Katsumata et al., 2005), ultrafiltration and nanofiltration process (Benitez et al., 2009) and $UV/TiO_2$ (Lopez et al., 2005). However, there has been no information available concerning the degradation of LNR by using $UV/O_3$ process and $TiO_2/H_2O_2/Vis$ (visble light) based on a review of the scientific literature. A detailed examination on the degradation of LNR by these two processes is, thus, important and of my major interest.

# Chapter 3 Materials and Methodology

## 3.1 Introduction

This chapter describes the methodology of experimental setup for the water treatment processes (i.e. $UV/O_3$, $UV/TiO_2$ and $TiO_2/H_2O_2/Vis$) employed in this study. The sampling and analytic methods of target compounds can be found in this chapter, and also how the generated intermediates are determined qualitatively and quantitatively is explicated in detail. The characterization of photocatalysts by X-ray diffraction (XRD), UV–Visible spectrophotometer and the generation of photocurrent are also depicted in this chapter.

## 3.2 Materials

All the chemicals used in this study were tabulated in Table 3-1. All the chemicals were used without further purification. The water used in the preparation of all the solutions was 18 MΩ deionized distilled water obtained from a Barnstead NANO pure water purification system. Linuron (LNR) has been chosen as the target pollutant. Selected physical properties of LNR were listed in Table 3-2.

Table 3-1: List of chemicals used in this study

| Chemicals | Molecular weight, g mol$^{-1}$ | Formula | Purchased from |
|---|---|---|---|
| Target Compounds | | | |
| Linuron (99.0%) | 249 | $C_9H_{10}Cl_2N_2O_2$ | SUPELCO |

*Cont'd*

| Semiconductors or Metal oxides | | | |
|---|---|---|---|
| Titanium dioxide (P25) | 79.87 | $TiO_2$ | Degussa |
| Titanium dioxide (Anatase) | 79.87 | $TiO_2$ | Shanghai |
| Titanium dioxide (Rutile) | 79.87 | $TiO_2$ | Shanghai |
| Zinc oxide | 81.38 | $ZnO$ | Aldrich |
| Tungsten (VI) oxide | 231.85 | $WO_3$ | Aldrich |
| Aluminium Oxide (99.9%) | 101.96 | $Al_2O_3$ | Alfa Aesar |
| Silicon Dioxide | 60.08 | $SiO_2$ | Alfa Aesar |
| Oxidants | | | |
| Hydrogen Peroxide (35%) | 34.00 | $H_2O_2$ | Riedel-deHaën |
| Intermediates | | | |
| 1-(3,4-dichlorophenyl)-3-methylurea (98%) | 218 | $C_8H_8Cl_2N_2O$ | Aldrich |
| 1-(3,4-dichlorophenyl)urea | 203 | $C_7H_6Cl_2N_2O$ | Aldrich |
| Solvents | | | |
| Acetonitrile (HPLC grade) | 41.05 | $C_2H_3N$ | Tedia |
| Acetone (AR grade) | 58.08 | $C_3H_6O$ | Tedia |
| Methanol (HPLC grade) | 32.04 | $CH_4O$ | Tedia |
| tert-butanol (99%) | 74.12 | $C_4H_9OH$ | Tedia |

*Cont'd*

| | | | |
|---|---|---|---|
| Acetic acid (99.8%) | 88.11 | $CH_3COOH$ | Lab-scan |

Others

| | | | |
|---|---|---|---|
| Sodium Carbonate (99.7%) | 105.99 | $NaCO_3$ | AnalaR |
| Sodium Bicarbonate (99.9%) | 84.01 | $NaHCO_3$ | AnalaR |
| Sodium Chloride (99.99%) | 58.44 | $NaCl$ | Riedel-dehaën |
| Sodium Sulfate (anhydrous) | 142.04 | $Na_2SO_4$ | BDH |
| | 141.96 | $Na_2HPO_4$ | BDH |
| titanium oxide sulfate hydrate (99.5%) | 69.00 | $TiOSO_4 \bullet_X H_2O$ | International Laboratory |
| Sulfuric Acid | 98.08 | $H_2SO_4$ | Tedia |
| Sodium Hydroxide (96%) | 40.00 | $NaOH$ | Uni-Chem |
| Sodium Azide | 65.00 | $NaN_3$ | Aldrich |
| Ammonia Acetate | 77.08 | $CH_3COONH_4$ | Aldrich |
| Sodium Thiosulfate | 158.11 | $Na_2S_2O_3$ | BDH |

Table 3-2: Physical properties of LNR

(http://pmep.cce.cornell.edu/profiles/extoxnet/haloxyfop-methylparathion/linuron-ext.html)
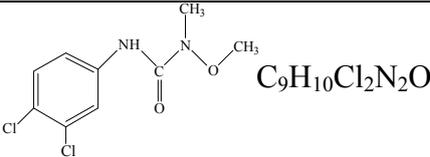
| Formula |  $C_9H_{10}Cl_2N_2O$ |
|---|---|
| Molecular mass | 249.11 |
| Physical state | White crystalline solid |
| Melting point (°C) | 93~94 |
| Boiling point (°C) | 180~190 |
| Vapor pressure | $1.5 \times 10^{-6}$ mm Hg at 24 °C |
| Water solubility | 75 mg/l at 25 °C |
| Solvent solubility | slightly soluble in aliphatic hydrocarbons, moderately soluble in ethanol, soluble in acetone |
| Maxima of absorption spectrum | 210 and 246 nm |

## 3.3 Experimental Setup

3.3.1 UV/O$_3$ process

For the tests involving UV photolysis, 600 mL sample was irradiated in a 800 mL (97.8 mm ID×125 mm H) quartz beaker with magnetic stirring. The beaker was

placed in the center of a Rayonet$^{TM}$ RPR-200 photoreactor manufactured by the Southern New England Ultraviolet Co., which was equipped with phosphor-coated low-pressure mercury lamps, emitting 253.7 nm monochromatic UV at a light intensity of $1.5 \times 10^{-6}$ Einstein L$^{-1}$s$^{-1}$ (See Figure 3-1).
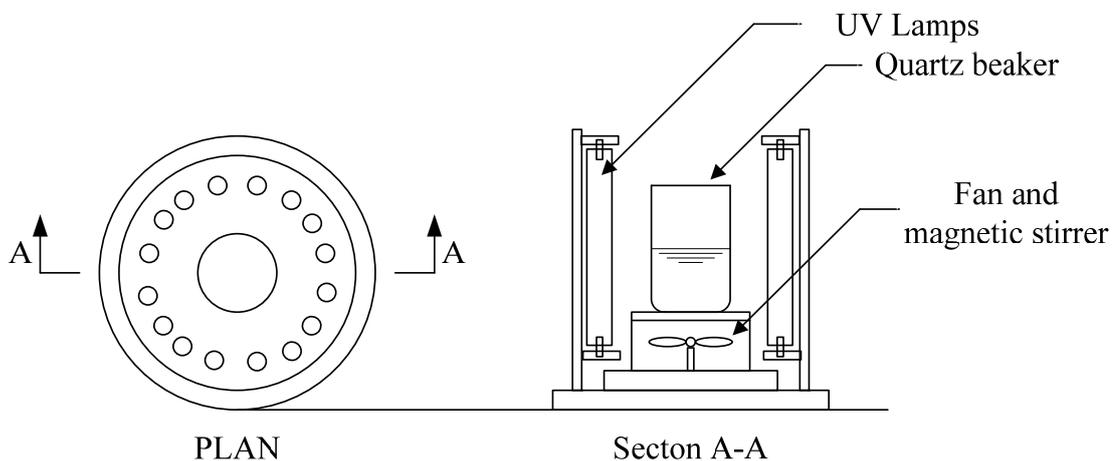


Figure 3-1: The top view and sectional view of the photoreactor Rayonet$^{TM}$.

For the tests involving ozonation, 400 mL of deioned water was pre-ozonated for 15 min (to produce a saturated ozone solution), after adding 200 mL of linruon stock solution into the pre-ozonated solution, a small reduction of dissolved ozone was observed at the beginning of the reaction, which was considered insignificant and could be replenished easily and quickly by continuous feeding of ozone gas into the reactor through a glass sparger (pore size ranges from 16-40 μm) located just above the bottom of the reactor. Ozone gas was produced by the OZAT ozone generator (CFS-1A from Ozonia, Ltd.). The flow rate of ozone/oxygen mixture into the reactor varied from 1.3-2.0 L min$^{-1}$, which resulted in a $9.96 \times 10^{-6}$ to $3.09 \times 10^{-5}$ M ozone concentration in the solution. The concentration of ozone was determined by the Indigo spectrometric method. For the UV/O$_3$ experiments, simultaneous UV irradiation was provided during the ozonation period. The remaining ozone in the

collected sample was quenched by sodium thiosulfate before quantification of linuron.

3.3.2 Photocatalysis process

For UV-induced photocatalytic reactions, they were also conducted in a Rayonet$^{TM}$ RPR-200 photochemical reactor. Six phosphor-coated low-pressure mercury lamps at 350 nm were installed on the photoreactor. To ensure a thorough mixing, 150 mL of solution was dispensed into a 300 mL quartz cylinder with mechanical stirring before and during the illumination.

For the investigation on the degradation kinetics of LNR by $TiO_2/H_2O_2/Vis$ system, the photodegradation of LNR was conducted in a Luzchem CCP-4V photochemical reactor controlled by a computer. To ensure a thorough mixing, 150 mL of solution was dispensed into a 300 mL quartz cylinder with mechanical stirring before and during the illumination. Twelve low-pressure mercury lamps centered at 420 nm were installed in the photoreactor as shown in Figure 3-2. The emission spectra of 420 nm lamp are shown in Figure 3-4.

For the examination on the degradation mechanism of LNR by $TiO_2/H_2O_2/Vis$ system, Vis (visible light)-induced photocatalytic reactions were conducted in a cylindrical glass vessel with a recycling water jacket to avoid overheating. To ensure a thorough mixing, 200 mL of solution was dispensed into the reactor with mechanical stirring before and during the illumination. The suspension was irradiated

by a 300 W Xe lamp (Beijing Perfectlight Co Ltd), which emits both UV and visible light over a wide wavelength as indicated in Figure 3-5. The experimental setup is shown in Figure 3-3. To limit the irradiation wavelength, the light beam was passed through both UV cutoff and other filters of varied wavelength (420, 435, 450, 500 nm).
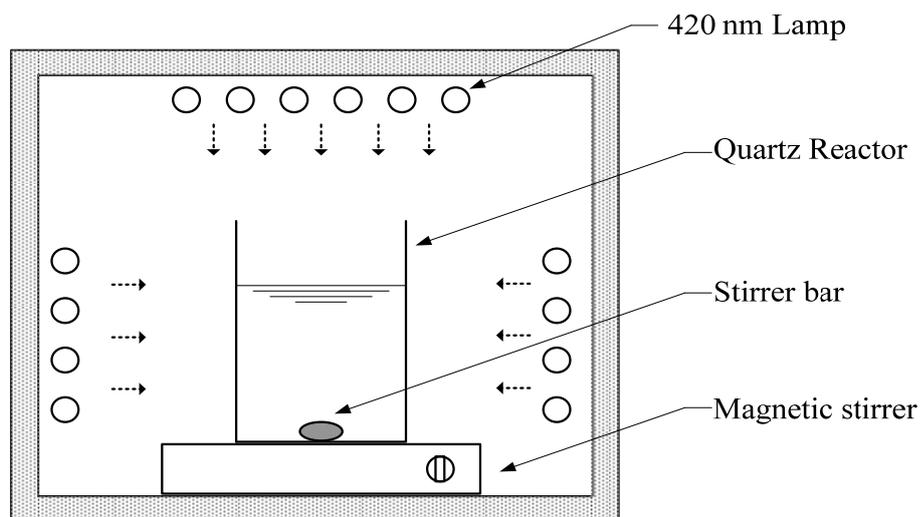


Figure 3-2: Schematic diagrams of the photoreactor Luzchem CCP-4V.
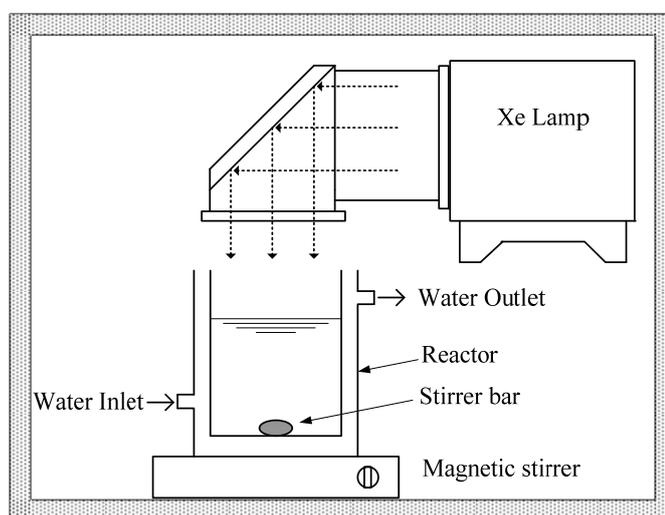


Figure 3-3: Schematic diagrams of the photoreactor with Xe lamp installed.

Samples were withdrawn at a predetermined interval and were filtered through a 0.2 μm PTFE membrane to keep the particles free from the solution prior to

quantification. All experiments were carried out at room temperature (air-conditioned) at 23 ± 2°C in duplicate.
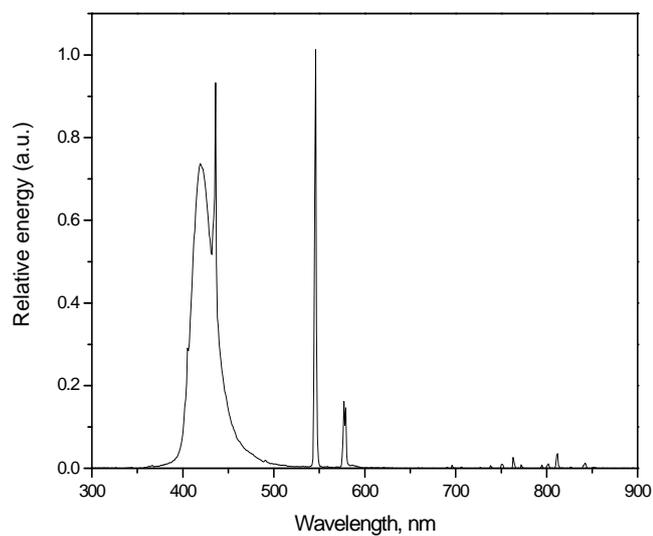
Figure 3-4: Emission spectra of 420 nm lamps
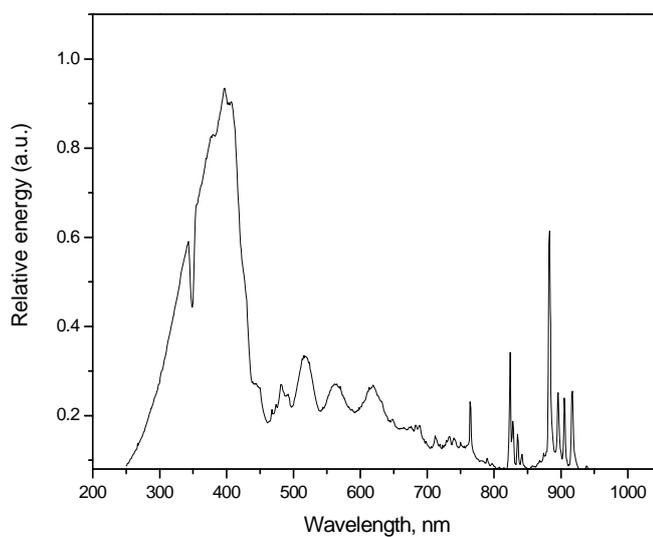
Figure 3-5: Emission spectra of Xe lamp

## 3.4 Instrumental Analysis

3.4.1 Analysis by high performance liquid chromatography (HPLC)

Remaining LNR after reaction was determined by HPLC (Waters). The system was comprised of a Waters 515 HPLC pump, Waters 2489 Dual λ Absorbance Detector, an Agilent Hypersil ODS column (5μm, 0.46×25 cm), and Waters 717plus Autosampler. The maximum adsorption wavelength ($\lambda_{max}$) was selected as 246 nm for LNR (spectrum was shown in Appendix III). A mixture of 60% acetonitrile and 40% water was used as the mobile phase running at a flow rate of 1 mL/min. Four-point calibration was conducted for every batch of analysis.

3.4.2 Analysis by LC/MS

The identification of intermediates was carried out at an initial [LNR] of 0.29 mM. A Thermo Quest Finnigan LCQ Duo Mass Spectrometer system was used to identify the reaction intermediates, which consisted of a PDA-UV detector, and an electrospray ionization with a quadrupole ion-trap mass spectrometer operating at a negative mode at a capillary temperature of 225 °C. The mobile phase was a mixture of (A) 5mM ammonia acetate (pH 4.6) and (B) acetonitrile (100%). The composition of the mobile phase was changed according to the following gradient: 95% of A was kept during the first 2 minutes. From 2 to 26 min, B was steadily increased from 5% to 95%. From 26 to 27 min, B was kept at 95%. Finally, the mobile phase turned to the initial composition until the end of the run. Ionization of the HPLC elute was performed with the following settings: vaporizer temperature 270 °C, spray voltage 4.0 kV, current 5 μA, sheath gas and auxiliary gas ($N_2$) flow rates (arbitrary units) 80 and 20, capillary temperature and voltage 150 °C and 3 V, respectively, and data collected from m/z 50–400.

Those intermediate compounds whose standards are not available commercially were quantified in terms of ion intensity relative to the initial LNR concentration for comparison. This approximation is acceptable on the basis of the fact that the UV absorbance may be ascribed to the resonance structure of the ring, which is basically identical (Adams and Randtke, 1992).

3.4.3 Analysis by ion chromatography (IC)

The generation of chloride, nitrite and nitrate ions were quantified by the ion chromatography (Dionex Series 4500i) composed of an anion column (Dionex IonPac® AS14 (4 mm × 250mm), Dionex CD25 Conductivity Detector and Dionex AS 40 Automated sampler. A mixture of 1 mM of $NaHCO_3$ and 3.5 mM of $Na_2CO_3$ was used as the mobile phase eluting at 1 mL $min^{-1}$. For the quantification of the ammonium ion produced during the reaction, Dionex IonPac® CS12 (4 mm × 250mm) was used as a cation column and 0.022 M MSA (methane sulphonic acid) was used as the mobile phase eluting at 1 mL $min^{-1}$.

3.4.4 TOC measurement

The total organic carbon (TOC) concentration was analyzed by a Shimadzu TOC-5000A analyzer equipped with an ASI-5000A autosampler to determine the total mineralization degree of the organic pollutants during the advanced oxidation process. The principle of it is to break down the single carbon units and convert them to single carbon molecular form (i.e. carbon dioxide) that can be measured quantitatively. The inorganic carbon is first removed by acidification and sparging. Each sample is acidified to pH 3 prior to TOC analysis. The analyzer is calibrated bi-

monthly. The sample is loaded into the analyzer by automatic sampler and the carrier gas, $O_2$, will carry the sample right into the reactor. A high temperature catalytic combustion is used to convert organic carbons to carbon dioxide ($CO_2$). The resulting $CO_2$ is then measured directly by an infrared analyzer. The TOC content is calculated and displayed in mg/L by the computer.

3.4.5 pH measurement

Solution pH was adjusted by the addition of diluted $H_2SO_4$ or NaOH. Measurement was carried out by the pH meter (Cole Parmer) and thorough mixing was ensured by magnetic stirrer.

3.4.6 X-ray diffraction analysis

X-ray diffraction (XRD) was employed to investigate the phase homogeneity of the titanium dioxide. Powder XRD patterns of the samples were recorded on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda =1.54178$ Å) at a scan rate of $0.05^{\circ}$ 2θ/s. The accelerating voltage and applied current were 40kV and 40mA, respectively. The XRD patterns of the three $TiO_2$ tested in this study are shown in Figure 3-6.
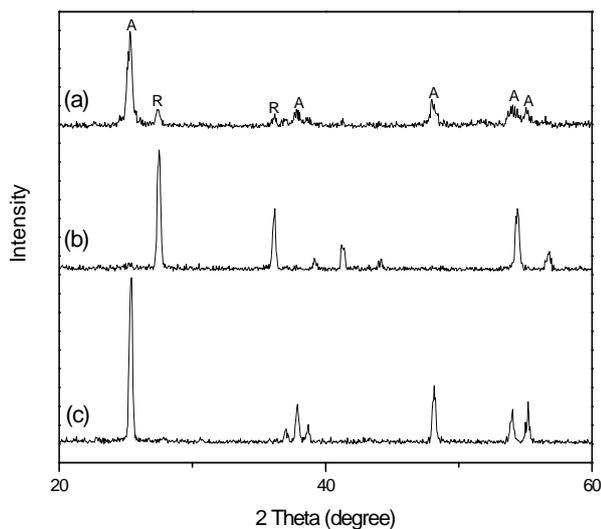
Figure 3-6: XRD patterns of different $TiO_2$ powders used in this study: (a) P25; (b) Rutile; (c) Anatase.

3.4.7 Diffuse reflectance absorption analysis

A Varian CARY 300 UV-Visible Spectrophotometer were used to obtain the ultraviolet-visible diffuse reflection spectra (UV-vis DRS) of the samples over a range of 200-800nm. Baseline correction was conducted using a calibrated sample of barium sulphate ($BaSO_4$).

3.4.8 Measurement of the emission spectra of lamps

The emission spectra of 420 nm lamp and Xe lamp were recorded by ILT900 Wideband Rapid Portable Spectroradiometer (InternationalLight TECHNOLOGIES).

3.4.9 Measurement of the photocurrent

Photocurrent generation was measured with $TiO_2$/ITO electrode immersed in aqueous solution of $H_2O_2$. For preparing the $TiO_2$/ITO electrode, the ITO plates were

first cleaned by sonication in acetone, ethanol and DDW for 30 min, respectively. Then ITO plates were spin-coated with $TiO_2$ film from 25 g/L P25 ethanol suspension with the addition of 25 g/L glycerol. The $TiO_2$-coated ITO plates were calcined at 450℃ for 30 min to burn off organics and bind the $TiO_2$ film to the ITO plate. The $TiO_2$/ITO electrode, a saturated calomel electrode (SCE), and Pt plate were immersed in the reactor as working, reference, and counter electrodes, respectively. Photocurrents were recorded in aqueous solution with or without $H_2O_2$ as a function of elapsed time with application of a potential (+0.5 V vs SCE) using a potentiostat (VersaSTAT 3) connected to a computer.

# Chapter 4 Degradation Kinetics of LNR with UV, Ozonation and UV/O₃ Processes

## 4.1 Introduction

The phenylurea herbicides have been widely applied as effective weed killers by inhibiting photosynthesis upon absorption in the roots in the conventional production of corn, cereals, vegetables and fruits since their discovery in 1950 (Sorensen et al., 2005). Generally, these chemicals are characterized as persistent in the environment (half-life in soil was reported to be 38-67 days) (Caux et al., 1998) and thus have been found frequently in surface and ground waters (Garmouma et al., 1997). Linuron (N-(3, 4-dichlorophenyl)-N'-methoxy-N'-methylurea) (LNR), one of the most commercialized phenylurea herbicides, was selected as probe compound. The toxicity and possible endocrine disrupting effects of LNR and its metabolites lead to pressing demand for effective treatment techniques to eliminate and mineralize this contaminant.

Ozone process has widely been applied in the treatment of particular organic substances of concern, such as 2, 4- dichlorophoxyacetic acid (Chu and Ching, 2003), trichlorophenol (Graham et al., 2003) and atrazine (Acero et al., 2000). However, the reactions between organic substances and ozone are highly electrophilic and selective (Yao and Haag, 1991), which limit the application of the ozonation as a sole treatment process in meeting drinking water requirements. Therefore, intensive efforts have been put into the research about ozone associated with other oxidation

processes, such as $O_3/H_2O_2$ (Chen et al., 2006), Ultrasound/$O_3$ (He et al., 2007b), UV/$O_3$ (Lau et al., 2007), ozonation coupled with photocatalysis (Sanchez et al., 1998), and ozonation combined with electrolysis (Kishimoto et al., 2008), in which hydroxyl radical oxidation is believed to play a key role in the mineralization of organic substances due to its non-selective property.

LNR is subjected to growing attentions for investigating its treatability by various techniques, such as biological methods (Sorensen et al., 2005; Dejonghe et al., 2003), $O_3/H_2O_2$ (Tahmasseb et al., 2002), direct photolysis (Faure and Boule, 1997), photo-Fenton procedure (Katsumata et al., 2005), and photocatalysis (Lopez et al., 2005). However, the study of LNR under UV/$O_3$ process in aqueous phase is still superficial and the inside study of the individual reaction pathway is very limited. The combined UV/$O_3$ process has been widely studied (Lau et al., 2007), and its overall oxidation reaction is believed to result from a synergistic effect of several individual reactions, such as direct ozonation, direct photolysis, and indirect radical oxidation. UV irradiation can lead to ozone being transformed into hydrogen peroxide which can be further photolyzed into $HO^\bullet$ and then initiate a chain of radical reactions (Gurol and Akata, 1996). It is believed that the UV/$O_3$ process could provide an effective treatment of LNR and its toxic intermediates present in contaminated waters.

In this chapter, the degradation and mineralization of LNR was examined under direct photolysis, $O_3$, and UV/$O_3$ processes in aqueous phase. In addition, the effects of initial pH levels, ozone dose and light intensity on the decay rate of LNR were also investigated. The information was used in subsequent model derivations and rate constants determination for the involved sole-UV, $O_3$ and UV/$O_3$ systems.

## 4.2 Results and Discussion

4.2.1 Decomposition and mineralization of LNR in UV/Ozone system

The degradation and mineralization of 0.1 mM LNR in sole UV, sole Ozone and combined UV/ozone system was investigated with pH level set at 6.0, ozone concentration and light intensity were fixed at 0.0171 mM and at $6.0 \times 10^{-6}$ Einstein $L^{-1} s^{-1}$, respectively. As indicated in Figure 4-1, the decay rate of LNR increases in the order of UV photolysis, ozone and UV/ozone. In addition, LNR (0.1 mM) can be completely removed by the three proposed processes. It takes 35 minutes to fully decompose 0.1 mM LNR for UV illumination, while 22.5 and 10 minutes were required for ozonation and UV/ozone, respectively. The photolysis and oxidation of LNR were found to follow pseudo first-order kinetics. As also demonstrated in Figure 4-1, no TOC removal was observed in sole UV process, and TOC removal was insignificant in ozonation process (about 15% mineralization after 100 minutes). However, nearly 80% mineralization was achieved by using UV/ozone process after 100 minutes, suggesting the use of UV/ozone is a promising and clean process for the final disposal of LNR.
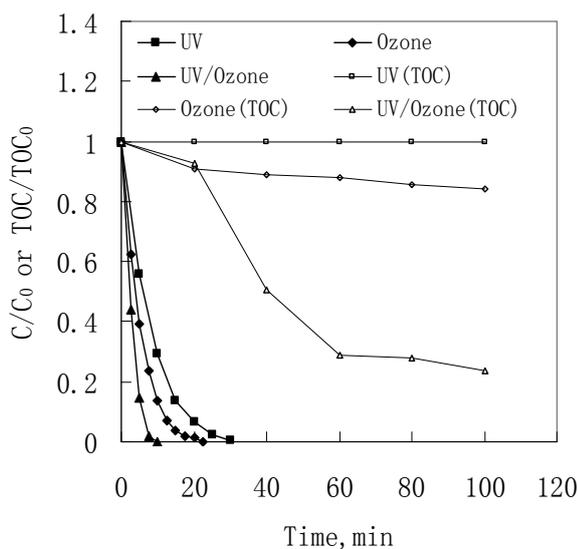
Figure 4-1: Comparison of LNR decay (C/C$_0$) and TOC removal by the different treatment processes at pH 6 (C$_0$ = 0.1 mM)

4.2.2 Effect of pH level on decay rate of the LNR ozonation

The decay rate of LNR was tested at various pH levels (from 3 to 11) by ozonation process with ozone concentration fixed at 0.0171 mM. As indicated in Figure 4-2, an increased degradation rate was observed at elevated pH levels. Furthermore, it is interesting to note that the overall rate constants increased linearly at lower pH level (< 9), but exponentially at higher pH level (> 9) as indicated in the inset of Figure 4-2. This can be rationalized by the different oxidation pathways. At lower pH level, the oxidation by ozone molecules is the dominant reaction, while a much faster oxidation by hydroxyl radicals plays a key role under basic conditions (Chu and Ma, 2000).
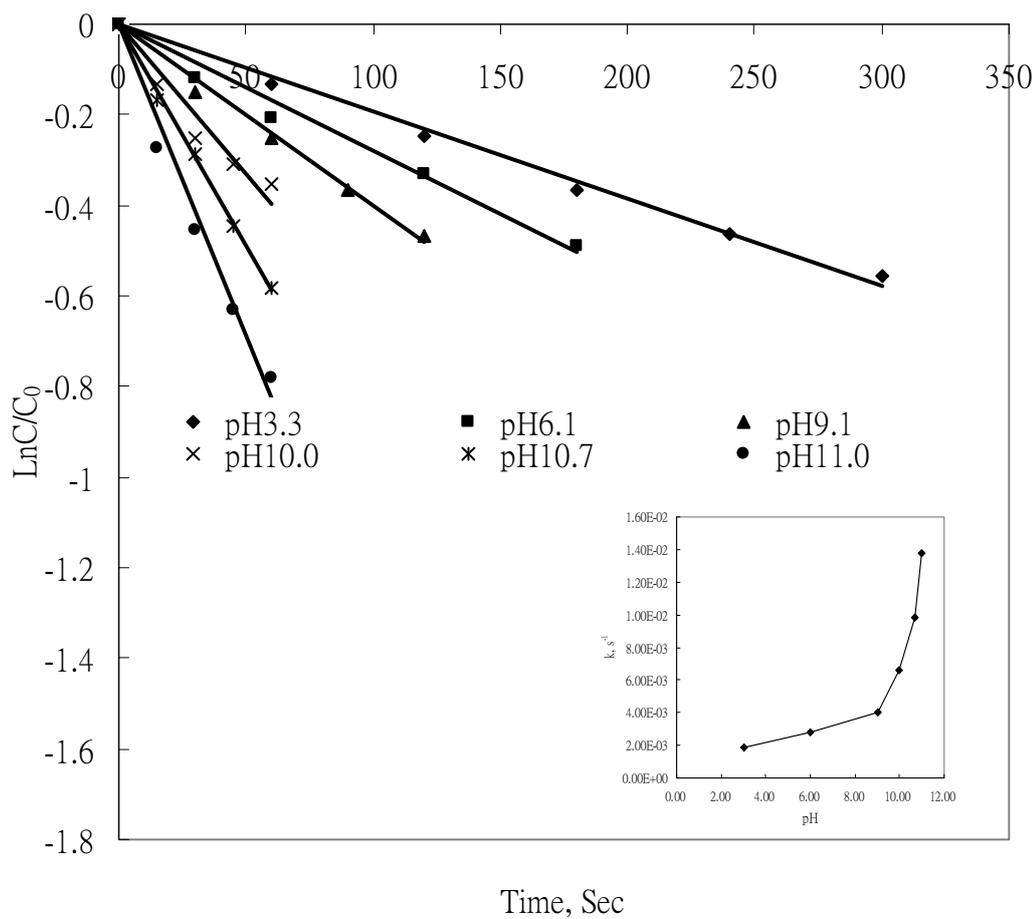
Figure 4-2: Pseudo first-order degradation of 0.1 mM LNR in ozone-alone system at

various pH levels ($[O_3] = 1.71 \times 10^{-5}$ M )


4.2.3 Quantum Yield determination in UV system

The photodecay of LNR by sole-UV (at 253.7 nm) was investigated by using four

different levels of light intensity at 3.0, 6.0, 9.0 and $12.0 \times 10^{-6}$ Einstein $L^{-1}$ $s^{-1}$ with

other parameters unchanged. The results shown in Figure 4-3 suggested that the LNR

decay rate constant is linearly increased with the intensity of light. Theoretically, it is

possible to determine the quantum yield of LNR decay by simple pseudo first-order

kinetics under an optical dilute condition. The decay rate of LNR by sole-UV

therefore can be formulated as:

$$-\frac{d[LNR]}{dt} = k_{obs}[LNR] = 2.303\phi_{LNR}\varepsilon_{LNR}lI_0[LNR] \tag{4-1}$$

$$k_{obs} = 2.303\phi_{LNR}\varepsilon_{LNR}lI_0 \tag{4-2}$$

where $\phi_{LNR}$ is the quantum yield of LNR decay, $k_{obs}$ is the observed pseudo first-order rate constant ($s^{-1}$), $I_0$ is intensity of the incident light at 253.7 nm (Einstein $L^{-1}s^{-1}$), $\varepsilon_{LNR}$ is the molar absorptivity of LNR at 253.7 nm (13,254 $M^{-1}cm^{-1}$), and $l$ is the optical path length of the quartz beaker (9.78 cm). The observed rate constant $k_{obs}$ was found to be linearly correlated to initial light intensity as shown in Figure 4-3. Therefore, $\phi_{LNR}$ is calculated to be 0.00122 by the slope of the curve divided by 2.303 $\varepsilon_{LNR}$ $l$.
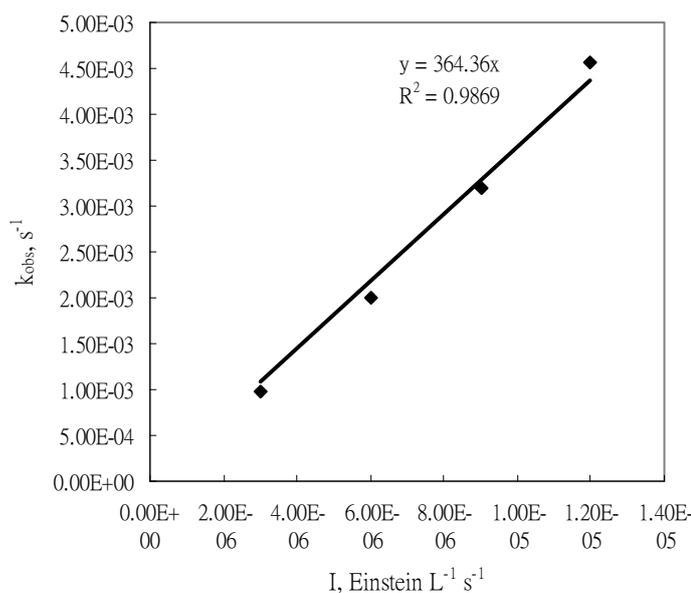


Figure 4-3: Pseudo first-order degradation of 0.1 mM LNR in sole-UV system under various light intensity irradiation

4.2.4 Rate Constant Determination in Ozone system

The degradation of LNR was found to follow a pseudo first-order reaction (See Figure 4-2) at different pH levels during ozonation. It is well known that the oxidization reaction in ozone system comes from either ozone molecule or hydroxyl

free radical with substrates. The decay rate of LNR therefore can be theoretically interpreted by Eqn. (4-3)

$$-\frac{d[LNR]}{dt} = k_{overall}[LNR] = k_{o_3,LNR}[LNR][O_3] + k_{OH,LNR}[LNR][HO^\bullet]$$  (4-3)

The formation of hydroxyl radicals depends on the pH level of the solution; under a pseudo steady state condition, the concentration of hydroxyl radicals can be estimated by the following equation (Benitez et al., 1994):

$$[HO^\bullet] = \frac{3k_{OOH}[O_3][OH^-]}{k_{OH,LNR}[LNR]}$$  (4-4)

where $k_{OOH}$ is the rate constant for the formation of free radical $HOO^{\bullet-}$ from ozone decomposition at high pH (Staehelin and Hoigne, 1982). By combining Eqns. (4-3) and (4-4), the oxidation rate of LNR in ozone system can be derived as following:

$$k_{overall}[LNR] = k_{o_3,LNR}[LNR][O_3] + 3k_{OOH}[O_3][OH^-]$$  (4-5)

in terms of rate constant, Eqn. (4-5) would be:

$$k_{overall} = k_{o_3,LNR}[O_3] + 3k_{OOH}[O_3]\frac{[OH^-]}{[LNR]}$$  (4-6)

In order to determine the $k_{O3}$ and $k_{OOH}$, the variations of overall rate constant at different levels of $[O_3]$ and $[OH^-]$ were investigated and plotted in Figure 4-4a. Depending on $[O_3]$, $k_{overall}$ has a good linear correlation with $[OH^-]$ ($r^2$ ranging between 0.967 and 0.997). According to Eqn. (4-6), the intercepts of these lines would be the $k_{o_3,LNR}[O_3]$ for the corresponding $[O_3]$, while the slopes stand for the

$3k_{OOH}\dfrac{[O_3]}{[LNR]}$ . Therefore, $k_{O3}$ can be determined by plotting the intercepts (from Figure 4-4a) at different $[O_3]$ as a function of the corresponding ozone concentration as shown in Figure 4-4b. Also, $k_{OOH}$ can be calculated by plotting the slopes (from

Figure 4-4a) at different [$O_3$] as a function of the term $\dfrac{3[O_3]}{[LNR]}$ (see Figure 4-4b). The

correlation lines going through the origin in Figure 4-4b result in $k_{O_3,LNR}$ and $k_{OOH}$ as

293 $M^{-1}s^{-1}$ and 14.2 $M^{-1}s^{-1}$, respectively. The different orders of these two rate

constants suggest that the second term of Eqn. (4-5) (i.e. the oxidation due to

hydroxyl radical) can be ignored when the hydroxide ion concentration level is much

lower than the concentration of the compound. In order to verify the hypothesis that

the ozone concentration was close to a constant during the reaction, Hatta number

was calculated to compare diffusion time with reaction time based on the Eqn. (4-7)

(Benitez et al., 1994).

$$Ha = \frac{\sqrt{k_{O_3,LNR}D_{O_3}C_{LNR} + 3k_{OOH}D_{O_3}[OH^-]}}{k_L} \tag{4-7}$$

where $D_{O_3}$ is the ozone diffusion coefficient in the liquid and $k_L$ is the ozone

transfer coefficient to the liquid. $D_{O_3}$ is reported to be $1.76 \times 10^{-9}$ $m^2\,s^{-1}$ in the water

at 20 ℃(Johnson and Davis, 1996). $k_La$ was determined to vary from 0.013 to 0.025

$s^{-1}$ according to Huang (Huang and Shu, 1995). The gas-liquid interfacial area per

unit of liquid volume ($a$) was estimated by the Eqn. (4-8) (Lan et al., 2008) and Eqn.

(4-9) (Bin et al., 2001).

$$a = \frac{6H_g}{d_{bs}} \tag{4-8}$$

$$H_g = 5.54U_g^{1.03} \tag{4-9}$$

where $U_g$ is superfacial velocity varied from $2.9 \times 10^{-3}$ to $4.4 \times 10^{-3}$ $m\,s^{-1}$ in this

study and $d_{bs}$is the Sauter bubble diameter calculated from the correlation of Bouaifi

and Roustan (Bouaifi and Roustan, 1998). As a result, Hatta number was estimated

to be ranged from 0.0046 to 0.0217 which is below 0.03, indicating the kinetic regime is very slow.

a



b
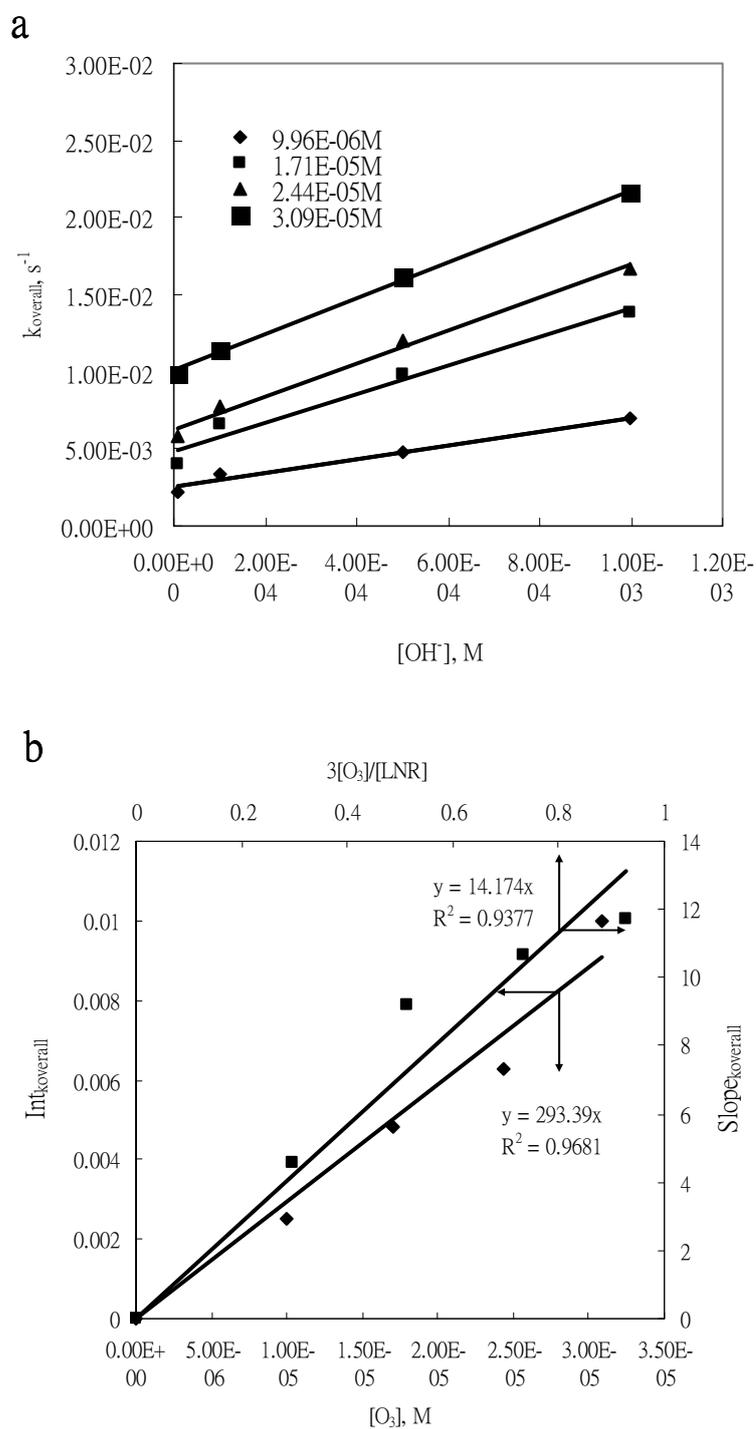


Figure 4-4: (a) Variation of decay rate constant of 0.1 mM LNR with various

hydroxide ion concentrations at different ozone concentration levels in

ozone-alone system; (b) Correlations between $int_{koverall}$ and $[O_3]$ or

Correlations between $slope_{koverall}$ and $3[O_3] / [LNR]$

To determine the $k_{OH,LNR}$, an independent $UV/H_2O_2$ experiment using ATZ as a

reference compound was conducted, where the LNR decay due to sole-UV has been

deducted from the reaction data. In theory, $k_{OH,LNR}$ can be determined by using Eqn.

4-10 under the same reaction conditions in oxidizing the model compound ATZ:

$$Ln\frac{[LNR]_0}{[LNR]_t} = \frac{k_{OH,LNR}}{k_{OH,ATZ}} Ln\frac{[ATZ]_0}{[ATZ]_t} \qquad (4\text{-}10)$$

By plotting $Ln\dfrac{[LNR]_0}{[LNR]_t}$ versus $Ln\dfrac{[ATZ]_0}{[ATZ]_t}$ as shown in Figure 4-5, a straight line

was observed, which gave a slope of 1.015 in terms of $\dfrac{k_{OH,LNR}}{k_{OH,ATZ}}$. Since $k_{OH,ATZ}$ was

reported to be $2.7 \times 10^9$ $M^{-1}s^{-1}$ (Acero et al., 2000), the value of $k_{OH,LNR}$ was

determined to be $2.74 \times 10^9$ $M^{-1}s^{-1}$.
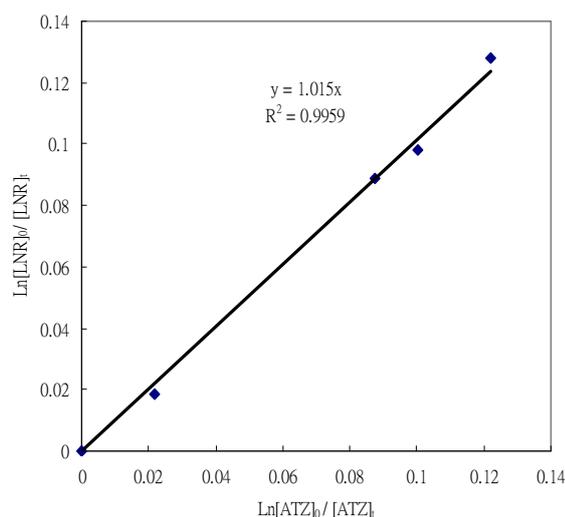


Figure 4-5: Relationship between the degradation of atrazine and LNR ($[LNR]_0 =$

$[ATZ]_0 = 10$ μM, $[H_2O_2]_0 = 20$ mM, Initial light intensity $= 3.0 \times 10^{-6}$

Einstein $L^{-1}$ $s^{-1}$ )

4.2.5 Derivation of Rate Models and rate constant determination in UV/O$_3$ system

The decomposition of LNR in UV/O$_3$ system is an extremely complicated process since many individual reactions, such as direct photolysis, direct (molecular) ozonation, and various free radical oxidation are believed to be involved in this system. According to Gurol and Akata, the principal reactions expected in UV/O$_3$ aqueous system are summarized in Table 4-1 (Gurol and Akata, 1996).

From the table, the inclusion of all sub-reactions to develop kinetic model in this system will be difficult and the result is likely impracticable due to the involvement of too many parameters. Therefore, a different approach using ozone molecule oxidation, hydroxyl radical oxidation, and UV-induced oxidation to describe the overall process were proposed. The decay of LNR in UV/O$_3$ system therefore can be described as below:

$$-\frac{d[LNR]}{dt} = k_{overall}[LNR] = k_{o_3,LNR}[LNR][O_3] + k_{OH,LNR}[LNR][HO^\bullet] +$$

$$2.303\phi_{LNR}\varepsilon_{LNR}lI[LNR] \tag{4-29}$$

The [HO$^\bullet$] of the second term in the Eqn. (4-29) theoretically may come from the hydroxide ion initiated decomposition of ozone and the photolysis of ozone by UV. Under acidic condition, however, the contribution of the hydroxide ion initiated decomposition of ozone to the production of HO$^\bullet$ is insignificant at low pH levels as discussed previously. The photolysis of ozone can be assumed as the only source of HO$^\bullet$ in UV/O$_3$ system.

Table 4-1: Summary of the principal reactions expected in UV/O$_3$ aqueous system

| Reaction | Rate Constant (M$^{-1}$s$^{-1}$) and Equilibrium Constant (pK$_a$) | eq |
|---|---|---|
| O$_3$ + $hv$ →H$_2$O$_2$ | | 4-11 |
| H$_2$O$_2$ + $hv$ → 2HO$^\bullet$ | | 4-12 |
| H$_2$O$_2$ ↔ HO$_2^-$ + H$^+$ | $pK_{a,10}$ = 11.8 | 4-13 |
| HO$_2^-$ + O$_3$ → O$_3^{\bullet-}$ + HO$_2^\bullet$ | k$_{11}$ = 2.8 × 10$^6$ | 4-14 |
| HO$_2^\bullet$ ↔ H$^+$ + O$_2^{\bullet-}$ | $pK_{a,12}$ = 4.8 | 4-15 |
| O$_2^{\bullet-}$ + O$_3$ → O$_3^{\bullet-}$ + O$_2$ | k$_{13}$ = 1.6 × 10$^9$ | 4-16 |
| O$_3^{\bullet-}$ + H$^+$ → HO$^\bullet$ + O$_2$ | k$_{14}$ = 5.2 × 10$^{10}$ | 4-17 |
| HO$^\bullet$ + H$_2$O$_2$ → HO$_2^\bullet$ + H$_2$O | k$_{15}$ = 2.7 × 10$^7$ | 4-18 |
| HO$^\bullet$ + HO$_2^-$ →HO$_2^\bullet$ + OH$^-$ | k$_{16}$ = 7.5 × 10$^9$ | 4-19 |
| HO$^\bullet$ + O$_3$ → HO$_2^\bullet$ + O$_2$ | k$_{17}$ = 3.0 × 10$^9$ | 4-20 |
| 2HO$^\bullet$ → H$_2$O$_2$ | k$_{18}$ = 5.5 × 10$^9$ | 4-21 |
| 2HO$_2^\bullet$ → H$_2$O$_2$ + O$_2$ | k$_{19}$ = 7.6 × 10$^5$ | 4-22 |
| HO$_2^\bullet$ + O$_2^{\bullet-}$ + H$_2$O→ H$_2$O$_2$ + O$_2$ + OH$^-$ | k$_{20}$ = 8.9 × 10$^7$ | 4-23 |
| O$_3$ + OH$^-$ → HO$_2^-$ + O$_2$ | k$_{21}$ = 14.2 | 4-24 |
| O$_3$ + LNR → products | $k_{O3,LNR}$ = 293 | 4-25 |
| LNR + $uv$ → products | | 4-26 |
| HO$^\bullet$ + LNR → products | $k_{OH,LNR}$ =2.74 × 10$^9$ | 4-27 |
| Other radicals + LNR → products | | 4-28 |

Since HO$^\bullet$ is so reactive that it does not accumulate to an appreciable level in the solution, a steady-state approximation can be made (from the equations listed in Table 4-1):

$$\frac{d[HO^\bullet]}{dt} = 2\frac{d[H_2O_2]}{dt} + k_{14}[O_3^{\bullet-}][H^+] - k_{15}[HO^\bullet][H_2O_2] - k_{16}[HO^\bullet][HO_2^-]$$
$$-k_{17}[HO^\bullet][O_3] - k_{18}[HO^\bullet]^2 - k_{OH,LNR}[HO^\bullet][LNR] = 0 \tag{4-30}$$

or $2\dfrac{d[H_2O_2]}{dt} + k_{14}[O_3^{\bullet-}][H^+] = k_{15}[HO^\bullet][H_2O_2] + k_{16}[HO^\bullet][HO_2^-] + k_{17}[HO^\bullet][O_3]$

$$+ k_{OH,LNR}[HO^\bullet][LNR] \tag{4-31}$$

Under acidic conditions (the reaction condition of this test), $HO_2^-$ concentration would be at extremely low level (judging from the pKa of 11.8 as shown in Eqn. (4-13)), which means $O_3^{\bullet-}$ as a source of $HO^\bullet$ is negligible (from Eqns. (4-14) to (4-17)) comparing to $H_2O_2$ (Eqn. 4-12). In addition, the contribution of Eqn. 4-16 to $HO^\bullet$ consumption can also be ignored. Furthermore, the termination of $HO^\bullet$ through radical-radical termination reactions as presented by Eqns. (4-21) to (4-23) is insignificant and can be neglected due to very low $HO^\bullet$ radical concentrations (Gurol and Akata, 1996). According to Table 1, $k_{15}$ is much smaller than $k_{17}$ and $k_{OH,LNR}$ (more than 100 times), while [$O_3$] (a continuous input) is much higher than [$H_2O_2$], the Eqn. (4-18) can therefore be ignored. Thus, Eqn. (4-31) can safely be simplified to:

$$2\frac{d[H_2O_2]}{dt} = k_{17}[HO^\bullet][O_3] + k_{OH,LNR}[HO^\bullet][LNR] \tag{4-32}$$

In Eqn. (4-32), [$HO^\bullet$] still cannot be calculated since the variation of [$H_2O_2$] is difficult to be determined. However, if Eqns (4-11) and (4-12) are merged together, the left-hand side of Eqn. (4-32) can be redefined as $-\alpha\dfrac{d[O_3]}{dt}$ ($\alpha$ is defined as the

ratio of the production rate of HO$^\bullet$ and/or the decay rate of ozone) since the rate of

Eqn. (4-11) is likely much faster than that of Eqn. (4-12). Then Eqn. (4-32) becomes:

$$-\alpha\frac{d[O_3]}{dt} = 2.303\alpha\phi_{O_3}I\varepsilon_{O_3}l = k_{17}[HO^\bullet][O_3] + k_{OH,LNR}[HO^\bullet][LNR] \tag{4-33}$$

where $\phi_{O_3}$ is the quantum yield of ozone decay, $l$ is the optical light path (i.e. the

diameter) of the quartz beaker and $\varepsilon_{O_3}$ is the molar absorptivity of ozone (3600 L

mol$^{-1}$ cm$^{-1}$) (Bahnemann and Hart, 1982)at 253.7nm.

or

$$[HO^\bullet] = 2.303\frac{\alpha\phi_{O_3}I\varepsilon_{O_3}l}{k_{17}[O_3] + k_{OH,LNR}[LNR]} \tag{4-34}$$

The decay rate of LNR can therefore be defined in Eqn. (4-35) by incorporating Eqs.

(4-29) and (4-34):

$$k_{overall} = k_{O_3,LNR}[O_3] + 2.303I\{k_{OH,LNR}\frac{\alpha\phi_{O_3}\varepsilon_{O_3}l}{k_{17}[O_3] + K_{OH,LNR}[LNR]} + \phi_{LNR}\varepsilon_{LNR}l\} \tag{4-35}$$

It should be noted that many chemicals in the solution are capable of absorbing UV

light at 253.7nm, which may result in an effect of light attenuation. This is specially

noticeable when their concentration or the associated molar absorptivity is high.

Since this study focused on the initial rate, the contribution to light attenuation from

intermediates can be negligible, which makes LNR and ozone the major components

contributing to the attenuation effect. The attenuated light intensity can be quantified

by the following equation in a cylindrical reactor (Chu et al., 2005):

$$I = \frac{I_0}{-2.303A}[e^{-2.303A} - 1] \tag{4-36}$$

Where A = $\sum_{i=1}^{n} \varepsilon_i c_i l = \varepsilon_{O3}C_{O3}l + \varepsilon_{LNR}C_{LNR}l$. Due to high molar absorptivity of ozone

and LNR (as indicated before), the term $e^{-2.303A}$ approaches zero, then the Eqn. (4-36)

can be further simplified to:

$$I = \frac{I_0}{2.303A} \qquad (4\text{-}37)$$

By substituting Eqn. (4-37) into Eqn. (4-35), the Eqn. (4-35) becomes:

$$k_{overall} = k_{O_3,LNR}[O_3] + \frac{I_0}{A} \{k_{OH,LNR} \frac{\alpha\phi_{O_3}\varepsilon_{O_3}l}{k_{17}[O_3] + K_{OH,LNR}[LNR]} + \phi_{LNR}\varepsilon_{LNR}l\} \qquad (4\text{-}38)$$

The tested results of $k_{overall}$ under different light intensity were correlated to $\frac{I_0}{A}$ as

shown in Figure 4-6, where a linear curve was observed as predicted in Eqn. (4-38).

The slope of the linear curve would be the complex term inside the bracket of Eqn.

(4-38), and the intercept revealed the $k_{o_3,LNR}[O_3]$. Because $\phi_{O_3}$ was reported to be 0.48

and the other parameters are all known, the $\alpha$ is determined to be $6.92 \times 10^{-5}$. The

calculated parameters and the corresponding equations and/or figures are

summarized in Table 4-2.
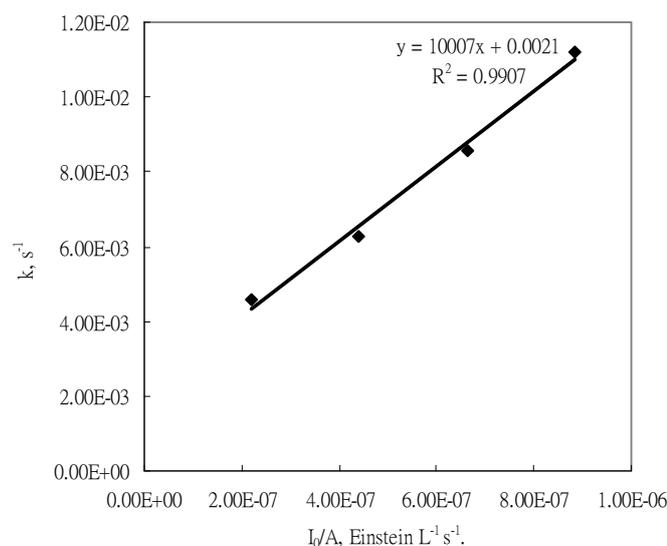


Figure 4-6: Variation of decay rate constant of 0.1 mM LNR under different light

intensity irradiation in UV/$O_3$ system (Notes: $pH_0 = 4.03$, $[O_3] = 1.71 \times 10^{-5}$ M)

Table 4-2: Summary of Rate Constant determination

| parameter | value | unit | Involved equations and figures |
|---|---|---|---|
| $\Phi_{LNR}$ | 0.00122 | mol Eistein$^{-1}$ | Eq. 4-2(slope) and Fig. 4-3 |
| $k_{o_3,LNR}$ | 293 | M$^{-1}$s$^{-1}$ | Eq. 4-6 (int.) and Fig. 4-4b |
| $k_{OOH}$ | 14.2 | M$^{-1}$s$^{-1}$ | Eq. 4-6 (slope) and Fig. 4-4b |
| $k_{OH,LNR}$ | $2.74 \times 10^9$ | M$^{-1}$s$^{-1}$ | Eq. 4-10 (slope) and Fig. 4-5 |
| $\alpha$ | $6.92 \times 10^{-5}$ | fraction | Eq. 38 (slope) and Fig. 4-6 |

A high $k_{o_3,LNR}$ value (293 M$^{-1}$s$^{-1}$)and low $k_{OOH}$ (14.2 M$^{-1}$s$^{-1}$) justifies the observation that OH$^-$ plays a much more important role at pH levels above 9 than pH levels below 9. It has been reported that $k_{o_3,LNR}$ is 1.9 M$^{-1}$s$^{-1}$ (Benitez et al., 2007a) or 3.1 M$^{-1}$s$^{-1}$ at pH 2.0 (DeLaat et al., 1996), which is lower than the value obtained in this study. This can be rationalized by the pKa value of LNR and the highly electrophilic property of ozone. The pKa of phenylurea was reported to vary in the range from 4.3 to 5.5 (Lopez et al., 2005), as a result, LNR would be charged positively at pH 2 while charged negatively at pH 9-11 in this study. The negatively-charged compounds show higher reactivity toward ozone than positively-charged one (Hoigne and Bader, 1983), leading to a higher $k_{o_3,LNR}$ value under basic conditions. The $k_{OOH}$ is lower than the value (48 $\pm$ 12 M$^{-1}$s$^{-1}$) reported previously (Forni et al., 1982). It is probably because the value reported by Forni was determined at pH levels of 11.2-12.3 while pH level in this study varied from 9 to 11. The $k_{OH,LNR}$ was

determined to be $2.74 \times 10^9 \, M^{-1}s^{-1}$ which is about the same order of the value $(4.2 \pm 0.4) \times 10^9 \, M^{-1}s^{-1}$ with 248 nm UV irradiation reported by López et. al. (Lopez et al., 2005).

The observed LNR decay rate and predicted overall decay rate by the proposed model under various conditions were compared and shown in Table 4-3, where the error ranges from 2.2% to 11.5%, indicating the proposed models offer an accurate way to predict the LNR decay in the UV, $O_3$ and $UV/O_3$ under varied conditions.

Table 4-3: Comparison between the predicted $k_{overall}$ from the proposed model and the observed $k_{overall}$

| Reaction conditions | Predicted $k_{overall}$ based on the proposed model ($s^{-1}$) | Observed $k_{overall}$ in this study ($s^{-1}$) |
|---|---|---|
| Sole-UV system $I_0 = 9.0 \times 10^{-6}$ Einstein $L^{-1}s^{-1}$ $[LNR]_0 = 0.1$ mM | $3.27 \times 10^{-3}$ | $3.20 \times 10^{-3}$ |
| Ozone system $[O_3] = 1.71 \times 10^{-5}$ M pH = 11.0 $[LNR]_0 = 0.1$ mM | $1.23 \times 10^{-2}$ | $1.38 \times 10^{-2}$ |
| Ozone system $[O_3] = 9.96 \times 10^{-6}$ M pH = 11.0 $[LNR]_0 = 0.1$ mM | $7.16 \times 10^{-3}$ | $7.00 \times 10^{-3}$ |
| UV/Ozone system $[O_3] = 3.09 \times 10^{-5}$ M $I_0 = 6.0 \times 10^{-6}$ Einstein $L^{-1}s^{-1}$ pH = 6.0 $[LNR]_0 = 0.1$ mM | $1.304 \times 10^{-2}$ | $1.154 \times 10^{-2}$ |

## 4.3 Summary

In this chapter, the degradation for LNR by UV, $O_3$, and UV/$O_3$ processes has been investigated. The decay rate of linuron by UV/$O_3$ process was found to be around 3.5 times and 2.5 times faster than sole-UV and ozone-alone, respectively. No TOC removal was observed in sole UV process, and TOC removal was insignificant in ozonation process (about 15% mineralization after 100 minutes). However, nearly 80% mineralization was achieved by using UV/ozone process after 100 minutes. The overall rate constants increase exponentially with pH above 9.0 while the increase of rate constants with pH below 9 is insignificant in $O_3$ system. All predominating parameters involved in the three processes were determined in the assistant of proposed linear models. The proposed approach could furnish a useful method to explore the major kinetic constants, while minimizing the requirement in defining the minor rate constants. This is helpful in real applications for determining a quick but accurate prediction in system design.

# Chapter 5 Reaction Mechanism of LNR Degradation by UV Photolysis, Ozonation and UV/O$_3$ Process

## 5.1 Introduction

Herbicides have been widely used as a regular and effective practice to increase the productivity of crop fields. The enormous majority of herbicides, however, are diffused into aquatic environment via agricultural runoff or leaching, only a tiny part of total applied herbicides reaching the target pests. (Pimentel, 1995). Herbicides, therefore, have been some of the most frequently detected organic contaminants in natural waters. On the other hand, increasing demand of high quality water results in intensive concern about the possible effect of such substances on human health and ecological environment (Colborn et al., 1993; Daam et al., 2009).

LNR was still chosen as target compound in this chapter. Various treatment techniques has been developed to destruct LNR in recent years (Faure and Boule, 1997; Dejonghe et al., 2003; Farre et al., 2007; Chen et al., 2008; ; Benitez et al., 2009). A major part of the investigation, however, focuses on the removal or decomposition of LNR. If the fate of the resulting products remains unanswered, the treatment process cannot be proposed as a trouble-free method since the decay of the parent compounds may result in the generation of more toxic organics than parent compounds. The intermediates from the transformation of LNR vary with treatment methods since different methods offer differed reaction mechanisms. Even LNR is treated by the same process, the identification and fate of intermediates could still

vary with researchers since the decay of LNR is condition-dependent. As a result, the investigation of the resulting products is necessary in each process.

Only four photoproducts have been identified during the phototransformation of LNR in aqueous phase under the irradiation of UV at 254nm in earlier study (Faure and Boule, 1997) and the evolution and destination of these products still remains unanswered. In addition, the information about the reaction mechanism of LNR by UV/$O_3$ process and the fate of intermediates generated during this process is scanty so far. Therefore, in this study, the degradation intermediates of LNR by UV, $O_3$, and UV/$O_3$ were investigated and the decay pathways were proposed accordingly for these three processes, respectively. The effect of initial pH level on the decay of LNR by these three processes and the influence of various anions on the decomposition of LNR by ozonation have aslo been examined. And some major products which escaped identification in the earlier studies are presented in this chapter.

## 5.2 Results and Discussion

5.2.1 The effect of initial pH level on the decay of LNR by UV, $O_3$ and UV/$O_3$ processes

The decomposition of LNR was tested at varied pH levels (from 3 to 11) by different treatment processes: (1) UV photolysis, (2) ozone, and (3) combined UV/ozone system. The photolysis and oxidation of LNR were found to follow pseudo-first-order kinetics at various initial pH levels and the observed rate constants are summarized in Figure 5-1a. As indicated in Figure 5-1a, an increased degradation rate was observed at elevated pH levels both in ozone and UV/ozone systems. It is

well-known that the hydroxide ion can initiate the decomposition of ozone to produce hydroxyl radicals which is a stronger oxidant than ozone in aqueous solution (Forni et al., 1982). The pH level, therefore, plays a major role in the reactions involved with ozone. It is also interesting to observe that photolysis of LNR is pH-independent. No decay of LNR after 50 min was observed at three different pH levels 3, 7, and 11 in a separate test, suggesting there is no acid-or-alkaline catalyzed hydrolysis.
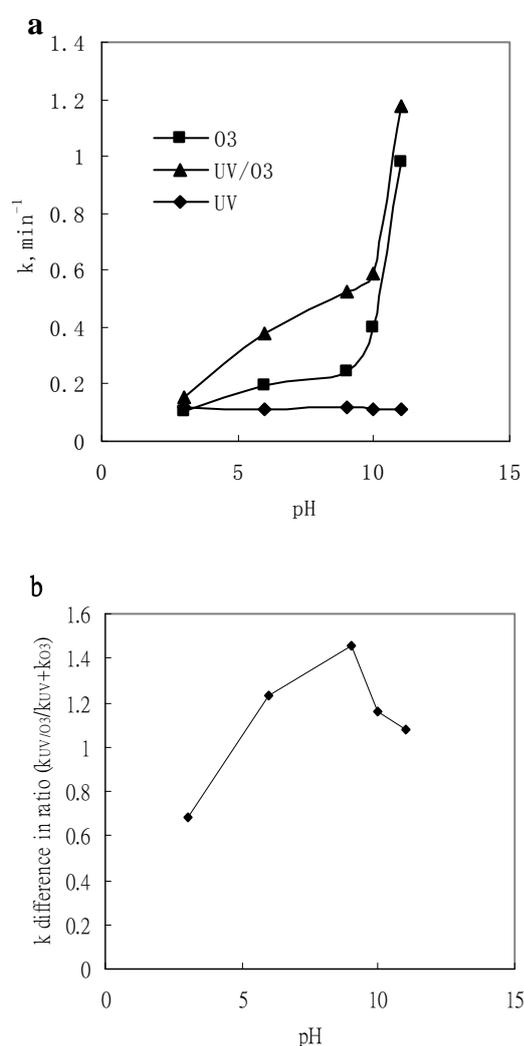


Figure 5-1: (a). Pseduo first-order rate constants at different initial pH level by different degradation process. (b). The ratio of $k_{UV/O3}$ and $k_{UV} + k_{O3}$ (Notes: $[LNR]_0 = 0.1$ mM, $[O_3]_0 = 0.0171$ mM, $[I_0] = 6.0 \times 10^{-6}$ Einstein L$^{-1}$ s$^{-1}$)

It is believed that the combined $UV/O_3$ system can offer a synergistic effect of individual reactions: direct ozonation, direct photolysis, and $HO^\bullet$ oxidation. In this study, the $UV/O_3$ process has proved that it is an effective treatment of LNR from neutral to high pH levels (Figure 5-1a) and 80% TOC removal could be achieved within 100 min reaction as presented in chapter 4. In order to optimize the $UV/O_3$ process at different pH levels, the synergistic effect was examined by comparing the ratio of reaction rate constants of $UV/O_3$ versus the summation of direct ozonation and direct photolysis as illustrated in Figure 5-1b. At pH 3, the ratio is smaller than unity indicating no synergistic effect at all. It was reported that UV irradiation at 254 nm led to all the ozone being photolyzed into hydrogen peroxide which is much weaker oxidant when compared to ozone and hydroxyl radicals (Canton et al., 2003). In addition, hydrogen peroxide is very stable at acidic pH, the chance for forming hydroxyl radicals due to the interaction between UV and $H_2O_2$ is minimal. Therefore, no significant rate improvement was observed by combining UV and $O_3$ at pH 3 (Chu, 2001).

As pH level gradually increased, the synergistic effect becomes more perceptible, and reaches a maximum at around pH 9. This is resulting from the formation of hydroxyl radicals from both ozone molecules and $UV/H_2O_2$ process.

However, it is interesting to note that the synergistic effect drops as pH is further increased. This is because the intermediate $H_2O_2$ is very unstable at very high pH levels. The $H_2O_2$ can easily decay into water and oxygen and the total oxidation capability of the process reduced. This phenomenon may be rationalized by another possible reason that high concentration of hydroxide ion can also initiate the

decomposition of ozone into hydroxyl radicals in sole-ozone system. UV, thus, may not play a key role in terms of the generation of hydroxyl radicals in UV/O$_3$ system.

5.2.2 The effect of varied anions on the LNR decay in sole-ozone system

The effect of various cations such as Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Cu$^{2+}$ and Ti$^{2+}$ on the performance of ozonation process has been well documented (Pines and Reckhow, 2002; Canton et al., 2003; Ni et al., 2003; Xiao et al., 2008). The information about whether or not the anions may influence the functioning of sole-ozone process still remains very limited.

In this section, the effect of various anions on the LNR decay was investigated at pH 3 and 7 in sole-ozone system. As indicated in Figure 5-2, the existence of 0.01 M chloride leads to the significant retardance in the decay rate of LNR at pH 3 while Chloride does not show considerable influence on the degradation of LNR at pH 7. It was reported chloride could react with ozone under acidic conditions as shown in Eqn. 5-1 and Eqn. 5-2 (Yeatts and Taube, 1949):

$$O_3 + Cl^- \rightarrow O_2 + ClO^- \tag{5-1}$$

$$2H^+ + Cl^- + ClO^- \Leftrightarrow Cl_2 + H_2O \tag{5-2}$$

The first reaction is the rate-determining reaction while the second one is reversible. High concentration of hydrogen ion favors the second reaction proceeding towards the right side. Therefore, at pH 3, chloride ions can effectively compete for O$_3$ with LNR to produce Cl$_2$ which is much weaker oxidant than ozone. On the other hand, at pH 7, lower proton concentration deactivates the above reactions, restricts the reaction between ozone and chloride, and minimizes the competition between

chloride and LNR for $O_3$. In addition, a little retardance in the LNR decay rate was observed after 4 min reaction at pH 7 with the existence of 10 mM chloride (See Figure 5-2b). This is possibly due to the decrease of pH during the reaction as shown in Figure 5-2c.

a

b

c
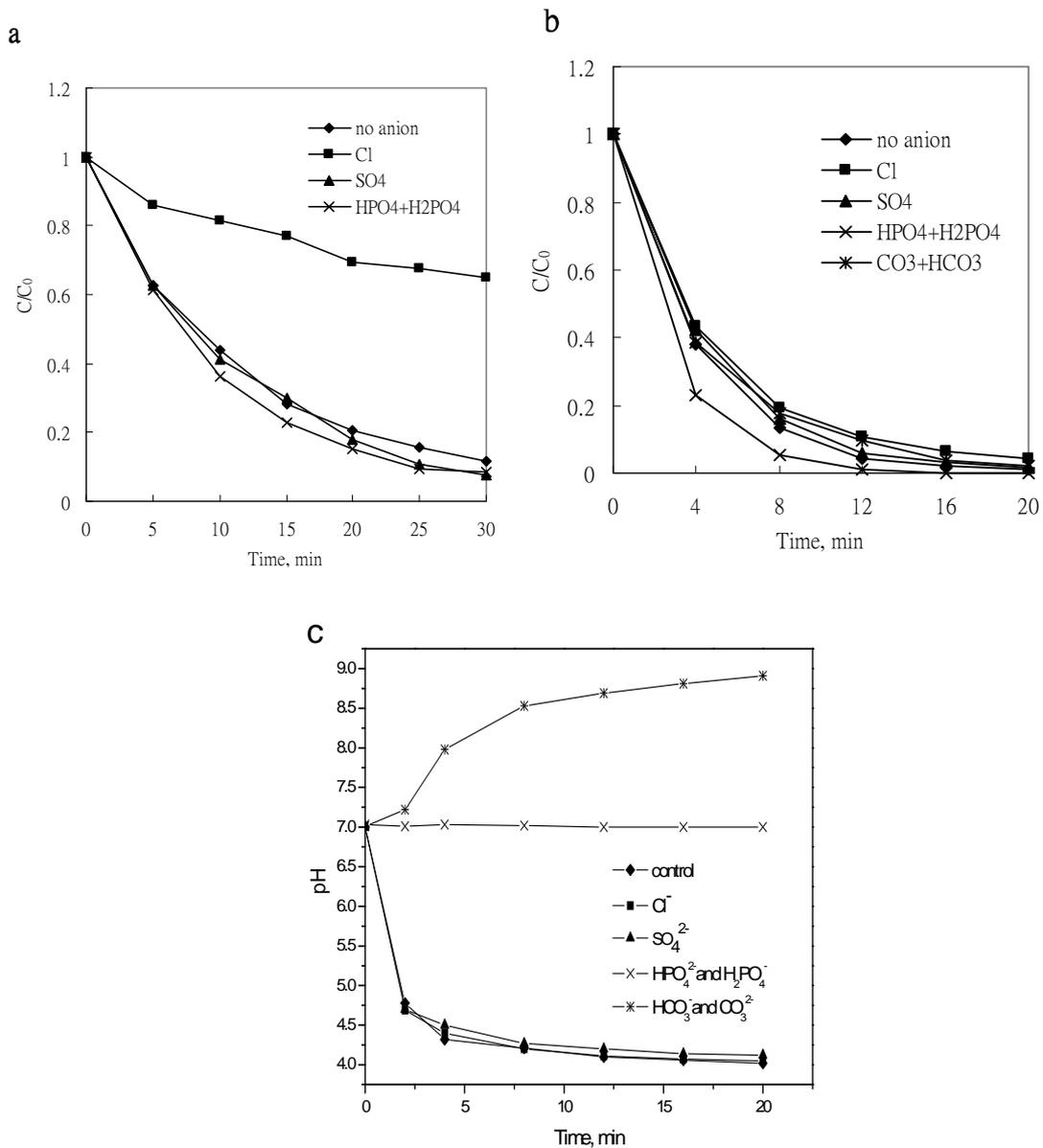
Figure 5-2: (a) The effect of varied anions on the performace of ozonation at pH 3;

(b) The effect of varied anions on the performance of ozonation at pH 7;

(c) The variation of pH during the ozonation of LNR with the presence

of various anions. (Notes: $[LNR]_0 = 0.1$ mM, $[O_3]_0 = 0.0245$ mM, [anions] $= 0.01$ M)

It is also interesting to note the LNR decay rate accelerates with the existence of $HPO_4^{2-}$ and $H_2PO_4^-$ at pH 7 while such an effect is not significant at pH 3, in which the solution pH remains stable during the reaction for every scenario (data not shown). At pH 7, the buffer ability of $HPO_4^{2-}$ and $H_2PO_4^-$ made the pH of the solution very stable during the reaction while the pH value decreased from 7 to 4.78 during the first 2 min reaction in the case of no anion as indicated in Figure 5-2c. The higher pH level may result in the faster decay of LNR in the reaction with the existence of $HPO_4^{2-}$ and $H_2PO_4^-$, as discussed previously.

When 0.01 M $Na_2CO_3$ was added into the solution at pH 7, another interesting point is the increase of pH level during the reaction did not guarantee an improvement of LNR decay rate even though the higher pH should theoretically favors the faster decay of LNR. This may be because carbonate ions can quench the hydroxyl radicals in the solution to generate hydroxide ions as described in Eqn. 5-3:

$$HO^\bullet + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-} \tag{5-3}$$

Since carbonate and bicarbonate can compete for hydroxyl radicals with LNR, which can hinder the beneficial effect resulting from the increment of pH level, these two effects counteract each other and this rationalizes no appreciable influence of bicarbonate and carbonate ions on the LNR degradation rate.

### 5.2.3 Reaction mechanism of LNR degradation

In order to gain a deep insight into the LNR degradation by UV, ozone and UV/ozone processes, the intermediates were identified and the evolution of major

intermediates was investigated in each process. Seventeen intermediates were identified during LNR degradation by these three processes. The information on the intermediates including the mass of deprotonated ion ($[M-H]^+$) of the daughter compounds, the proposed molecular structure, and the proposed fragments is summarized in Table 5-1. Actually, [M + acetate]$^-$ ions were obtained as a base peak of the mass spectra for most intermediates and LNR (See Appendix II) due to 5 mM ammonium acetate being used as mobile phase and negative-ion mode being employed in this study (Barcelo and Albaiges, 1989). Some of their mass spectra are shown in Appendix II.

Table 5-1: Identified degradation products and their main fragments determined by LC/ESI-MS

| Compound | Retention time | Molecular weight | Molecular ion and main fragments | Structural formula | Detected in | | |
|---|---|---|---|---|---|---|---|
| | | | | | UV | O₃ | UV/O₃ |
| LNR | 20.93 | 248 | 247, 217, 188, 160, 109 |  | √ | √ | √ |
| 1 | 10.25 | 278 | 277, 250, 233, 217,119 |  | | | √ |
| 2 and 3 | 10.61, 12.62 | 200 | 199,142 |  or  | √ | √ | √ |
| 4 | 11.61 | 186 | 185,165,141,119 |  or  | √ | | √ |

| No. | $t_R$ | [M] | Fragment ions | Structure | | | |
|---|---|---|---|---|---|---|---|
| 5 | 13.12 | 214 | 213 |  | √ | | √ |
| 6 and 7 | 14.11 and 15.40 | 230 | 229, 37,119,109 |  | √ | √ | √ |
| 8 | 14.90 | 250 | 249,219,202,176, 137,119,109 |  | | | √ |
| 9 | 15.44, 15.56 | 220 | 219,203,176, 137 119,109 |  | | | √ |
| 10 | 15.68 | 234 | 233,203,160, 137,119,109 |  | √ | √ | √ |
| 11 | 16.31 | 204 | 203, 160, 137,119,109 |  | √ | √ | √ |
| 12 | 16.93 | 234 | 233, 202,176, 137,119,109 |  | √ | √ | √ |
| 13 | 17.46 | 218 | 217, 160, 137,119,109 |  | √ | √ | √ |
| 14 | 18.74 | 248 | 247, 202, 204 |  | √ | | √ |
| 15 | 18.93 | 232 | 231,202,188 160, 137,119.109 |  | √ | √ | √ |
| 16 and 17 | 19.30, 19.72 | 264 | 263, 233, 217, 202,188,156,119, 109 |  or  | | √ | √ |
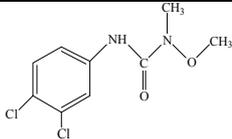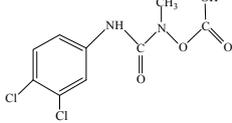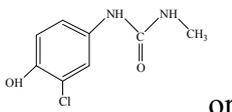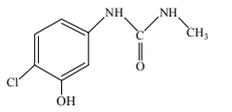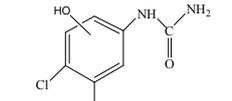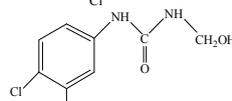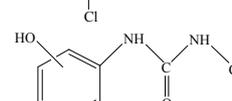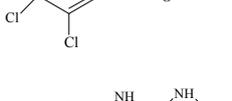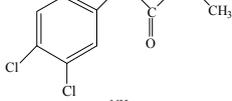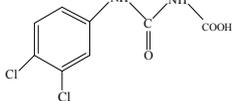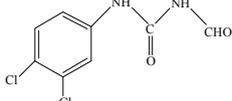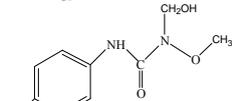
(1) UV photolysis

The direct photolysis of LNR and evolution profiles of intermediates by UV at 254 nm is shown in Figure 5-3. The LC-MS analysis revealed that twelve intermediates were produced during the reaction. The "demethoxylation" pathway is believed to be one of major reaction pathways since compound 13 (DCPMU) is the dominating intermediate during photolysis of LNR as indicated in Figure 5-3a. Similar observation has been reported earlier (Faure and Boule, 1997). The formation of intermolecular hydrogen bond between one hydrogen atom of *N*-methoxyl and the oxygen of neighboring C=O bond and subsequent generation of formaldehyde was proposed to be the mechanism of this demethoxylation pathway. Faure and Boule reported four intermediates (compounds 6, 7, 11 (DCPU) and 13 (DCPUM)) in the photolysis of LNR by UV at 254 nm (Faure and Boule, 1997) while eight new intermediates (compounds 2, 3, 4, 5, 10, 12, 14 and 15) were detected in this study. Photohydrolysis-dechlorination is believed to be another major reaction mechanism during the photolysis of LNR by UV at 254 nm, judging from the yields of the products from photohydrolysis-dechlorination and chloride ions during the reaction (See Figure 5-3c). There are two pairs of isomers (6 and 7, 2 and 3) which are the products of Photohydrolysis-dechlorination among these intermediates. Compounds 6 and 7 are believed to come from the hydroxylation on the ring with simultaneous dechlorination of LNR. Compounds 2 and 3 originate from the photohydrolysis-dechlorination of compound 13 (DCPMU), and the photohydrolysis-dechlorination of compound 11 (DCPU) produces compound 4, which have been corroborated by two individual tests using compound 13 (DCPMU) and 11 (DCPU) as initial probe compounds by UV process at 254 nm. In addition, compound 12 was detected in the degradation of both LNR and compound 13 (DCPMU) by UV irradiation at 254 nm, indicating this product is from the hydroxylation of benzene ring of DCPMU. The

hydroxylation of benzene ring has been reported by other researchers (Jin et al., 1995; Lau et al., 2007). Jin et al. proposed two possible mechanisms (One is the presence of oxygen leading to the production of $O_2^{\bullet-}$ and $HO_2^{\bullet}$, and another one is that benzene ring of the parent compound is hydroxylated via endoperoxide not involving free radicals). Oxygen was believed to be involved in both mechanisms, and it was suggested that the presence of oxygen could significantly increase the decay rate of tyrosine (Jin et al., 1995). This, however, is not observed in this study. In a separate test that the LNR solution was deoxygenated by argon before and during the irradiation by UV at 254 nm, the same twelve intermediates were identified and no reduction in LNR decay rate was observed in the absence of oxygen.

A different mechanism---direct hydrolysis of benzene ring of DCPMU, not involving oxygen, thus, is proposed and may rationalize the generation of compound 12. Compound 10 also escaped from the identification in earlier study. It is reasonable to assume that compounds 10 and 11 (DCPU) originate from *N*-oxidation and subsequent demethylation of DCPMU, respectively as observed in the work of Jirkovsky et al. (Jirkovsky et al., 1997). However, it is interesting to note that compounds 10 and DCPU were not detected in the photolysis of DCPMU, indicating DCPMU is not the source of compound 10. Compound 10 and 11 were detected in the photolytic degradation of LNR without the existence of oxygen, suggesting that oxygen was not involved in the production of these two compounds, either. The possible mechanism for the generation of compound 10, therefore, was proposed as below:

(5-4)
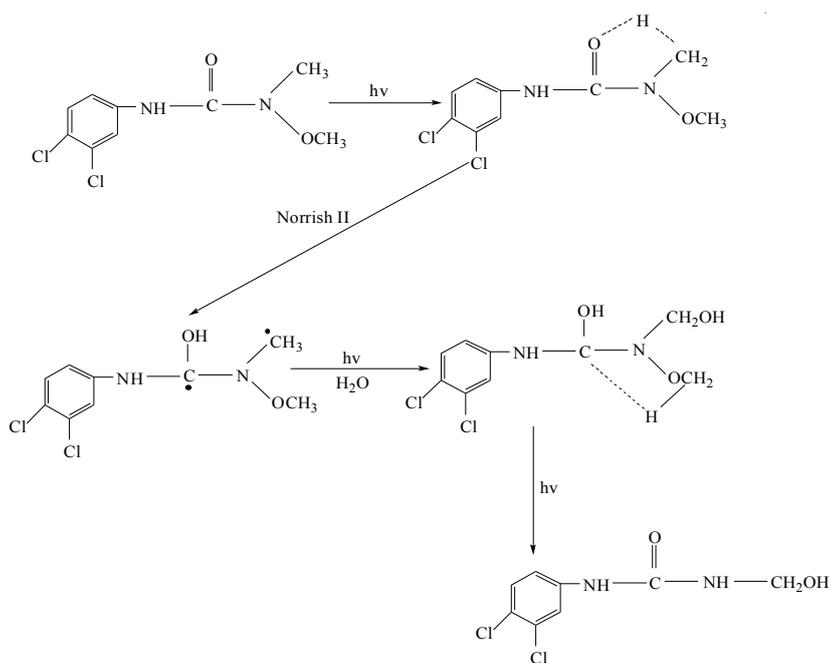
DCPU is believed to result from compound 10 since the photolysis of DCPMU does not generate DCPU. Therefore, the decay pathway of LNR by UV process was proposed (Figure 5-5) on the basis of the evolution profile analysis of intermediates during the photolysis of LNR and the information about the intermediates from the photolysis of DCPMU and DCPU. The percentages in Figure 5-5 stand for the fraction of LNR transformed to a particular product during the initial phase (30 minutes). Figure 5-5 also reveals that demethoxylation is predominant decay mechanism of LNR by UV process at 254 nm since 63.1% ([DCPMU] + [compound 2 and 3] + [compound 12] / [LNR]$_{removed}$) of LNR was eliminated via this pathway. Furthermore, the individual test using DCPMU as the initial compound reveals that photohydrolysis-dechlorination is the dominating mechanism in terms of the photolysis of DCPMU (96.9% of DCPMU was removed via this pathway) (See Figure 5-4).

Figure 5-3b shows UV spectrum of the reaction solution at different time intervals. It is well-known that a benzene ring has two absorption bands (One occurs near 205

nm, and another one appears near 250 nm). As indicated in Figure 5-3b, both absorption bands are dwindling during the photolysis reaction. Judging from the mass balance of benzene ring and the decreased absorbance of the solution at 254 nm (See Figure 5-3a and Figure 5-3b), it is believed that ring-opening occurs during the photolytic decomposition of LNR. Unfortunately, mineralization of LNR was not observed in this process due to the lack of oxidants as demonstrated in the TOC curve (Figure 5-3c). Figure 5-3c also demonstrates that photohydrolysis-dechlorination led to considerable decrease of pH level from 6.0 to 3.59. It was observed that around 98% of chlorine on the benzene ring was released and trace amount of $NH_4^+$ and $NO_3^-$ was detected, indicating de-nitrogenation could be achieved in the photolytic degradation of LNR by UV at 254 nm.
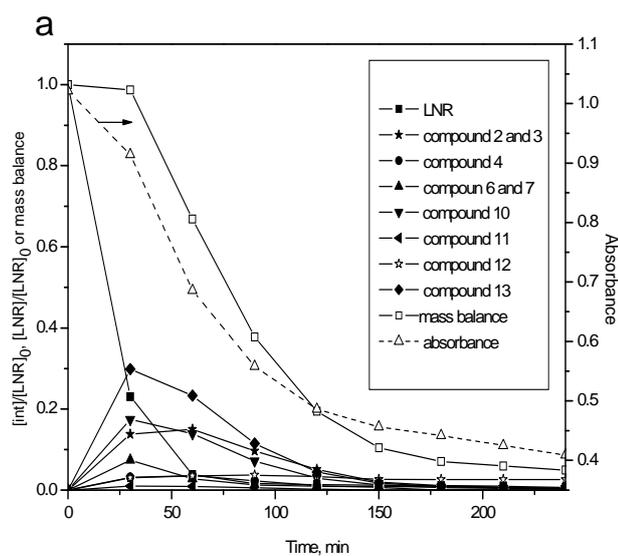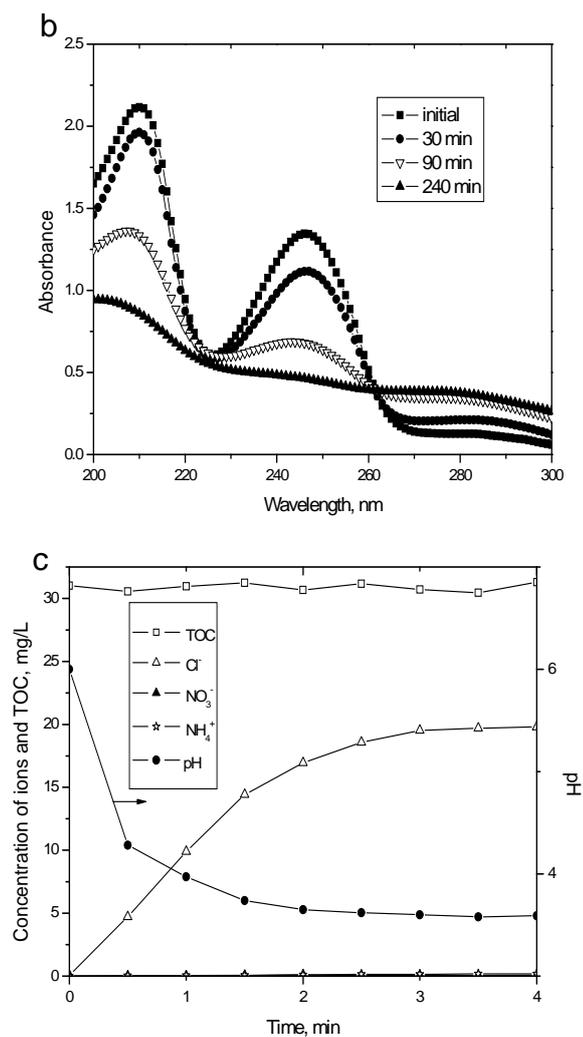
Figure 5-3: (a) The evolution profiles of LNR and intermediates in the photolysis of LNR at 254 nm; (b) UV absorption spectrum of the solution at different time intervals; (c) The evolution profiles of TOC, pH, $Cl^{-1}$, $NO_3^{-1}$, and $NH_4^+$.

(Notes: $[LNR]_0 = 0.285$ mM, $pH_0 = 6.0$, $[I_0] = 9.0 \times 10^{-6}$ Einstein $L^{-1}$ $s^{-1}$)
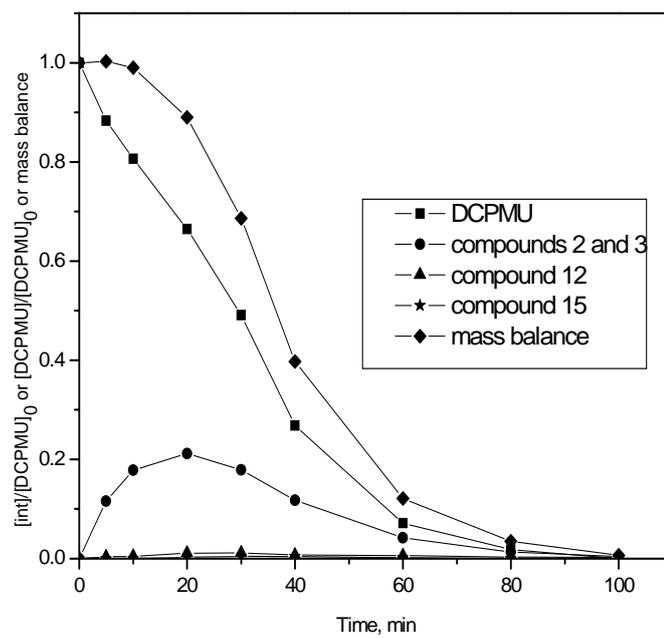
Figure 5-4: The evolution profiles of DCPMU and intermediates in the photolysis of

DCPMU at 254 nm
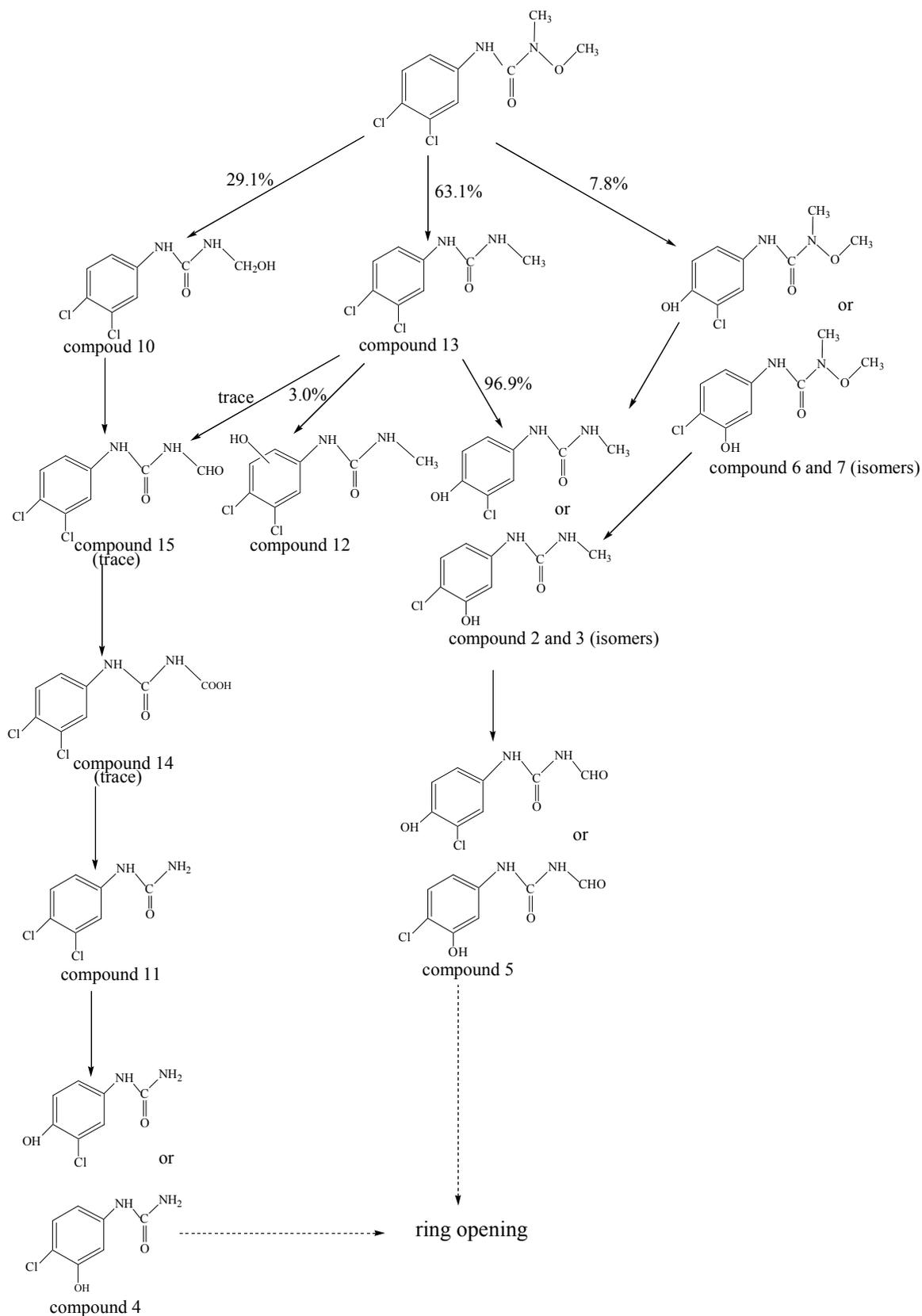
Figure 5-5: The decay pathways of LNR under the irradiation by UV at 254 nm.

(2). Ozonation

Benzene ring is susceptible to electrophilic attack (by electrophilic agents) due to its exposed π electrons. However, substituted groups on the benzene ring are believed to exert a significant influence on the reactivity of electrophilic reaction. LNR is tri-substituted by two chlorines and a side chain ( $\underset{\text{NHCHON}}{\overset{\text{OCH}_3}{\diagdown}}_{\text{CH}_3}$ ). Bi-substitution by chlorine may result in decrease on the electron density of benzene ring due to electron-withdrawing ability of chlorine while the side chain can be a moderately activating substituent because the unshared electron pair on the nitrogen atom adjacent to the benzene ring may make a contribution to the electron density on the benzene ring through resonance (Solomons, 2006). Ozone is highly electrophilic agent. The degradation of LNR by ozonation, therefore, becomes very complicated. Ten intermediates were identified and summarized in Table 1 in this study. The evolution profiles of LNR and four major intermediates (compound 6 or 7, 10, 11, 13) were demonstrated in Figure 5-6a. It is interesting to note that the profile of mass balance is quite similar to that of LNR, indicating the intermediates only account for a small portion to the total mass. This may be because most intermediates are susceptible to ozonation process. In addition, trace amount of six intermediates (compound 2 and 3, 12, 15, 16 and 17) were detected in this system. Compound 6 or 7 is believed to come from the dechlorination-hydroxylation of LNR while compound 16 and 17 may originate from the *N*-terminus oxidation of LNR. Demethoxylation of LNR leads to the generation of compound 13 (DCPMU). All six other intermediates (compounds 2 and 3, 10, 11, 12 and 15) are believed to come from DCPMU, which was confirmed by an independent test using DCPMU as initial probe compound in this system. Compounds 2 and 3 are from dechlorination-

hydroxylation of DCPMU. *N*-terminus oxidation of DCPMU produces compound 10 and 15. Compound 11 (DCPU) is believed to result from the demethylation of DCPMU while hydroxylation of benzene ring of DCPMU gives rise to the production of compound 12. A decay pathway of LNR by ozonation, thus, was proposed accordingly (See Figure 5-8).

Judging from the low yield of compound 6 or 7, the dechlorination is likely to be minor mechanism of LNR decay by ozonation while *N*-terminus oxidation may be major mechanism. However, more than 50% of total chlorine was released after 20 min of reaction as shown in Figure 5-6b, which contradicts to the previous assumption. One possible explanation is that dechlorination-hydroxylation intermediates may not accumulate to appreciable level due to fast decay. When chlorine is substituted by hydroxyl, the electron-donating resonance effect of hydroxyl favors the enhancement of the electron density on the benzene ring and the susceptibility of these dechlorination-hydroxylation intermediates to ozonation.

Although mass balance of benzene ring nearly approaches zero, the TOC removal is only around 25% after 120 min (See Figure 5-6b). This may be due to the high selectivity of ozone leading to its incapability to degrade some small organic compounds resulting from the cleavage of benzene ring. As shown in Figure 5-6b, pH decreases significantly during the initial 20 minutes of the reaction due to the release of chloride and probably the generation of aliphatic acid. Figure 5-6b also reveals that 13% of nitrogen was released to the solution as nitrate and ammonia ions after 120 min.
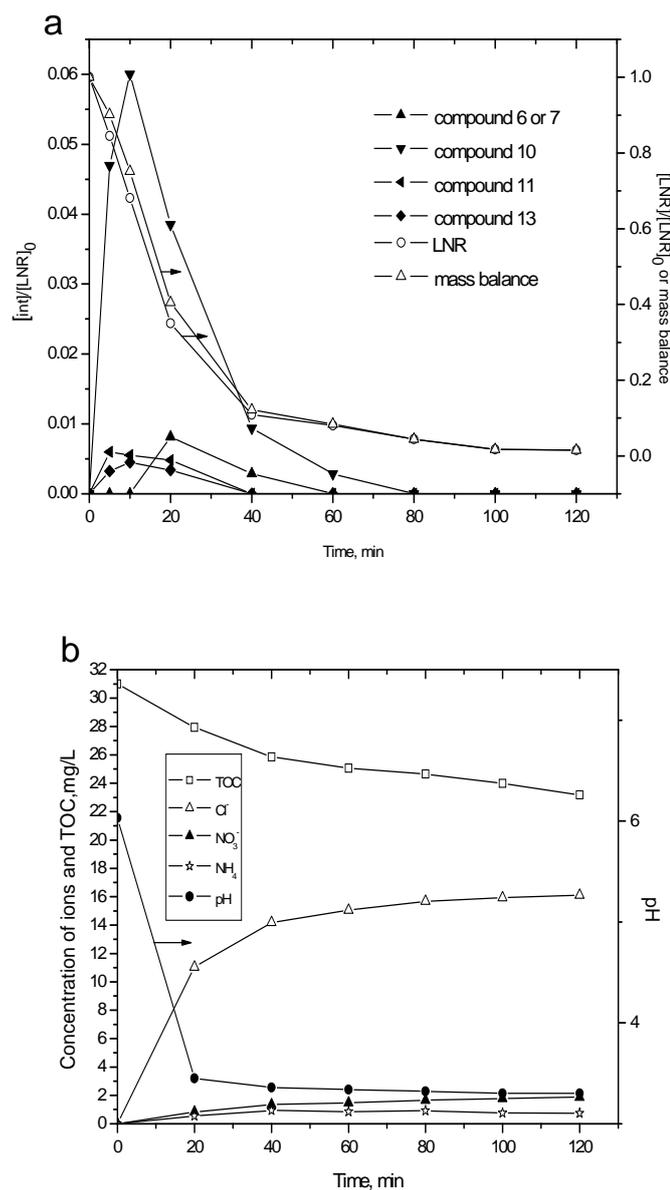
Figure 5-6: (a) The evolution profiles of LNR and intermediates for the degradation of LNR by ozonation; (b) The evolution profiles of TOC, pH, $Cl^{-1}$, $NO_3^{-1}$, and $NH_4^+$ for the degradation of LNR by ozonation.

(Notes: $[LNR]_0 = 0.285$ mM, $[O_3] = 0.0245$ mM, $pH_0 = 6.0$)

(3) UV/$O_3$ process

It is generally agreed that several individual reactions such as direct (molecular) ozonation, direct photolysis, and radical oxidation (mainly hydroxyl radical) involve

the degradation of organic compounds by UV/O$_3$ process. Therefore, more intermediates (seventeen) were detected in this system than sole-ozone and sole-UV (See Table 5-1). The evolution profiles of LNR and major products were shown in Figure 5-7 a. The decay pathway of LNR by UV/O$_3$ was proposed as illustrated in Figure 5-8, where the degradation pathways by UV/O$_3$ are quite similar to that of ozonation. However, the yield of major intermediates is much higher in UV/O$_3$ system than that of major products in sole-ozone system as indicated in Figure 5-7a. This is likely because these intermediates originate from more decay mechanisms in parallel including photolysis, radical oxidation and oxidation offered by ozone molecule. At the initial stage of reaction, photolysis may play a major role in the degradation of LNR since both UV/O$_3$ and UV processes produce the same dominating intermediates (the yield of compound 13 is the highest and followed by compound 10) (See Figure 5-3a and Figure 5-7a). This phenomenon can be rationalized by the following:

(a) Ozone can be rapidly photolyzed into hydrogen peroxide under UV irradiation at a wavelength of 254 nm due to its high molar absorptivity (3600 M$^{-1}$ cm$^{-1}$) and quantum yields (0.48) (Gurol and Akata, 1996); and

(b) The low absorption coefficient of H$_2$O$_2$ (19.6 M$^{-1}$ cm$^{-1}$) (Gurol and Akata, 1996) may make H$_2$O$_2$ incapable of competing with LNR (the absorption coefficient of LNR is 13254 M$^{-1}$ cm$^{-1}$) for photons to produce hydroxyl radical.

The evolution of TOC, pH and varied ion products in this system was also investigated in this study (See Figure 5-7b). As demonstrated in Figure 5-7, the UV/O$_3$ process have shown several advantages over sole-UV and ozonation including: (1) more than 86% mineralization; (2) faster degradation of LNR (Complete decomposition of LNR was observed after 25 min); (4) greater and faster

removal in terms of mass balance; (3) greater and faster dechlorination and denitrogenation (Complete release of chlorine was achieved after 80 min and around 56% of nitrogen was released as ammonia and nitrate ions after 120 min).
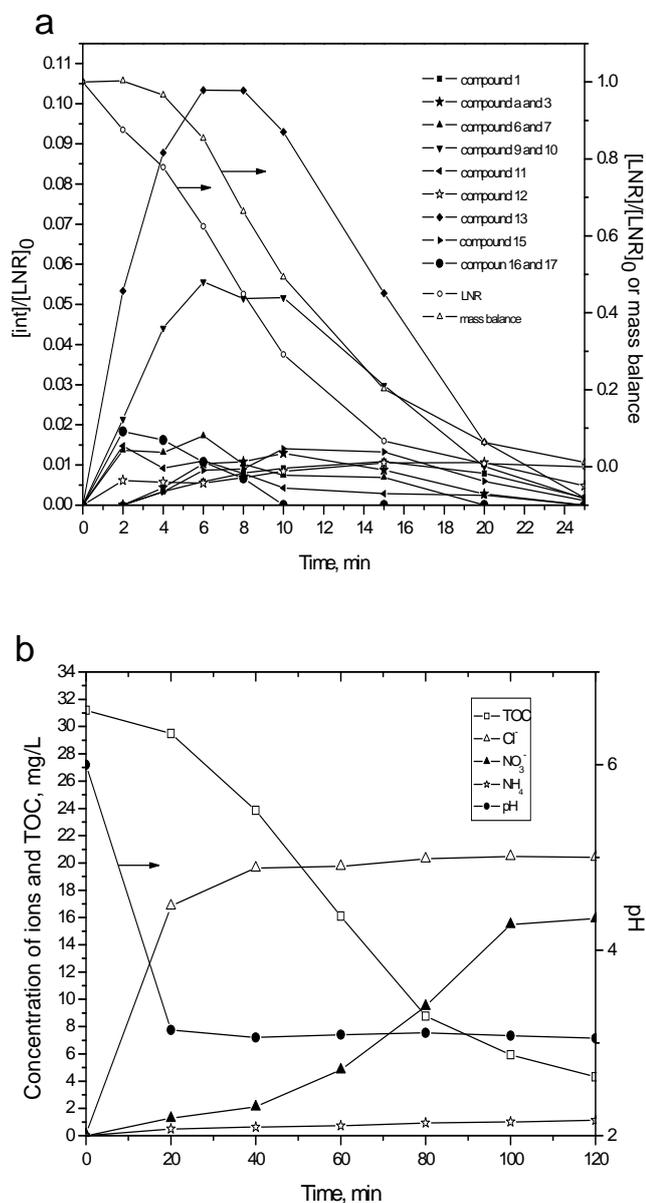


Figure 5-7: (a) The evolution profiles of LNR and intermediates for the degradation of LNR by UV/$O_3$; (b) The evolution profiles of TOC, pH, $Cl^{-1}$, $NO_3^{-1}$, and $NH_4^+$ for the degradation of LNR by UV/$O_3$. (Notes: $[LNR]_0 = 0.285$ mM, $[O_3] = 0.0245$ mM, $[I_0] = 9.0 \times 10^{-6}$ Einstein $L^{-1}$ $s^{-1}$, $pH_0 = 6.0$)

Figure 5-8: The degradation pathways of LNR by ozonation and UV/O$_3$ processes.

(Notes: Solid arrows indicate UV/O$_3$ process while dashed arrows indicate ozonation)

## 5.3 Summary

The degradation of LNR by UV, $O_3$ and $UV/O_3$ processes was examined. It has been found the LNR decay is highly pH-dependent (especially in basic range) in both ozonation and $UV/O_3$ processes while UV process is pH-independent in terms of LNR decay. The effect of varied anions on the performance of ozonation was also investigated. Chloride ion was observed to significantly retard the degradation of LNR at pH 3 while it exerted no effect on the performance of ozonation at pH 7. The presence of phosphate ion led to the increase of LNR decay rate at pH 7 due to its buffer ability to keep pH stable and had no influence on the LNR degradation. In addition, the reaction mechanisms were proposed via identification of intermediates and evolution profile analysis of intermediates in UV, $O_3$ and $UV/O_3$ system. Among these three treatment processes, $UV/O_3$ process has exhibited the best overall performance. It demonstrated significant advantages not only in the decay rate of LNR but also achieving 86% mineralization at the end of the process (120 min).

# Chapter 6 LNR Decomposition in Aqueous Semiconductor Suspension under Visible Light Irradiation-with and without $H_2O_2$

## 6.1 Introduction

Semiconductor-induced photocatalysis has received intensive attention as an environmental remediation technology over the past decades (van Schalkwyk et al., 2003; Spamer et al., 2003; Fu et al., 2006; Liu and Sun, 2007; Garcia-Lopez et al., 2007). Among all semiconductors, Titanium dioxide ($TiO_2$) is believed to be one of the most appropriate photocatalysts in terms of environmental application owing to its particularly optical properties, innocuity, low cost and enduring stability regarding photo- and chemical corrosion (Augugliaro et al., 1995; Hoffmann et al., 1995a). In general, a photon with energy higher than the bandgap energy (Eg = 3.2 eV and 3.0 eV for anatase and rutile phases, respectively) of $TiO_2$ can initiate the excitation of electron from the valence band (VB) to the conduction band (CB), leaving a hole, $h_{vb}^+$ behind (Hossain et al., 2008). These charged species are believed to induce the generation of free radicals such as $HO^\bullet$ and $O_2^{\bullet-}$ which play a major part coupling with $h_{vb}^+$ in the oxidation of organic compounds (Hoffmann et al., 1995a). The widespread use of $TiO_2$ as an effective photocatalyst, however, has been curbed by its poor light absorption in the visible region due to its large band gap. Therefore, efforts have been devoted to improve the utility of $TiO_2$ by shifting its optical response from the UV to the visible spectral range. Using transition metal and nonmetal doping to lower the threshold energy for the excitation of electron in the valence band plays a

big part in these efforts (Asahi et al., 2001; Piera et al., 2003; Tachikawa et al., 2004; Huang et al., 2006; Niishiro et al., 2007; Zaleska et al., 2008). In addition, recently photosensitization via surface adsorbed organic dyes and coordination metal complexes also holds promise for extending $TiO_2$ absorption into the visible region (Cho et al., 2001; Fung et al., 2003; Wang et al., 2007). Whereas both doping and photosensitization have demonstrated successful performance in either narrowing the band gap of $TiO_2$ or sensitizing photocatalytic properties of $TiO_2$ towards visible light irradiation, the preparation process of photocatalyst is time-consuming and expensive, which may hinder the use of $TiO_2$ in practical applications. In this chapter, a novel and cost-efficient process was developed to allow the degradation of organic compounds in $TiO_2$ suspension under visible light irradiation with the assistant of $H_2O_2$.

The widespread application of herbicides as a regular and effective practice to control weed growth has led to increasing environmental concerns in the past decades because of their low biodegradability and long-term persistence in soil. Most herbicides are diffused into aquatic environment via agricultural runoff or leaching (Canle et al., 2001), which makes them ubiquitous. Linuron (LNR), selected as the probe contaminant in this chapter, has received particular attention in recent years due to the toxicity, being frequently detected in the surface and underground waters, and possible endocrine disrupting properties of LNR and/or its metabolites (Sorensen et al., 2005). Therefore, various treatment techniques have been developed to remove LNR in the aqueous phase, including biological methods(Dejonghe et al., 2003; Sorensen et al., 2005), direct photolysis (Faure and Boule, 1997), $O_3/H_2O_2$ (Tahmasseb et al., 2002), photo-Fenton procedure (Katsumata et al., 2005; Farre et

al., 2007), UV/$H_2O_2$ (Benitez et al., 2006) and photocatalysis under UV irradiation (Lopez et al., 2005). The information regarding the photocatalytic decay of LNR under visible light, however, is very limited.

In view of these, the major objectives of this chapter are to explore a new and effective approach to utilize visible light to degrade LNR with the aid of $H_2O_2$ in semiconductor suspension. The performance of the LNR degradation was investigated in this study under different conditions, such as selection of semiconductors, the effects of $TiO_2$ phase composition, $TiO_2$ dosage, the concentration of $H_2O_2$, and initial pH levels.

## 6.2 Results and Discussion

6.2.1 LNR degradation under visible light irradiation in $TiO_2$-$H_2O_2$ system

Many studies have shown that, under UV irradiation, $H_2O_2$ play a dual role in enhancing the semiconductor-sensitized photocatalytic degradation of organic compounds by acting either as an electron scavenger to prevent the recombination of $e^-$ and $h^+$ or as a direct source of hydroxyl radicals (Poulios et al., 2003; Wong and Chu, 2003; Kaniou et al., 2005; Nienow et al., 2008). However, under visible light, such information is limited.

In this section, the degradation of LNR was investigated under various conditions including the presence or absence of $TiO_2$ (P25), the processes with or without $H_2O_2$, and the use of visible light irradiation or in the dark. As shown in Figure 6-1a, it is interesting to observe that the elimination of LNR is insignificant in the systems of

$P25/H_2O_2$ (in the dark), $Vis/P25$ and $Vis/H_2O_2$ with LNR decay level of 8%, 10% and 8%, respectively, after a 3 hr of reaction. However, in the system of $P25/H_2O_2/Vis$, a pronounced enhancement of the reaction rate was observed resulting in a nearly complete decay of LNR.

Though the $H_2O_2$ itself could not degrade the LNR directly, by using $P25/H_2O_2$ in the dark about 8% of LNR removal was observed. This may result from the $TiO_2$ surface adsorption and the formation of an oxidizing agent, i.e., a titanium peroxide complex due to the interaction between $H_2O_2$ and valance-unfilled Ti (IV) on $TiO_2$ surface (Ohno et al., 2001; Li et al., 2001). It could be verified by both the color change on $TiO_2$ surface (turned into pale yellow) after the addition of $H_2O_2$ and the increase of $H_2O_2$ consumption to 9% comparing to that of 0% when no $TiO_2$ was involved (Figure 6-1b).

The use of visible light irradiation in the presence of P25, however, can slightly increase the LNR degradation to 10%. The upper threshold wavelength that P25 can absorb is 410 nm (Figure 6-2), which is within the emission spectra of the 420 nm lamps (Figure 3-4) and therefore likely leading to the production of trace amount of $e^-$ and $h^+$. However, another mechanism that might also contribute to the LNR decay was the surface complexation between organic compounds and $TiO_2$. It was reported that the formation of complex between the organic compounds harboring function groups such as $- OH, - COOH , -NH_2$ and $\equiv TiOH$ groups on the $TiO_2$ surface might initiate the degradation of organic compound upon absorbing visible light through ligand-to-metal charge transfer (Agrios et al., 2004; Paul et al., 2007). An additional test was conducted to verify the latter mechanism by adding 1 M MeOH, a well

known hydroxyl radical scavenger, into the reaction and no LNR decay was observed as demonstrated in Figure 6-1c. The result suggested that the hydroxyl radical, not the complex, was responsible for the LNR decay.
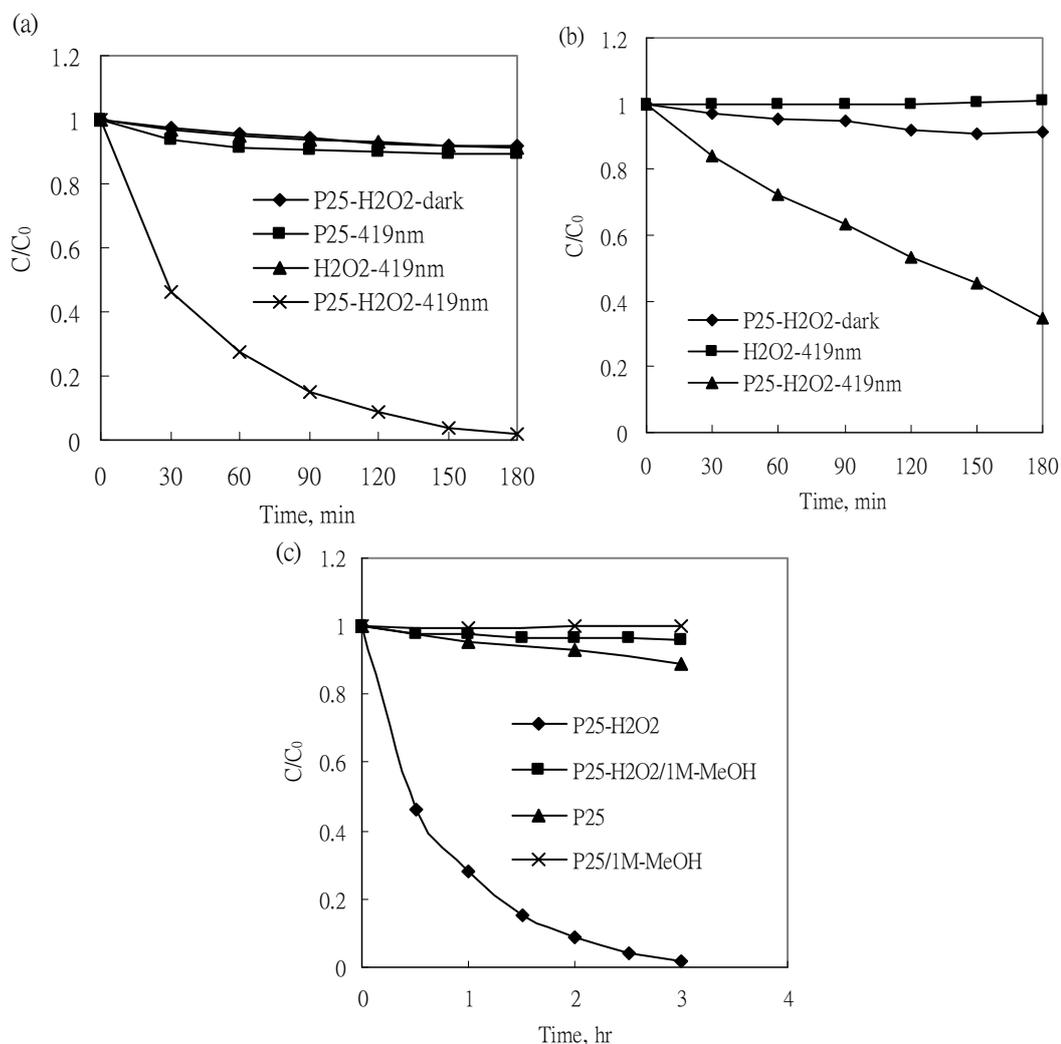


Figure 6-1: (a) LNR degradation under different reaction conditions; (b) $H_2O_2$ decomposition under different reaction conditions; (c) Effect of radical scavenger on visible-light photocatalysis of LNR with and without $H_2O_2$. (Notes: initial LNR concentration is 0.1 mM, $TiO_2$ loading is 0.6 g/L, the initial concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0)

It was interesting to reveal a synergistic effect in the process of P25/H$_2$O$_2$/Vis for a quick and complete removal of LNR. The possible explanations for this synergistic effect are: (1) H$_2$O$_2$ acts as an electron acceptor to prevent the recombination of e$^-$ and h$^+$ and/or offering additional hydroxyl radicals (Eqn. 6-1); (2) The interaction between H$_2$O$_2$ and TiO$_2$ leads to the formation of titanium peroxide complex on the TiO$_2$ surface which may act as oxidizing species under visible light (Ohno et al., 2001); (3) Titanium peroxide complex on the TiO$_2$ surface extend the photoresponse of TiO$_2$ to the visible region, leading to the visible-light-induced surface electron transfer from surface complexes to the conduction band of TiO$_2$. The electrons on the conduction band of TiO$_2$ initiate the decomposition of H$_2$O$_2$, which gives rise to the generation of hydroxyl radicals (Eqn. 6-2) (Li et al., 2001); and (4) It was reported that the water-oxide interface can lower the energy barrier for the H$_2$O$_2$ decomposition (Hiroki and LaVerne, 2005). As a result, additional hydroxyl radicals might be produced by the breakdown of H$_2$O$_2$ on the surface of TiO$_2$ under the irradiation of visible light (Eqn. 6-3).

$$H_2O_2 + e_{direct}^- \rightarrow HO^\bullet + OH^- \tag{6-1}$$

$$H_2O_2 + e_{transfer}^- \rightarrow HO^\bullet + OH^- \tag{6-2}$$

$$H_2O_2 + TiO_2 \rightarrow 2\, HO^\bullet \tag{6-3}$$

where $e_{direct}^-$ is the electron directly excited from the valence band to the conduction band of TiO$_2$ and $e_{transfer}^-$ is the electron transferred from surface complexes to the conduction band of TiO$_2$. The addition of 1 M MeOH significantly inhibits the LNR degradation in this process as shown in Figure 6-1c, indicating that the LNR decay is dominated by various radicals that generated upon the irradiation of visible light while the direct oxidation of titanium peroxide complex may make a trivial contribution to the LNR decay.
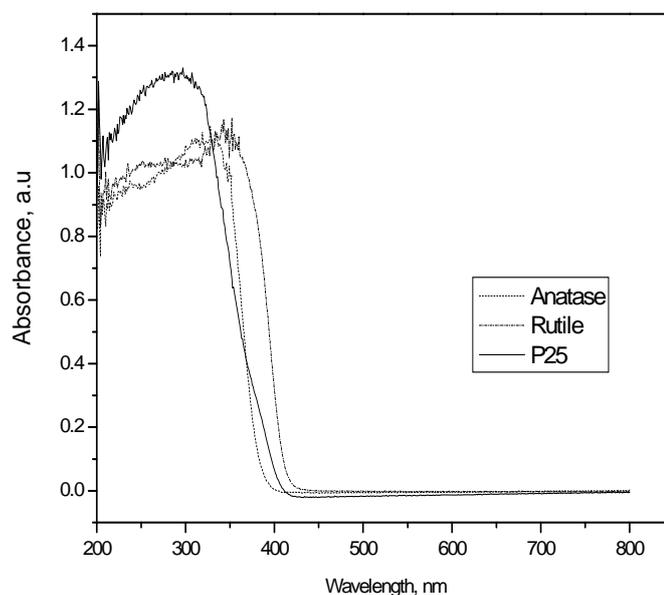
Figure 6-2: Diffuse reflection spectra of various $TiO_2$ powder

6.2.2 Effect of $TiO_2$ phase composition

The LNR degradation has been investigated in three different $TiO_2$ suspensions with or without $H_2O_2$ under visible light irradiation. Figure 6-3 shows that, in the absence of $H_2O_2$, anatase exhibited the highest reactivity (nearly 20% decomposition of LNR was achieved) and rutile was the worst. However, in the presence of $H_2O_2$, P25 demonstrated the best performance and followed by rutile and anatase. It is not unexpected that rutile displayed the lowest photocatalytic activity due to its narrow band gap unfavorable for the separation of photo-induced charges (Jing et al., 2008).

On the contrary, in the presence of $H_2O_2$, rutile showed a much better performance than anatase. The advantage of rutile in comparison with anatase is that the former can absorb a larger fraction of the emission spectrum of 419 lamps. Rutile powder can absorb photon up to 440nm while anatase shows absorption only up to 402nm

(data are not shown here). In addition, it was reported that Ti-$\eta^2$-peroxide and Ti-$\mu$-peroxide were the dominant bonds to be formed on the surface of rutile and anatase, respectively, in the presence of $H_2O_2$ (Ohno et al., 2001). By combining with our previous findings, it's very likely that the Ti-$\eta^2$-peroxide has a better performance than the Ti-$\mu$-peroxide in generating free radicals. The P25 demonstrated the best performance when using $H_2O_2$ as the additional hydroxyl radical source and this is because of its finest particle sizes (or largest surface area) as suggested by many researchers (Ohno et al., 2001; Hiroki and LaVerne, 2005).
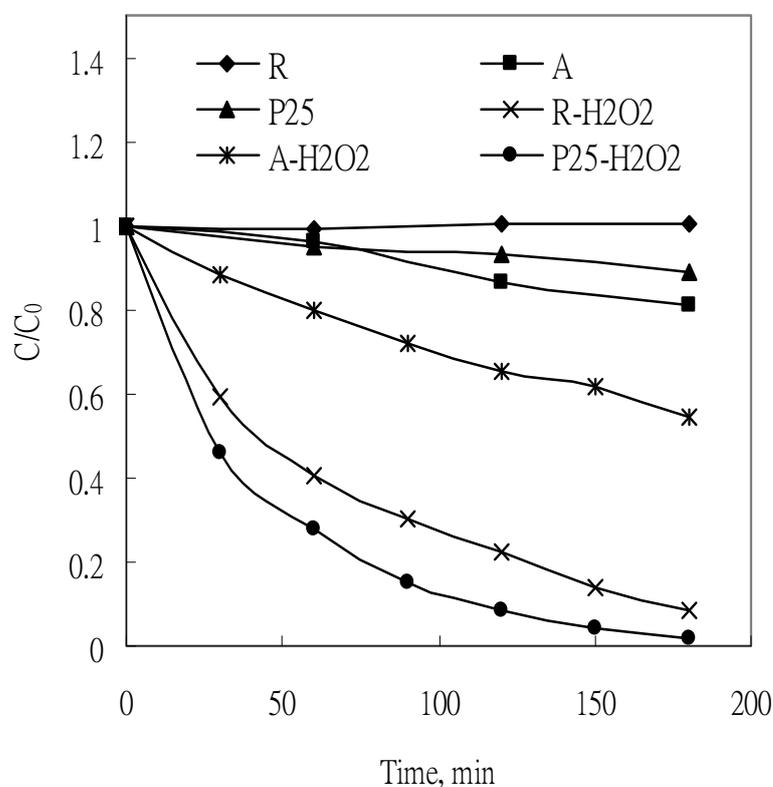


Figure 6-3: LNR degradation using different $TiO_2$ as photocatalysts with and without $H_2O_2$ (Notes: initial LNR concentration is 0.1 mM, $TiO_2$ loading is 0.6 g/L, the initial concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0, R denotes rutile, A represents anatase.)

6.2.3 The performance of different semiconductors under various conditions

Several semiconductors were also examined as alternatives in this study. ZnO has been considered as a suitable replacement to $TiO_2$ since both are relatively inexpensive and have almost the same band gap energy. While the positive conduction band level of $WO_3$ (around 0.37 V vs NHE) might limit its use as a photocatalyst in terms of the oxidative degradation of organic compounds (Scaife, 1980), the addition of $H_2O_2$ to the system may exert a positive effect on the LNR decay by acting as an electron acceptor because the potential for the single-electron reduction of $H_2O_2$ was reported to be 0.32V vs NHE ( $H_2O_2 + e \rightarrow OH^- + HO^\bullet$, 0.32 V vs NHE) (Castagna et al., 2008).

The profile of LNR decomposition in the suspension of the above three semiconductors under a variety of conditions is shown in Figure 6-4. It can be seen that purging $O_2$ led to a significant increase on the reaction rate in all cases. However, the mechanisms for the positive effect which $O_2$ exerts are different for the three semiconductors. In the case of $TiO_2$-P25 and ZnO, $O_2$ acts as an electron acceptor through single-electron reduction to prevent the recombination of photoinduced charges due to their conduction band level (-0.31V and -0.29 V vs NHE for ZnO and $TiO_2$, respectively) (Xu and Schoonen, 2000) were more negative than the potential for single-electron reduction of $O_2$ ($O_2 + e^- = O_2^-$, -0.284V vs NHE). In the presence of $WO_3$, however, the $O_2$ accepts electrons through multielectron reduction ($O_2 + 2H^+ + 2e^- = H_2O_2$, + 0.682V vs NHE; $O_2 + 4H^+ + 4e^- = 2H_2O$, +1.23V vs NHE) (Abe et al., 2008). Figure 6-4 also shows the addition of $H_2O_2$ resulted in a significant improvement on the LNR decay in the cases of P25 and $WO_3$, while no positive effect was observed for ZnO. This is likely due to the amount of $H_2O_2$ adsorbed onto

the surface of ZnO is negligible in comparison with that in the case of $TiO_2$ and $WO_3$ (Kormann et al., 1988; Evgenidou et al., 2005).
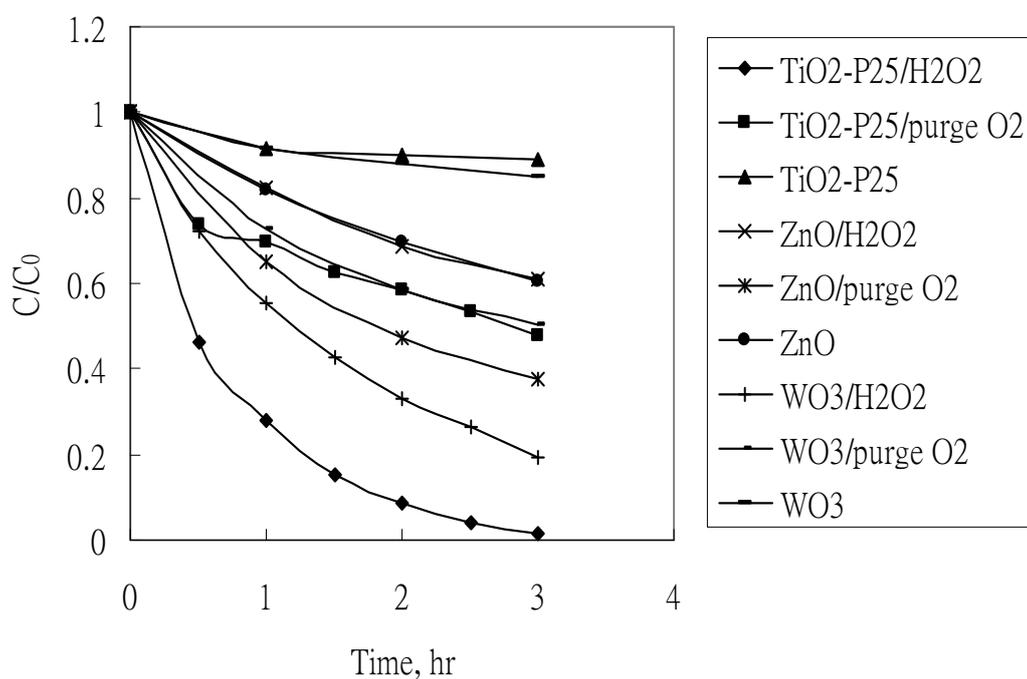


Figure 6-4: The performance of various semiconductors under different reaction conditions. (Notes: initial LNR concentration is 0.1 mM, semiconductor loading is 0.6 g/L, the initial concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0)

6.2.4 Effect of $TiO_2$-P25 dosage

Because $TiO_2$-P25 has exhibited the best performance comparing to other combinations as described above, it was chosen as the exclusive photocatalyst for the detail study. The influence of $TiO_2$-P25 dosage (ranged from 0.05 to 1.0 g/L) on the LNR degradation was investigated with the concentration of $H_2O_2$ and LNR fixed at 10 and 0.1 mM, respectively, and the results were illustrated in Figure 6-5. It can be observed that the decay rate of LNR increases with the increment of $TiO_2$ dosage. It is also interesting to perceive that the pseudo first-order decay rate constants

increased linearly with the increment of $TiO_2$ dosage, but could be clearly divided into two stages with a breakpoint of 0.4 g/L dosage (Figure 6-5b). This suggested that the LNR decay was gradually retarded when $TiO_2$ dosage was increased over 0.4 g/L. This is because the increase in the opacity of the suspension with the abundance of $TiO_2$ particles resulted in a reduction in the light penetration (Inel and Okte, 1996). The most cost-efficient dose of 0.4 g/L $TiO_2$, therefore was employed in the following studies.
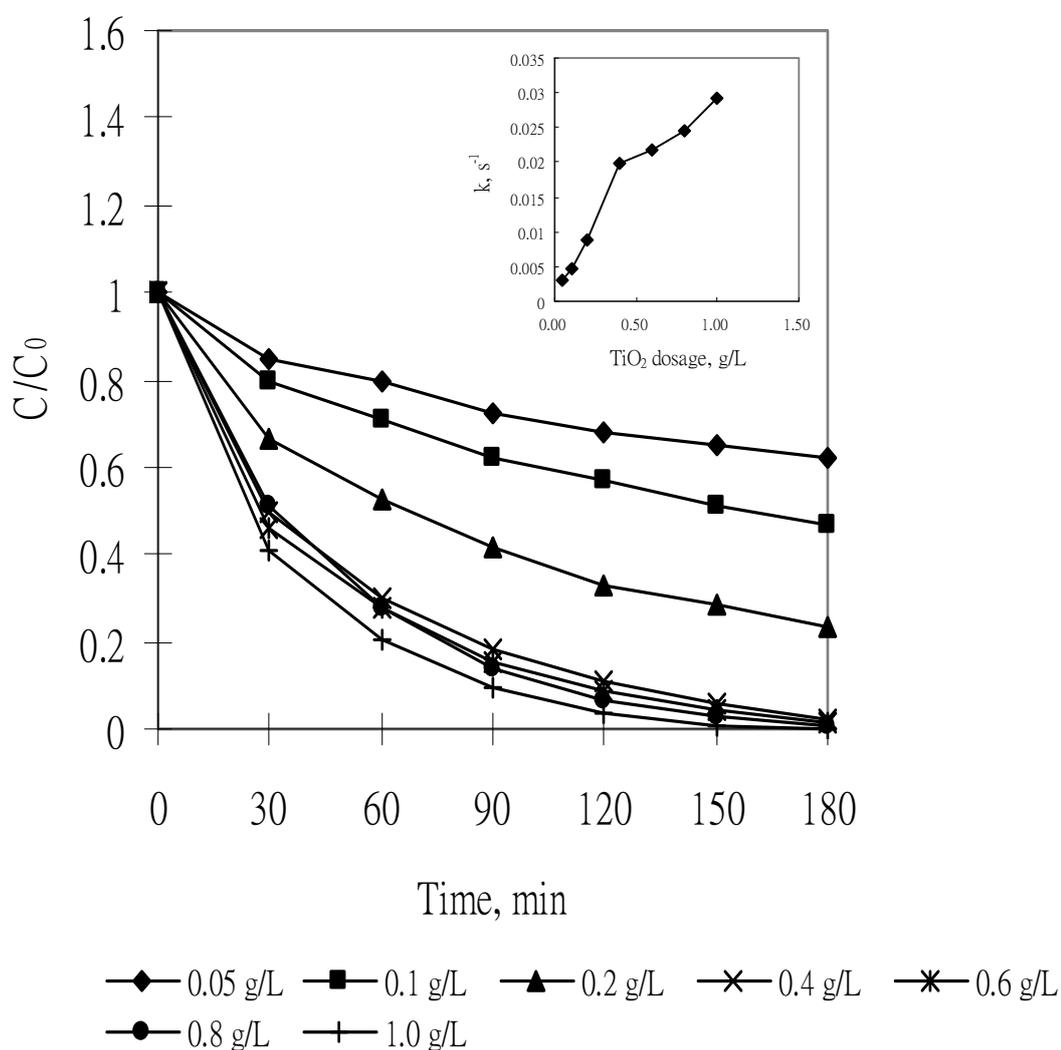


Figure 6-5: The effect of $TiO_2$-P25 dosage on the LNR decay rate (initial LNR concentration is 0.1 mM, the initial concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0)

6.2.5 Effect of $H_2O_2$ concentration

As described previously, hydroxyl radicals play a key role in the LNR decomposition in $TiO_2/H_2O_2$ system under the irradiation of visible light. However, if the $H_2O_2$ is in excess, $H_2O_2$ may compete for $HO^\bullet$ with the organic compound (Eqn. 6-4) and results in a negative effect. The determination of an optimum concentration of $H_2O_2$, thus, is critical for this system in any practical application.

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{6-4}$$

The LNR degradation at 0.4 g/L $TiO_2$ with $H_2O_2$ concentration varying from 1 to 20 mM is indicated in Figure 6-6. It is interesting to observe that the increase of $H_2O_2$ concentration did not accelerate the LNR decay significantly, even at the low $H_2O_2$ concentrations. This result is different from the results by using UV as the light source (Choy and Chu, 2005; Kaniou et al., 2005). A possible explanation is that the total available electrons produced from the direct excitation from the valence band to the conduction band of $TiO_2$ and the transfer from surface complexes to the conduction band of $TiO_2$ under visible light are much less than the number available under UV irradiation, making the amount of the available electrons (but not the $H_2O_2$ concentration) a rate-limiting factor in the production of hydroxyl radicals.

As also demonstrated in Figure 6-6, the decay rate of LNR with 1 mM $H_2O_2$ and 2 mM $H_2O_2$ was retarded after 60 minutes and 150 minutes, respectively, which occurred as the $H_2O_2$ concentration reduced to around 0.1 mM in the solution as shown in Figure 6-6b. This indicates that the $H_2O_2$ concentration might become a rate-limiting factor when it was below 0.1 mM in the solution.

**a**



**b**
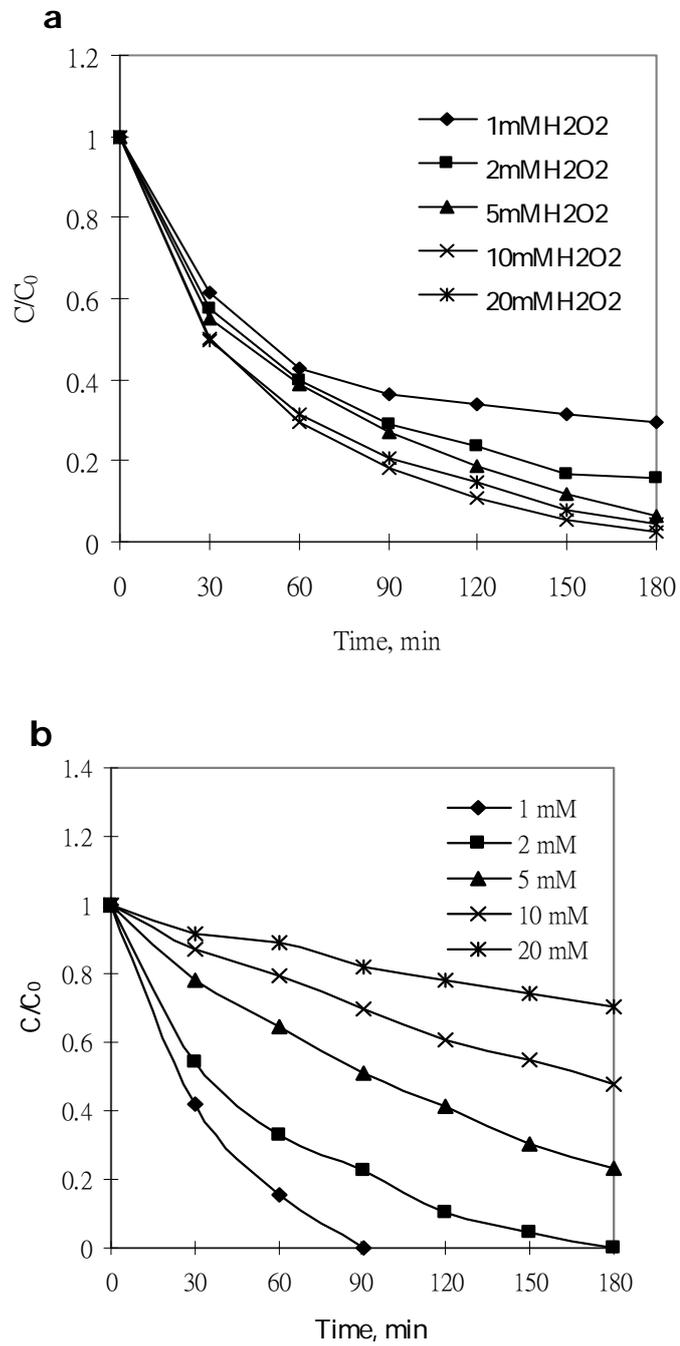


Figure 6-6: (a) The effect of $H_2O_2$ concentration on the LNR degradation; (b) The variation of $H_2O_2$ concentration during the reaction. (Notes: initial LNR concentration is 0.1 mM, $TiO_2$-P25 dosage is 0.4 g/L, initial pH value is 6.0)

6.2.6 Effect of pH level

The effect of initial pH on LNR decay with the addition of 5 mM $H_2O_2$ and 0.4 g/L $TiO_2$ was then examined as shown in Figure 6-7a. Under extremely acidic (pH 2.0) and basic conditions (pH 9 and 11), LNR degradation rate was significantly retarded and an optimal pH was found at 6 (see Figure 6-7b). Since $H_2O_2$, as a dominant resource of hydroxyl radicals, play a major role in this system under visible light, the simultaneous decomposition of $H_2O_2$ in this system was also examined. Figure 6-7c shows the decay of $H_2O_2$ was noticeably inhibited at pH 2. At pH 2, $H_2O_2$ exists in the form of $H_3O_2^+$ and $TiO_2$ carries positive charges since the point of the zero charge (pzc) of $TiO_2$ is around pH 6. The positive charges on the surface of $TiO_2$ may hamper the adsorption of $H_3O_2^+$ on the surface of $TiO_2$ due to electrostatic repulsion, leading to the retardation of the formation of Titanium peroxide complex and the decomposition of $H_2O_2$ on the surface of $TiO_2$. On the other hand, it is well known that $H_2O_2$ is unstable in an alkaline medium and breaks down rapidly into water and oxygen as demonstrated in Figure 6-7c, indicating less $H_2O_2$ molecules are available for the reactions that can produce hydroxyl radicals. Another minor possible reason for low LNR decay rate under basic condition is the dissolution of $CO_2$ from the air during the mixing and from the end product of LNR decay. The first and second pKa of $H_2CO_3$ are 6.4 and 10.3, respectively; when the pH level is higher than 6.4, the predominant species of a carbonate system will either be bicarbonate or carbonate ions. Since both of them are radical scavengers, these ions may compete with LNR for hydroxyl radicals (Wong and Chu, 2003).
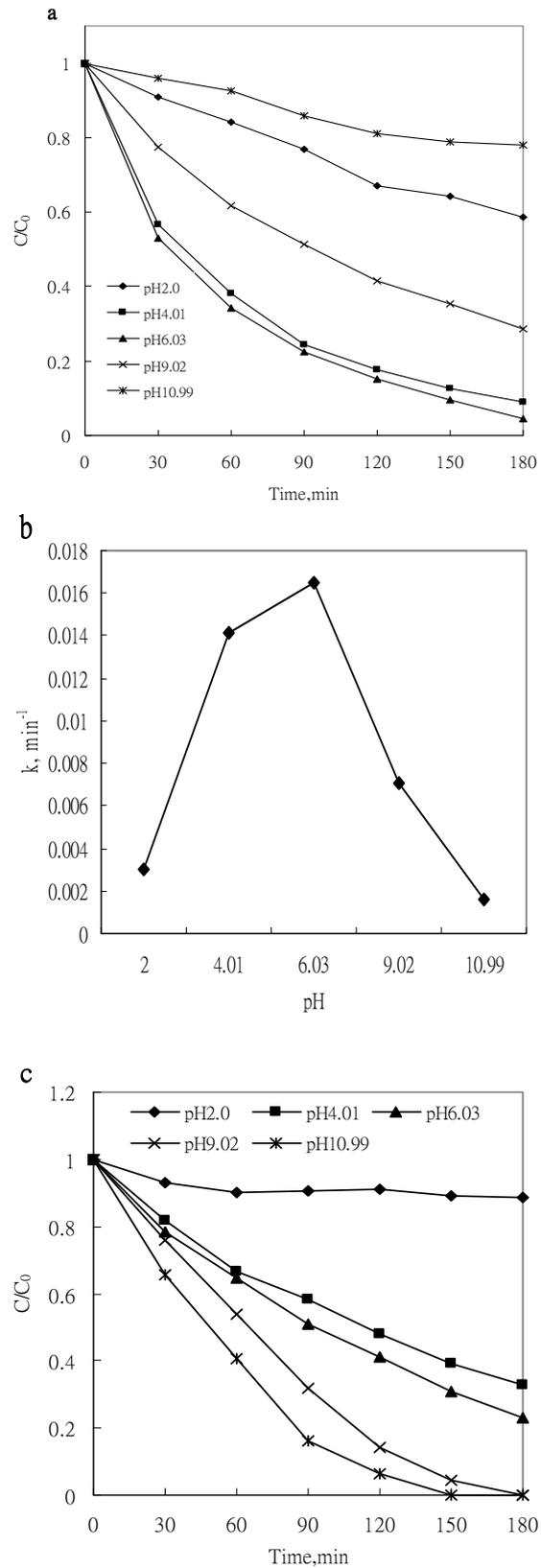
Figure 6-7: (a) LNR decomposition at different pH levels; (b) Observed rate constant

at different pH levels; (c) $H_2O_2$ decomposition at different pH levels.

(Notes: initial LNR concentration is 0.1 mM, TiO$_2$-P25 dosage is 0.4 g/L,

the initial concentration of H$_2$O$_2$ is 5 mM.)

6.2.7 Effect of initial concentration of LNR

LNR concentration in waters from various sources may range considerably (Caux et al., 1998), which makes the investigation on the effect of initial LNR concentration on the degradation rate of LNR interesting for the real application. The decay rate of LNR was tested with varied initial LNR concentrations by TiO$_2$/H$_2$O$_2$/vis system as shown in Figure 6-8a. The decay of LNR in TiO$_2$/H$_2$O$_2$/vis system was found to follow pseudo first-order kinetics. As also demonstrated in Figure 6-8, higher initial LNR concentration results in lower decay rate under the same reaction conditions.

The Langmuir-Hinshelwood (LH) kinetics is usually applied to quantitatively delineate such surface reactions. It is also possible to use the LH kinetics in heterogeneous photocatalysis systems only when homogeneous reaction is assumed to be insignificant (Fox and Dulay, 1993). The initial rate for the first 90 min, $r_0$, can be expressed as:

$$r_0 = -\frac{d[LNR]_0}{dt} = \frac{kK[LNR]_0}{1 + K[LNR]_0} \qquad (6\text{-}5)$$

where $K$ is the equilibrium absorption constant of LNR on the surface of catalyst (mM$^{-1}$) and $k$ represents the limiting reaction rate at maximum coverage (mM min$^{-1}$). For pseudo first-order kinetics, the incorporation of $-d[LNR]_0/dt = k_{observed}[LNR]_0$ into Eqn 6-5 gives

$$k_{observed}[LNR]_0 = \frac{kK[LNR]_0}{1 + K[LNR]_0} \qquad (6\text{-}6)$$

The linearization of Eqn 6-6 gives

$$\frac{1}{k_{observed}} = \frac{1}{k}[LNR]_0 + \frac{1}{kK} \qquad (6\text{-}7)$$

with an intercept of $1/kK$ and slope of $1/k$.

$1/k_{observed}$ versus $[LNR]_0$ was plotted in Figure 6-8b. The degradation of LNR at various initial concentrations fits well to the LH model with a linear regression ($r^2$) of 0.9873. The two constants, $k$ and $K$, were calculated to be 0.00213 mM min$^{-1}$ and 59.50 mM$^{-1}$ from the slope and intercept, respectively. The good correlation may indicate the degradation reaction of LNR in $TiO_2/H_2O_2$/vis system dominatingly occurs on the surface of $TiO_2$ while homogeneous reaction is insignificant.

**a**



**b**
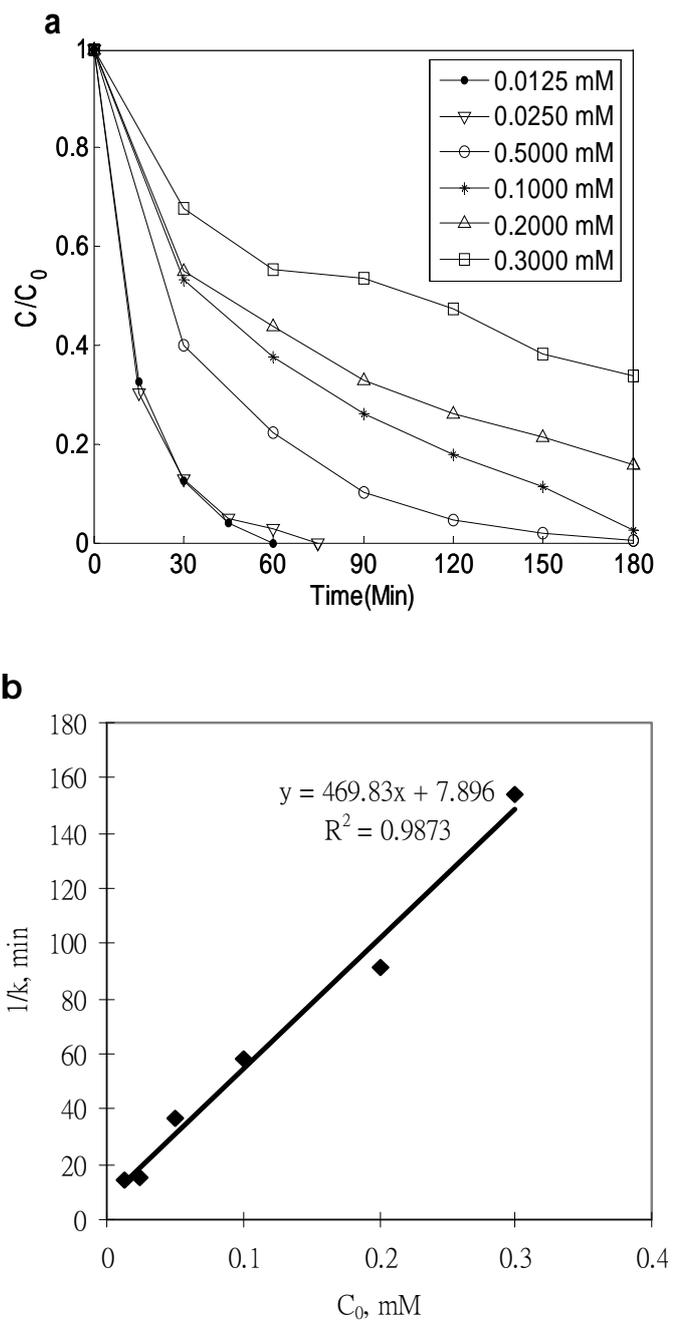


Figure 6-8: (a) Degradation of LNR at different initial concentrations; (b) L-H plot of

LNR decay (Notes: TiO$_2$-P25 dosage is 0.4 g/L, the initial concentration

of H$_2$O$_2$ is 5 mM, initial pH is 6.0)

## 6.3 Summary

The degradation of LNR in $TiO_2$ suspension with and without $H_2O_2$ was investigated under the irradiation of visible light. When no $H_2O_2$ involved, only 10% removal of LNR was observed. However the removal can be significantly increased to nearly 100% upon the addition of $H_2O_2$ to the process. In the absence of $H_2O_2$, anatase exhibited higher photocatalytic activities than $TiO_2$-P25 and no LNR decay was observed in rutile suspension; while in the presence of $H_2O_2$, $TiO_2$-P25 demonstrated the best performance and rutile showed higher activities than anatase.

The performance of various semiconductors under varied conditions was also investigated. ZnO showed the highest photocatalytic activities under visible light without using $H_2O_2$. The addition of $H_2O_2$ led to a considerable enhancement on the decay rate of LNR in the cases of $TiO_2$-P25 and $WO_3$, while no positive effect was observed for ZnO.

The process is optimized by examining the reaction rate under various reaction conditions. The decay rate of LNR, generally, increased with the increment of $TiO_2$ dosage. However, the LNR degradation could be gradually retarded when $TiO_2$ was overdosed (above 0.4 g/L) due to the reduction of light penetration.

The $H_2O_2$ concentration of the tested range (1 to 20 mM) did not show a significant influence on the LNR decay. This is likely due to the amount of the available electrons on the $TiO_2$ surface is much less than the $H_2O_2$ dosage in the solution, the former therefore becomes the rate-limiting factor rather than the concentration of $H_2O_2$. However, if the initial $H_2O_2$ is at low end (e.g. 1 or 2 mM) the retardation of

LNR decay will be observed as the remaining $H_2O_2$ in the solution reduced (consumed) to 0.1 mM. The optimal pH level for the $H_2O_2$-assisted photocatalysis under visible light was found at neutral range, which is beneficial for the purpose of application. Furthermore, it was found that the Langmuir-Hinshelwood kinetics fitted well to the degradation of LNR throughout the examined concentration range of LNR, implying that surface reaction is dominant while homogeneous reaction is insignificant in this system.

# Chapter 7 Reaction Mechanism of LNR Degradation in TiO$_2$ Suspension under Visible Light Irradiation with the Assistance of H$_2$O$_2$

## 7.1 Introduction

TiO$_2$-induced photocatalysis has attracted intensive attention as a water and wastewater treatment technology to eliminate toxic and recalcitrant organic compounds over the past decades due to its particularly optical properties, innocuity, low cost and enduring stability in terms of photo and chemical corrosion (Augugliaro et al., 1995, Hoffmann et al., 1995a). The widespread use of TiO$_2$ as an effective photocatalyst in practical application, however, has been curbed by its optical property that TiO$_2$ is only sensitive to UV light (Ding et al., 2000). The sun can furnish an abundance of photons; however, UV light only accounts for a small portion (~5%) of the sun spectrum in comparison to the visible region (~45%). Therefore, efforts have been devoted to shift the optical response of TiO$_2$ from the UV to the visible spectral range in order to make an effective utilization of solar energy. In recent years, doping (transmit metal and nonmetal) and dye-sensitization technologies have demonstrated successful performance in either narrowing the band gap of TiO$_2$ or sensitizing photocatalytic properties of TiO$_2$ towards visible light irradiation (Asahi et al., 2001, Cho et al., 2001, Huang et al., 2006, Lin et al., 1999, Zaleska et al., 2008). It has also been reported that the oxidation reaction of organic compounds occurs even under irradiation of visible light when TiO$_2$ particles are used as photocatalyst with the addition of H$_2$O$_2$ (Li et al., 2001, Ogino et al., 2008,

Ohno et al., 2001). It is known that the chemisorption of $H_2O_2$ on the surface of $TiO_2$ can result in the formation of yellow complex "Titanium peroxide" (Boonstra and Mutsaers, 1975). Ohno et al. proposed that the epoxidation reaction of 1-decene could be initiated by a photochemical reaction of Ti-$\eta^2$-peroxide with 1-decene (Ohno et al., 2001). On the other hand, the formation of active hydroxyl radicals was proven in $TiO_2/H_2O_2$ suspension under visible light irradiation in the work of Li et al. (Li et al., 2001). They proposed a possible mechanism of the generation of hydroxyl radicals in this system. Titanium peroxide complex formed on the $TiO_2$ surface could extend the photoresponse to the visible region and can be excited by visible light. The excited surface complex injects an electron to the conduction band of $TiO_2$. The electrons on the conduction band of $TiO_2$, then, further initiate the decomposition of $H_2O_2$ to produce hydroxyl radicals. It was also reported that the water-oxide interface can lower the energy barrier for the $H_2O_2$ decomposition (Hiroki and LaVerne, 2005). As a result, hydroxyl radicals might be produced by the breakdown of $H_2O_2$ on the surface of $TiO_2$ under the irradiation of visible light ($H_2O_2 + TiO_2 + vis \rightarrow 2HO^{\bullet}$). Although the interaction between $H_2O_2$ and $TiO_2$ is well-documented, the oxidation mechanism of organic compounds in the $TiO_2/H_2O_2$ system under visible light irradiation is not well-understood.

LNR was also chosen as a probe compound in this chapter. The degradation kinetics of LNR and the influence of varied parameters such as $TiO_2$ dosage, $H_2O_2$ concentration, pH level and LNR initial concentration on the performance of $TiO_2/H_2O_2/vis$ system have been investigated in chapter 6. This chapter will focus on the photocatalytic decomposition mechanism of LNR under visible range irradiation with the assistance of $H_2O_2$.

## 7.2 Results and Discussion

7.2.1 LNR Degradation in Various Systems

Many studies have demonstrated that, under UV irradiation, $H_2O_2$ plays a dual role in enhancing the $TiO_2$-based photocatalytic degradation of organic compounds by acting either as an electron scavenger to prevent the recombination of $e^-$ and $h^+$ or as a direct source of hydroxyl radicals (Poulios et al., 2003; Wong and Chu, 2003; Kaniou et al., 2005; Nienow et al., 2008). However, under visible light, the mechanism behind the degradation of organic compounds in the system of $TiO_2/H_2O_2$ is still not well-defined.

In this section, the degradation of LNR was investigated under various conditions including the presence or absence of $TiO_2$, the processes with or without $H_2O_2$, and the use of visible light irradiation or in the dark. As shown in Figure 7-1, it is interesting to note that no decay of LNR was observed in the systems of $TiO_2/H_2O_2$ (in the dark), $TiO_2$ with or without purging $O_2$ under the irradiation of visible light (420 nm) and Vis/$H_2O_2$ after 5 hr of reaction. However, in the system of $TiO_2/H_2O_2$ under visible light (420 nm), more than 70% decay of LNR was observed.

No LNR decay was observed in $TiO_2$ suspension under the irradiation of visible light even with the purge of $O_2$ (a well-known electron acceptor) indicating no electron-hole pairs are generated and no trace of UV light leaking into the reactor in this system. It is expected that no LNR degradation was achieved in the system of $H_2O_2$/Vis because direct dissociation of $H_2O_2$ to $HO^{\bullet}$ can be attained only through absorbing UV light ($\lambda$ < 320 nm). It has been reported that the degradation of

methylene blue can be accomplished in the presence of $H_2O_2$-pretreated $TiO_2$ in the dark, which was ascribed to the formation of a stable oxidant - titanium peroxide on the surface of $TiO_2$ particles (Ogino et al., 2008). In the presence of $H_2O_2$, the $-$ OOH groups of $H_2O_2$ substitute for the $-$ OH groups of basic $\equiv TiOH$, leading to the generation of a yellow surface complex--titanium peroxide (Boonstra and Mutsaers, 1975; Ohno et al., 2001). It has also been reported that the interaction between $H_2O_2$ and rutile $TiO_2$ can form surface $O_2^-$ anions and S = 1 triplet radical anion pairs (Murphy et al., 1997). However, no LNR decay was observed in the $TiO_2/H_2O_2$ system in the dark in this study. This may suggest that the oxidizing power of both titanium peroxide and radical anions is too weak to effectively oxidize LNR.
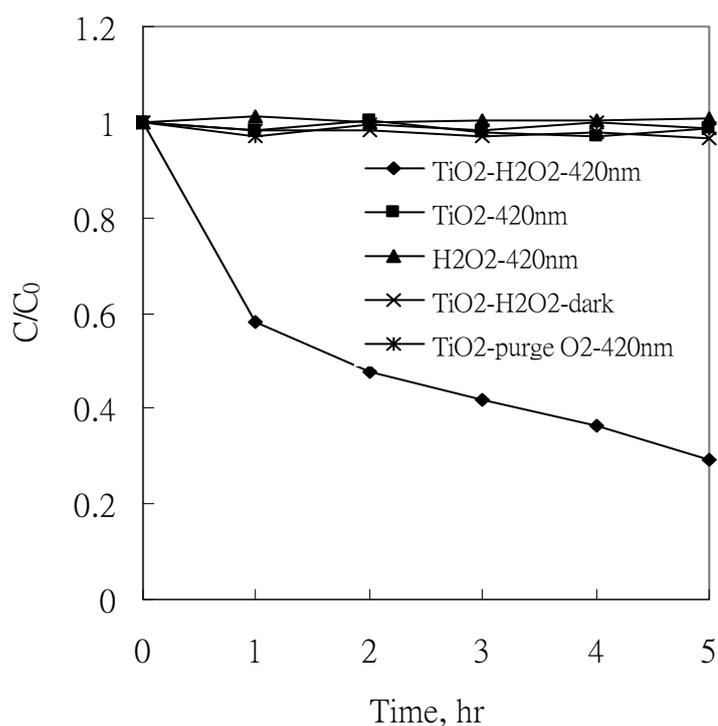


Figure 7-1: LNR degradation under different reaction conditions (Notes: initial LNR concentration is 0.1 mM, $TiO_2$ loading is 0.6 g/L, the initial concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0).

7.2.2 Photocatalytic Degradation Mechanism of LNR under Visible Light

It was interesting to observe a synergistic effect in the system of $TiO_2/H_2O_2/Vis$ for the decomposition of LNR. This synergistic effect may be rationalized by: (1) The interaction between $H_2O_2$ and $TiO_2$ leads to the formation of titanium peroxide complex and various radical anions on the $TiO_2$ surface which may act as oxidizing species with the assistance of visible light (Ohno et al., 2001); (2) Titanium peroxide complex on the $TiO_2$ surface extend the photoresponse of $TiO_2$ to the visible region, leading to the visible-light-induced surface electron transfer from surface complexes to the conduction band of $TiO_2$. The electrons on the conduction band of $TiO_2$ initiate the decomposition of $H_2O_2$, which gives rise to the generation of hydroxyl radicals (Eqn. 7-1) (Li et al., 2001); and (3) It was reported that the water-oxide interface can lower the energy barrier for the $H_2O_2$ decomposition (the presence of oxides leads to the activation energy of the cleavage of the $O - O$ bond in $H_2O_2$ being decreased from 210 kJ/mol to 40 kJ/mol)(Hiroki and LaVerne, 2005). As a result, additional hydroxyl radicals might be produced by breaking down $H_2O_2$ on the surface of $TiO_2$ under the irradiation of visible light (Eqn. 7-2).

$$H_2O_2 + e_{transfer}^- \rightarrow HO^\bullet + OH^- \tag{7-1}$$

$$H_2O_2 + TiO_2 \rightarrow 2\ HO^\bullet \tag{7-2}$$

where $e_{transfer}^-$ is the electron transferred from surface complexes to the conduction band of $TiO_2$.

In order to investigate the photodegradation mechanism of LNR, three selective radical scavengers were utilized to assess the contribution of various radicals or other oxidizing species to the LNR decay. Bicarbonate and tert-butanol selectively quench

hydroxyl radical while azide reacts with both singlet oxygen and hydroxyl radical (Xu et al., 2008). The addition of 100 mg/L bicarbonate and azide almost inhibited the LNR degradation completely in this process; 100 mg/L tert-butanol caused a significant reduction in the LNR removal (decrease from 64% to 28% at 4th hour after using the quencher) while 3 g/L tert-butanol completely hinders the LNR degradation (See Figure 7-2), indicating that the LNR decay is likely dominated by the oxidation of hydroxyl radicals. It is interesting to note the addition of 100 mg/L bicarbonate retards the LNR degradation more effectively than 100 mg/L tert-butanol does although tert-butanol is more reactive toward OH radicals than bicarbonate. This may be because bicarbonate can not only compete for hydroxyl radicals with LNR but also compete for the adsorption sites on the $TiO_2$ surface with $H_2O_2$ and LNR. It has been reported that the anions exerted an inhibiting effect on the photocatalytic degradation of organic pollutants due to the occurrence of the competitive adsorotion (Liang et al., 2008).

It was reported that the water-oxide interface could lower the energy barrier for the $H_2O_2$ decomposition and the activation energy was around 42 kJ/mol for the decomposition of $H_2O_2$ (independent on the type of oxide) (Hiroki and LaVerne, 2005). Therefore, it may be interesting to examine both the $H_2O_2$ and LNR decay in the suspension of other metal oxides under the irradiation of visible light. Alumina ($Al_2O_3$), silica ($SiO_2$), and Gallium oxide ($Ga_2O_3$), known to be insensitive to visible light nor producing electron-hole pairs, were therefore selected as probe oxides. It has been proven that, in the presence of $Al_2O_3$ or $SiO_2$, the decomposition of $H_2O_2$ can be achieved at 80℃(Hiroki and LaVerne, 2005). However, no $H_2O_2$ and LNR decomposition was observed under visible light in the presence of these additionally

tested oxides. Only $TiO_2$ can initiate the reaction as shown in Figure 7-3. This is likely because the visible light from 300 W Xe lamp cannot furnish enough energy (42 kJ/mol) for the cleavage of O – O bond in $H_2O_2$ to produce hydroxyl radicals.
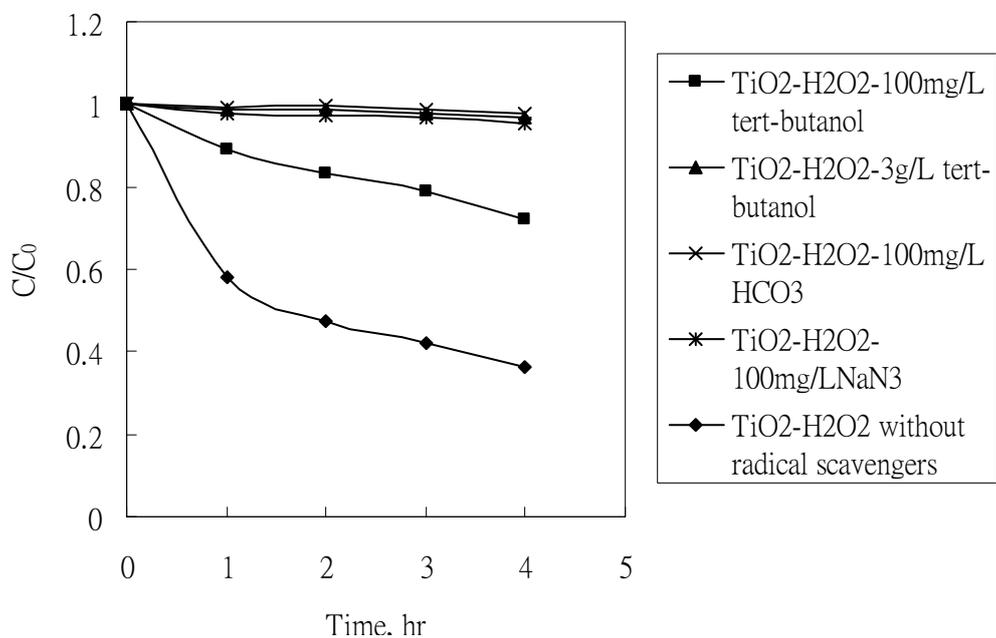


Figure 7-2: Effect of radical scavengers on visible-light photocatalysis of LNR with the assistance of $H_2O_2$. (Notes: initial LNR concentration is 0.1 mM, $TiO_2$ loading is 0.6 g/L, the initial concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0)
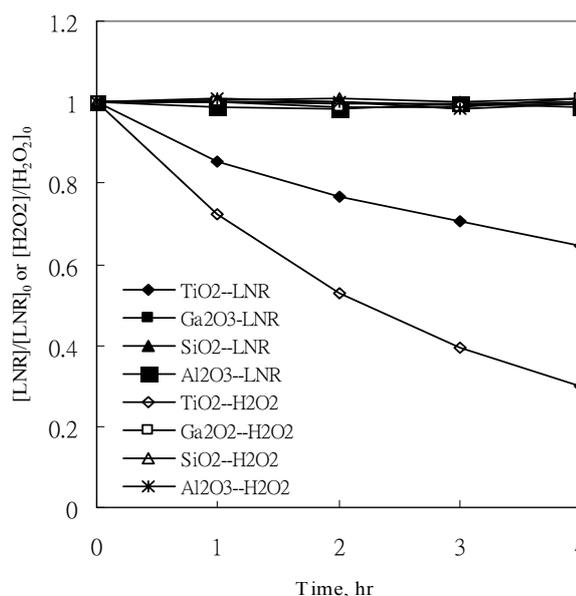
Figure 7-3: LNR and $H_2O_2$ decomposition in various oxides suspension under visible

light irradiation (Notes: initial LNR concentration is 0.1 mM, all oxides

loading is 0.6 g/L, the initial concentration of $H_2O_2$ is 1 mM, initial pH

value is 6.0).

It was proposed that the titanium peroxide complex formed on the surface of $TiO_2$

can be excited by visible light to produce electrons which can be transferred to the

conduction band of $TiO_2$ and subsequently initiate the decomposition of $H_2O_2$ to

produce hydroxyl radicals in the study of Li et al. (Li et al., 2001). However, the

production of electrons was not confirmed in their study. Thus, in order to investigate

if electrons can be generated in this system, photocurrent generation was monitored

from a $TiO_2$/ITO electrode immersed in aqueous 0.03 M $H_2O_2$ solution or DDW. The

time profiles of photocurrents generated under visible light ($\lambda = 420 \pm 10$ nm)

irradiation are demonstrated in Figure 7-4. When the visible light is on, the

generation of around 410 nA photocurrent can be observed in aqueous $H_2O_2$ solution

while no photocurrent is produced in DDW, indicating only the surface complex can

be excited by visible light to generate an electron which is transferred to the electrode to generate visible-light-induced current (Iph).
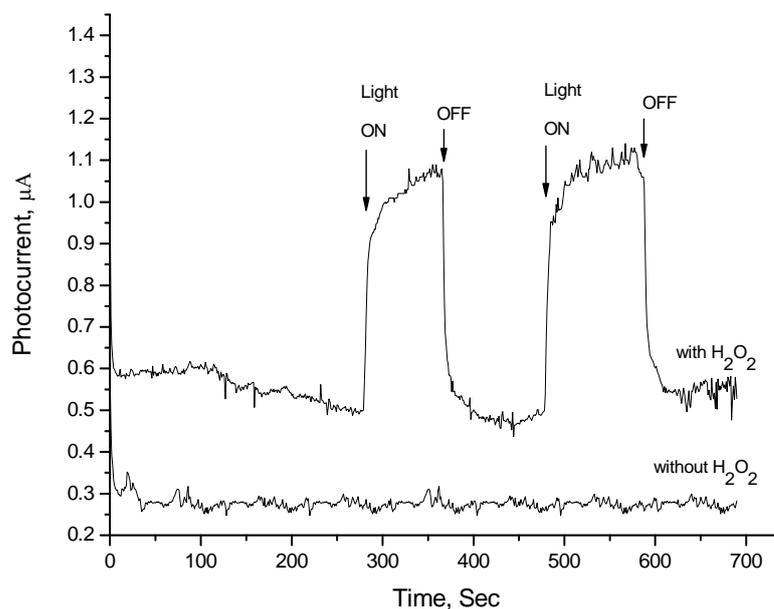


Figure 7-4:  Visible-light-induced current (Iph) generation on a $TiO_2$/ITO electrode in water with or without $H_2O_2$ (Notes: the concentration of $H_2O_2$ solution is 0.03 M).

7.2.3 Effect of Wavelength

The effect of wavelength of visible light on the LNR decay rate and the generation of photocurrent was also examined (See Figure 7-5). Figure 7-5a shows that the degradation rate of LNR decreased with the increment of irradiation wavelength, where less than 12% LNR was removed by using 500 nm light after 6-hour of irradiation. Figure 7-5b demonstrates the generated photocurrent and the consumption of $H_2O_2$ after 6 hours of reaction in the presence of $H_2O_2$ under different wavelength irradiations. It can be seen that the correlation between the generated photocurrent and the consumed $H_2O_2$ is well established under various wavelengths; shorter the wavelength (i.e. higher the energy), higher the photocurrent,

and subsequently faster the consumption of $H_2O_2$. This suggests the electrons initiate the decomposition of $H_2O_2$. However, it is interesting to note that no photocurrent was generated under the irradiation of 500 nm visible light, although the formation of $TiO_2$ surface complexes could be extended to 550 nm visible light (Li et al., 2001), and 3.6 μmol $H_2O_2$ was consumed after 6 hours by 500 nm irradiation (from this study). This is likely because the signal of photocurrent produced is too weak to be detected by the potentiostat used in this study. In addition, the light intensity has also been measured in this study. The photo intensity at different wavelength is 178.6, 164.3, 167.8 and 203.6 $Wm^{-2}$ for 420, 435, 450 and 500 nm, respectively. Although the photo intensity is the highest at 500 nm, the weak absorbance of titanium peroxide complex at 500 nm (Li et al., 2001) results in its weak response to light at this wavelength.
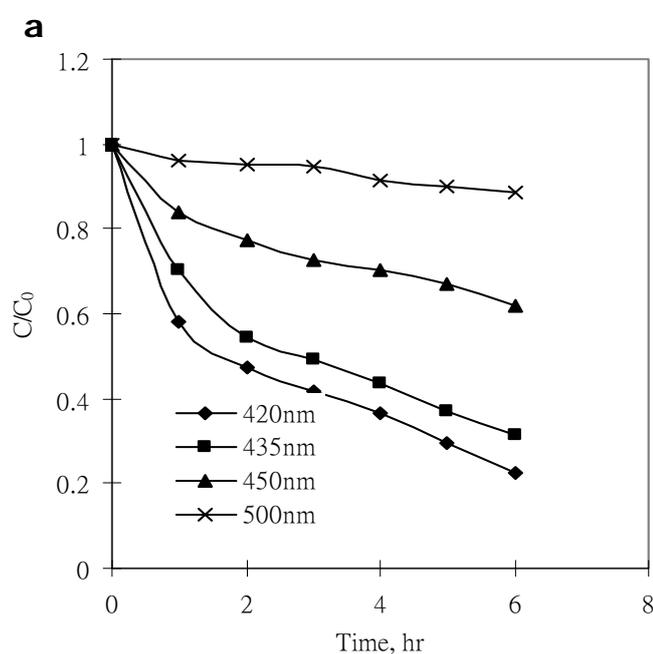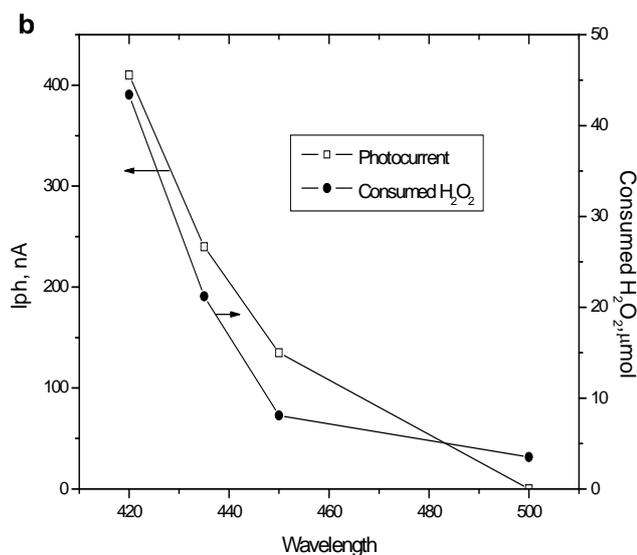
Figure 7-5: (a) The effect of wavelength of visible light on the LNR decay rate; (b) $I$ph and the $H_2O_2$ consumption are compared as a function of the wavelength (Notes: initial LNR concentration is 0.1 mM, $TiO_2$ loading is 0.6 g/L, the initial concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0).

7.2.4 Photocatalytic Degradation Pathway of LNR under Visible Light or UV Irradiation

It is believed that hydroxyl radicals play a key role in the decomposition of organic compounds by $UV/TiO_2$ process. The investigation on the transformation products of LNR produced both in visible light and UV-induced photocatalytic process may cast a bright light on the degradation mechanism of LNR by $TiO_2/H_2O_2/Vis$ process. The same concentration of LNR was degraded under irradiation of UV or visible light, where 16 and 17 intermediates were identified during the process on the basis of the molecular ions and mass fragment ions detected by MS spectrum for UV and visible light, respectively. The information on the intermediates including the mass of

deprotonated ion ([M − H] $^{+}$) of the daughter compounds, the proposed molecular structure, the relative abundances, and the proposed fragments is summarized (See Table 7-1). Actually, [M + acetate]$^{-}$ ions were obtained as a base peak of the mass spectra for most intermediates and LNR (See Appendix II) due to 5 mM ammonium acetate being used as mobile phase and negative-ion mode being employed in this study (Barcelo and Albaiges, 1989). The evolution profiles of major intermediates were organized and shown in Figure 7-6a and 7-6b (trace intermediates not included). As indicated in Figure 7-6, the formation/degradation profiles of the intermediates generated during these two processes are quite similar. It was also found that the decay of LNR was involved with *N*-demethoxylation and *N*-demethylation through alkylic-oxidation, dechlorination (hydroxylation at the chlorine site), and hydroxylation of the benzene ring in both processes. Direct dechlorination (no hydroxylation at the chlorine site) reported by other researchers (Lopez et al., 2005) was not observed in this study. Untill now, it is believed that hydroxyl radicals also play a predominant role in $Vis/TiO_2/H_2O_2$ process similar to that in $UV/TiO_2$ process for the LNR decay. It can also be believed LNR suffers the same decay pathway by both $Vis/TiO_2/H_2O_2$ and $UV/TiO_2$ process.

Table 7-1: Identified degradation products and their main fragments determined by LC/ESI-MS

| Compound | Retention time | Molecular weight | Molecular ion and main fragments | Structural formula | Detected in | |
|---|---|---|---|---|---|---|
| | | | | | UV | Vis |
| LNR | 20.93 | 248 | 247, 217, 188, 160, 109 |  | √ | √ |

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 8.96 | 186 | 185,165,141,119 | | √ | √ |
| 2 | 9.49 | 278 | 277, 250, 233, 217,119 | | √ | √ |
| 3 | 10.02 | 262 | 261, 156, 119,109 | | | √ |
| 4 | 10.65 | 200 | 199, 42,137,119 | | √ | √ |
| 5 | 12.62 | 200 | 199, 137, 119 | | √ | √ |
| 6 | 13.90 | 230 | 229, 37,119,109 | | √ | √ |
| 7 | 14.61 | 264 | 263,176,119,109 | | √ | √ |
| 8 | 14.83 | 250 | 249,219,202,176, 137,119,109 | | √ | √ |
| 9 | 15.44, 15.56 | 220 | 219,203,176, 137 119,109 | | √ | √ |
| 10 | 15.68 | 234 | 233,203,160, 137,119,109 | | √ | √ |
| 11 | 16.31 | 204 | 203, 160, 137,119,109 | | √ | √ |
| 12 | 16.69 | 248 | 247,203,88,160, 137,119,109 | | √ | √ |
| 13 | 16.93 | 234 | 233, 202,176, 137,119,109 | | √ | √ |
| 14 | 17.46 | 218 | 217, 160, 137,119,109 | | √ | √ |

| 15 | 18.93 | 232 | 231,202,188 160, 137,119.109 |  | √ | √ |
| 16 and 17 | 19.30, 19.72 | 264 | 263, 233, 217, 202,188,156,119, 109 |  or  | √ | √ |
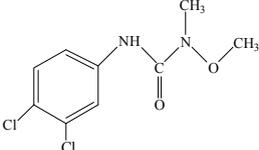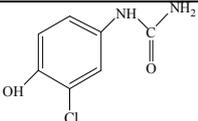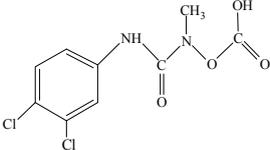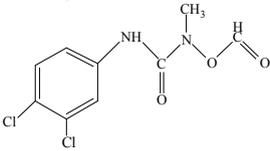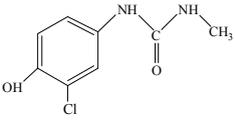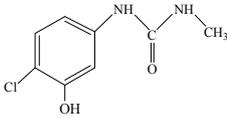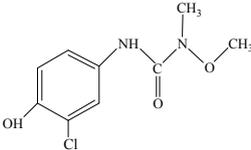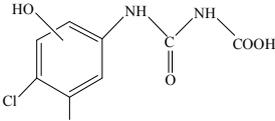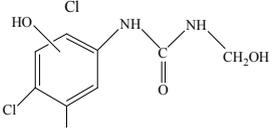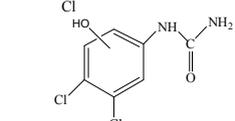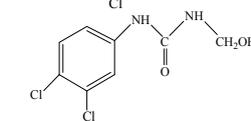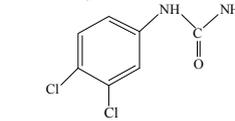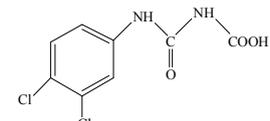
a



b



Figure 7-6: (a). The evolution profiles of generated intermediates in Vis/TiO$_2$/H$_2$O$_2$; (b).

The evolution profiles of intermediates in UV/TiO$_2$ system. (Notes: The

initial concentration of LNR is 0.25 mM, the initial concentration of H$_2$O$_2$

is 10 mM, initial pH value is 6.0; for UV/TiO$_2$ system, six 350 nm UV

lamps were used)

Therefore, the degradation pathway of LNR by Vis/TiO$_2$/H$_2$O$_2$ or UV/TiO$_2$ process

was proposed on the basis of the profile analysis as illustrated in Figure 7-7. The

decomposition of LNR was initiated by the attack of HO$^\bullet$ on the chlorine site of the

benzene ring, *N*-terminus methyl, and methoxyl groups, leading to the generation of

compounds 6, 16 and 17, respectively at the first step. The emergence of compound 6

was accompanied by the release of chlorine at the beginning of the reaction, which

has been quantified (See Figure 7-9). The oxidation of *N*-terminus methoxyl group of

compound 16 led to the formation of compounds 2, 3 and 14 through dealkylation

(alkylic side chain cleavage). The direct demethoxylation of compounds 6 and 17

resulted in the generation of compound 4 or 5 and 10, respectively. Compound 10 is

believed to have another source (the oxidation of N-terminus methyl of compound

14), which gives rise to high yield of compound 10 at the beginning of the reaction as

demonstrated in Figure 7-6. In addition, dechlorination of compound 14

(hydroxylation at the chlorine site) also could form compounds 4 or 5, which was

confirmed by an individual test using the standard of compound 14 as the initial

probe in Vis/TiO$_2$/H$_2$O$_2$ system. This individual test also verified that 13.6% of

compound 14 was transformed into compound 13 while 4.2% of compound 14 was

converted to compound 4 and 5 after 7 hours of reaction by Vis/TiO$_2$/H$_2$O$_2$ process

(data not shown), which may rationalize higher yield of compound 13 than

compounds 4 and 5 although compound 14 is the only possible source of compound

13. The further N-terminus oxidation of compound 10 produced compounds 15, 12

and 11 while the N-terminus oxidation of compound 13 caused the generation of

compounds 8, 7 and 9. Compound 1 is believed to come from the *N*-terminus

demethylation of compound 4. It should be noted that Compound 13 may not be the only source responsible for the formation of compound 9, while compound 4 may not be the only source contributed to the production of compound 1. Compound 11 can also make contribution to the yield of compound 1 and 9 through dechlorination (hydroxylation at the chlorine site on the benzene ring) and direct hydroxylation on the benzene ring without dechlorination, respectively, which was confirmed by an additional test using the compound 11 as the initial probe compound in this process. It was believed that 2,3-dichloroaniline was the terminal product of LNR decomposition (Farre et al., 2007). However, it was not detected in this study.

All intermediates were categorized into alkylic-oxidation derivatives (AOD), dechlorination-hydroxylation derivatives (DHD) and derivatives from the hydroxylation of benzene ring (HBD). In order to elucidate the major mechanism involved in these two processes, the transformation of LNR, the intermediates (in terms of AODs, DHDs and HBDs), and the mass balance of benzene ring were reorganized and incorporated in Figures 7-8a and 7-8b. Figure 7-8 shows the concentration of AODs is much higher than that of DHDs and HBDs, indicating alkylic-oxidation is a dominant degradation mechanism while dechlorination (hydroxylation at the chlorine site) and hydroxylation of the aromatic ring are minor in terms of LNR decay in both UV/TiO$_2$ and Vis/TiO$_2$/H2O$_2$ processes. This can be rationalized by the following: the di-substitution of the phenyl ring by chlorine atoms lowers its susceptibility towards any electrophilic or radical attack due to electron-drawing property of chlorine leading to the lower electron density on the benzene ring, resulting in the attack on the urea N-terminus group more competitive.
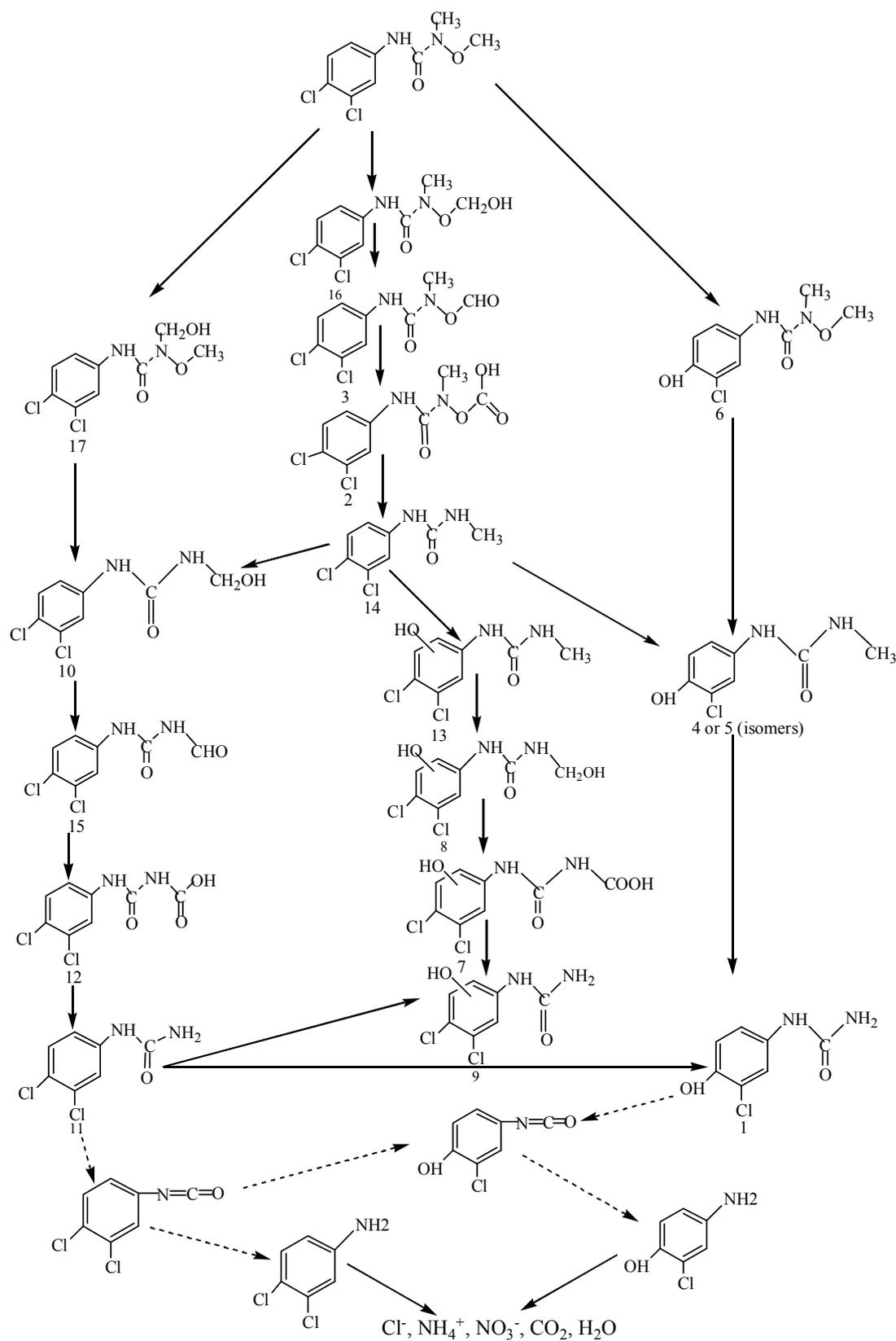
Figure 7-7: Degradation pathways of LNR for both Vis/TiO$_2$/H$_2$O$_2$ and UV/TiO$_2$ processes.

a



b
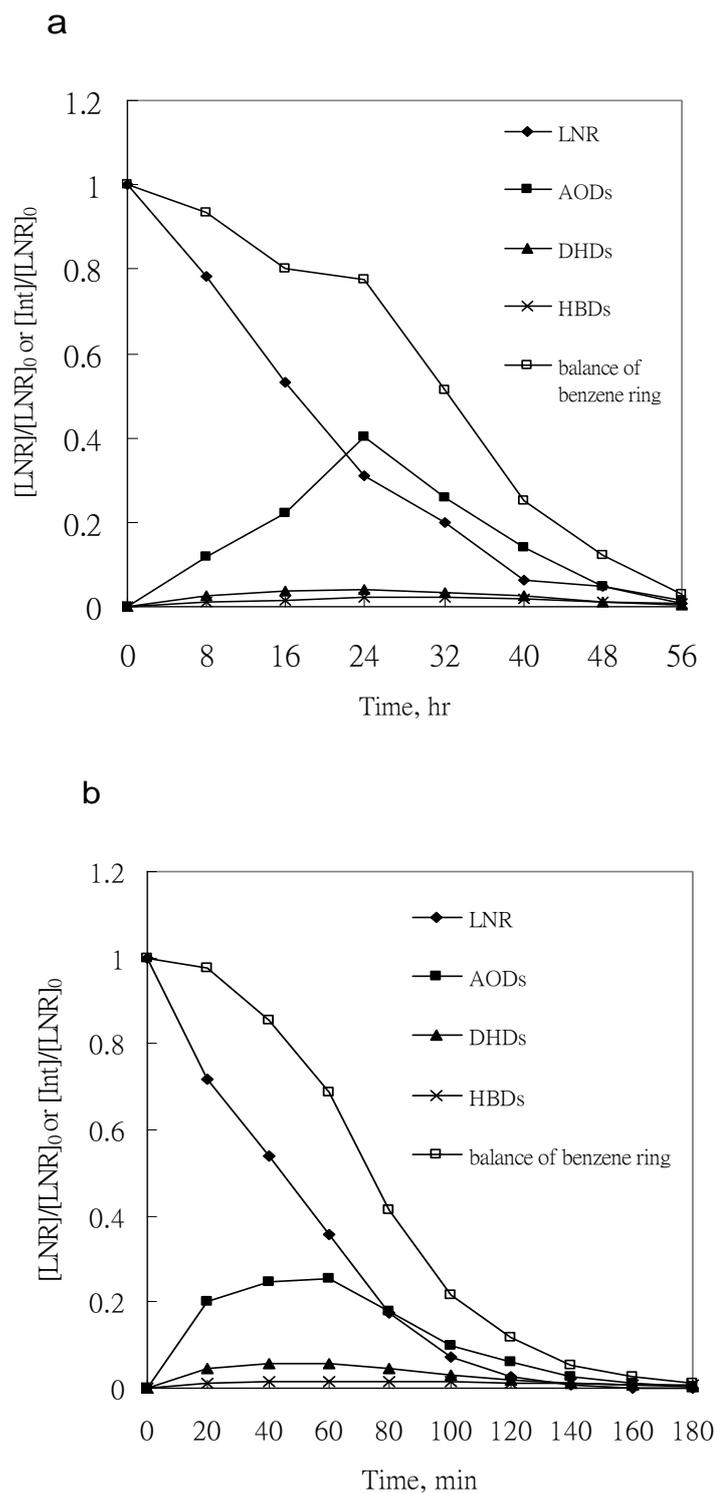


Figure 7-8: (a) Process summary of Vis/TiO$_2$/H$_2$O$_2$ (where [Int] stands for the concentration of intermediates); (b) Process summary of UV/TiO$_2$ (where [Int] stands for the concentration of intermediates)

The evolution of chloride, ammonium, nitrate and TOC was also monitored during the LNR decay reaction by $Vis/TiO_2/H_2O_2$ process (see Figure 7-9). Nearly 70% chlorine and 37% nitrogen were released after 56 hours of reaction as shown in Figure 7-9. Judging from the mass balance of benzene ring in Figure 7-8, ring opening was completed at the end of the reaction. However, only around 32% TOC was removed (see Figure 7-9). This suggests all aromatic compounds were broken down into simple aliphatic acids, which account for the dominating part of TOC. Furthermore, it is interesting to note that the $TiO_2$ particles sunk down to the bottom of the reactor automatically in 10 minutes right after the stirring was stopped. The release of chlorine due to dechlorination-hydroxylation and the generation of organic acid led to pH level dropping from 6.0 to 3.07. At pH 3.07, the $TiO_2$ surface is positively charged $(Ti-OH_2)^+$, which may favor the adsorption of the anions released during the reaction. The anion adsorption may weaken the repulsion of $TiO_2$ particles positively charged and start the aggregation of $TiO_2$ particles.
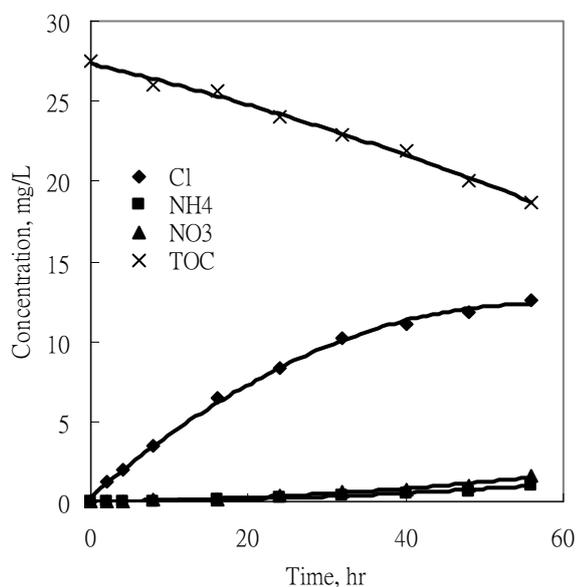


Figure 7-9: The evolution of TOC, chloride, ammonium and nitrate ions during the Vis-induced photocatalytic reaction (The initial concentration of LNR is

0.25 mM, the initial concentration of $H_2O_2$ is 10 mM, initial pH value is 6.0).

## 7.3 Summary

The application of $TiO_2/H_2O_2/Vis$ (visible light) process for the aqueous degradation of linuron (LNR) has been investigated. in this chapter. The degradation mechanism of LNR by $TiO_2/H_2O_2/Vis$ process has been verified through the investigation of the effects of various radical scavengers, monitoring the generation of photocurrent, examining the performance of other metal oxides in place of $TiO_2$ in this system, and comparing the intermediates and decay pathways of LNR by $UV$-$TiO_2$ and $TiO_2/H_2O_2/Vis$ processes with 16 and 17 intermediates identified, respectively. It has been revealed that demethoxylation and demethylation through alkylic-oxidation is the major mechanism of LNR degradation while dechlorination (hydroxylation at the chlorine site) and direct hydroxylation on the benzene ring is minor in both processes.

It is believable that $Vis/TiO_2/H_2O_2$ process is cost efficient and practically applicable in the removal of persistent organic contaminants in natural waters since it can work under the irradiation of visible light which accounts for a much larger part of solar light than UV.

# Chapter 8  Conclusion and Recommendation

## 8.1 Conclusion

The treatability of LNR has been investigated in depth by using various water treatment processes including continuous UV irradiation, ozonation, UV/ozonation, and $TiO_2/H_2O_2/Vis$ (visible light). These findings based on lab-scale studies provide important information for engineers to design reactors or tackle specific problems they may encounter in real application, not confined to the effect of those critical parameters, but extended to the interference of intermediates and final products. In particular, the study on the mechanism of LNR degradation by $TiO_2/H_2O_2/Vis$ process may perfect the theory about how $TiO_2$ work under the irradiation of visible light with the assistance of $H_2O_2$.

### 8.1.1 The Degradation of LNR by using UV, Ozonation, and UV/Ozone

The degradation for LNR by UV, $O_3$, and $UV/O_3$ processes were conducted under a wide range of conditions. The decay rate of LNR by $UV/O_3$ process was found to be around 3.5 times and 2.5 times faster than sole-UV and ozone-alone, respectively. No TOC removal was observed in sole UV process, and TOC removal was insignificant in ozonation process (about 15% mineralization after 100 minutes). However, nearly 80% mineralization was achieved by using UV/ozone process after 100 minutes. The overall rate constants increase exponentially with pH above 9.0 while the increase of rate constants with pH below 9 is insignificant in $O_3$ system. It was also observed that UV/ozone process was pH-dependent while UV photolysis was pH-independent in terms of LNR decay. The optimum synergistic effect of UV

combined with $O_3$ was found to be achieved at pH 9. The apparent photolysis rate constant of LNR is linearly increased with the increment of light intensity under the irradiation of UV at 254 nm. All predominating parameters such as quantum yield ($\Phi_{LNR}$), $k_{OOH}$ (rate constant for the formation of free radical $HOO^{\bullet-}$ from ozone decomposition at high pH), rate constant of linuron with ozone ($k_{o_3, LNR}$), rate constant of linuron with hydroxyl radical ($k_{OH, LNR}$), and $\alpha$ (the ratio of the production rate of $HO^{\bullet}$ and the decay rate of ozone in UV/$O_3$ system), involved in these three processes were determined in the assistant of proposed linear models. The proposed models offer an accurate way to predict the LNR decomposition by the UV, $O_3$ and UV/$O_3$ processes under varied conditions.

In addition, the influence of various anions on the performance of ozonation has also been examined. Chloride ion was observed to significantly retard the degradation of LNR at pH 3 while it exerted no perceptible effect on the performance of ozonation at pH 7. The presence of phosphate ion led to the increase of LNR decay rate at pH 7 due to its buffer ability to keep pH stable and had no influence on the LNR degradation at pH 3. Both carbonate and sulfate ions were not observed to affect the performance of ozonation in terms of LNR decomposition.

The intermediates and end products generated during LNR decay by these three processes have been investigated in detail. Eight intermediates escaped from previous studies were detected in sole-UV system in this study. A new decay pathway of LNR was proposed on the basis of information about the identified intermediates during the LNR and DCPMU (a dominating intermediate generated during LNR decay) degradation by UV photolysis compared to previous studies.

Furthermore, *N*-terminus demethoxylation, photohydrolysis with dechlorination, and *N*-terminus demethylation were found to be the major mechanisms in the LNR decay while hydroxylation on benzene ring might make a minor contribution to LNR removal under the irradiation of UV at 254 nm. *N*-terminus demethoxylation, dechlorination and hydroxylation on benzene ring were observed to be involved in the ozonation process. It was observed that around 98% of chlorine on the benzene ring was released after 4 hr and trace amount of $NH_4^+$ and $NO_3^-$ was detected, indicating de-nitrogenation could be achieved in the photolytic degradation of LNR by UV at 254 nm. For ozonation process, around 80% of chlorine and 13% of nitrogen were found to be released to the solution as chloride, nitrate and ammonia ions, respectively after 120 min. Among these three treatment processes, $UV/O_3$ process has exhibited the best overall performance in terms of LNR removal, mineralization, de-chlorination and de-nitrogenation (Complete release of chlorine was achieved after 80 min and around 56% of nitrogen was released as ammonia and nitrate ions after 120 min).

8.1.2 The Degradation of LNR by $TiO_2/H_2O_2/Vis$ (visible light) process

The degradation of LNR in $TiO_2$ suspension with and without $H_2O_2$ was investigated under the irradiation of visible light (420 nm lamps were used as light source). When no $H_2O_2$ involved, only 10% removal of LNR was observed. However the removal can be significantly increased to nearly 100% upon the addition of $H_2O_2$ to the process after 3 hr of reaction. We also examined the effect of $TiO_2$ phase composition on the performance of this system. In the absence of $H_2O_2$, anatase exhibited higher photocatalytic activities than $TiO_2$-P25 and no LNR decay was

observed in rutile suspension; while in the presence of $H_2O_2$, $TiO_2$-P25 demonstrated the best performance and rutile showed higher activities than anatase.

The performance of various semiconductors under varied conditions was also investigated. ZnO showed the highest photocatalytic activities under visible light without using $H_2O_2$. The addition of $H_2O_2$ led to a considerable enhancement on the decay rate of LNR in the cases of $TiO_2$-P25 and $WO_3$, while no positive effect was observed for ZnO.

The process is optimized by examining the reaction rate under various reaction conditions. The decay rate of LNR, generally, increased with the increment of $TiO_2$ dosage. However, the LNR degradation could be gradually retarded when $TiO_2$ was overdosed (above 0.4 g/L) due to the reduction of light penetration.

The $H_2O_2$ concentration of the tested range (1 to 20 mM) did not show a significant influence on the LNR decay. However, if the initial $H_2O_2$ is at low end (e.g. 1 or 2 mM) the retardation of LNR decay will be observed as the remaining $H_2O_2$ in the solution reduced (consumed) to 0.1 mM. The optimal pH level for the $H_2O_2$-assisted photocatalysis under visible light was found at neutral range, which is beneficial for the purpose of application.

Furthermore, it was found that the Langmuir-Hinshelwood kinetics fitted well to the degradation of LNR throughout the examined concentration range of LNR, implying that surface reaction is dominant while homogeneous reaction is insignificant in this system.

The reaction mechanism of LNR degradation by $TiO_2/H_2O_2/Vis$ process using Xe lamp as the light source has been verified through the investigation of the effects of various radical scavengers, monitoring the generation of photocurrent, examining the performance of other metal oxides in place of $TiO_2$ in this system, and comparing the intermediates and decay pathways of LNR by $UV-TiO_2$ and $TiO_2/H_2O_2/Vis$ processes. Hydroxyl radicals are believed to play a dominant role in LNR degradation in $Vis/TiO_2/H_2O_2$ system, judging from LNR decay being completely hampered after the application of radical scavengers as well as the comparison of the identical intermediates and decay mechanism between $Vis/TiO_2/H_2O_2$ and $UV/TiO_2$ processes. The generation of electrons was first confirmed by monitoring photocurrent while $TiO_2$-coated ITO electrode was immersed in $H_2O_2$ solution. Subsequent reaction between electron and $H_2O_2$ can produce hydroxyl radicals.

It is believable that $Vis/TiO_2/H_2O_2$ process is cost efficient and practically applicable in the removal of persistent organic contaminants in natural waters since it can work under the irradiation of visible light which accounts for a much larger part of solar light than UV.

## 8.2 Limitation and Recommendation

In this study, all photochemical reactions were conducted in a batch reactor and the destruction of single target organics was focused. For practical application, it is suggested to examine the performance of $UV/O_3$ and $TiO_2/H_2O_2/Vis$ systems in the presence of multiple organic pollutants. In the real treatment plant, influent are in flowing condition. The performance of these processes should be investigated in continuous flow reactor.

In addition, $TiO_2$ fine particles were used as photocatalyst in this study, which makes post-treatment necessary in real application. In order to overcome the disadvantages of the commercial $TiO_2$ fine powder, thus, coating $TiO_2$ on substrates such as glass beads, glass fiber, and activated carbon is recommended. The selection of substrates should be given special caution.

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# APPENDIX I: Experimental runs

| Experiment No. | Compound | Initial Concentration | Parameters | | | | |
|---|---|---|---|---|---|---|---|
| | | | *pH* | *$O_3$* (mM) | *UV* (nm) | *Intensity* (Einstein $L^{-1}$ $min^{-1}$) | *$H_2O_2$* (mM) |
| 4-1 | LNR | 0.1 mM | 6.0 | | 254 | $3.0 \times 10^{-6}$ | |
| 4-2 | LNR | 0.1 mM | 6.0 | | 254 | $6.0 \times 10^{-6}$ | |
| 4-3 | LNR | 0.1 mM | 6.0 | | 254 | $9.0 \times 10^{-6}$ | |
| 4-4 | LNR | 0.1 mM | 6.0 | | 254 | $1.2 \times 10^{-5}$ | |
| 4-5 | LNR | 0.1 mM | 3.0 | 0.0171 | | | |
| 4-6 | LNR | 0.1 mM | 6.0 | 0.0171 | | | |
| 4-7 | LNR | 0.1 mM | 9.0 | 0.0171 | | | |
| 4-8 | LNR | 0.1 mM | 10.0 | 0.0171 | | | |
| 4-9 | LNR | 0.1 mM | 10.7 | 0.0171 | | | |
| 4-10 | LNR | 0.1 mM | 11.0 | 0.0171 | | | |
| 4-11 | LNR | 0.1 mM | 9.0 | 0.00996 | | | |
| 4-12 | LNR | 0.1 mM | 10.0 | 0.00996 | | | |
| 4-13 | LNR | 0.1 mM | 10.7 | 0.00996 | | | |
| 4-14 | LNR | 0.1 mM | 11.0 | 0.00996 | | | |
| 4-15 | LNR | 0.1 mM | 9.0 | 0.0244 | | | |
| 4-16 | LNR | 0.1 mM | 10.0 | 0.0244 | | | |
| 4-17 | LNR | 0.1 mM | 10.7 | 0.0244 | | | |
| 4-18 | LNR | 0.1 mM | 11.0 | 0.0244 | | | |
| 4-19 | LNR | 0.1 mM | 9.0 | 0.0309 | | | |
| 4-20 | LNR | 0.1 mM | 10.0 | 0.0309 | | | |

| 4-21 | LNR | 0.1 mM | 10.7 | 0.0309 | | | |
|------|-----|--------|------|--------|-----|---------------------|----|
| 4-22 | LNR | 0.1 mM | 11.0 | 0.0309 | | | I-2 |
| 4-23 | LNR and ATZ | 10μM | 6.0 | | 254 | $3.0 \times 10^{-6}$ | 20 |
| 4-24 | LNR | 0.1 mM | 4.0 | 0.0171 | 254 | $3.0 \times 10^{-6}$ | |
| 4-25 | LNR | 0.1 mM | 4.0 | 0.0171 | 254 | $6.0\times10^{-6}$ | |
| 4-26 | LNR | 0.1 mM | 4.0 | 0.0171 | 254 | $9.0\times10^{-6}$ | |
| 4-27 | LNR | 0.1 mM | 4.0 | 0.0171 | 254 | $1.2\times10^{-5}$ | |
| 5-1 | LNR | 0.1 mM | 3.0 | | 254 | $6.0\times10^{-6}$ | |
| 5-2 | LNR | 0.1 mM | 9.0 | | 254 | $6.0\times10^{-6}$ | |
| 5-3 | LNR | 0.1 mM | 10.0 | | 254 | $6.0\times10^{-6}$ | |
| 5-4 | LNR | 0.1 mM | 11.0 | | 254 | $6.0\times10^{-6}$ | |
| 5-5 | LNR | 0.1 mM | 3.0 | 0.0171 | 254 | $6.0\times10^{-6}$ | |
| 5-6 | LNR | 0.1 mM | 6.0 | 0.0171 | 254 | $6.0\times10^{-6}$ | |
| 5-7 | LNR | 0.1 mM | 9.0 | 0.0171 | 254 | $6.0\times10^{-6}$ | |
| 5-8 | LNR | 0.1 mM | 10.0 | 0.0171 | 254 | $6.0\times10^{-6}$ | |
| 5-9 | LNR | 0.1 mM | 11.0 | 0.0171 | 254 | $6.0\times10^{-6}$ | |
| 5-10 | LNR | 0.29 mM | 6.0 | | 254 | $9.0\times10^{-6}$ | |
| 5-11 | LNR | 0.29 mM (purge Argon) | 6.0 | | 254 | $9.0\times10^{-6}$ | |
| 5-12 | DCPMU | 0.18 mM | 6.0 | | 254 | $9.0\times10^{-6}$ | |
| 5-13 | DCPU | 0.20 mM | 6.0 | | 254 | $9.0\times10^{-6}$ | |
| 5-14 | LNR | 0.29 mM | 6.0 | 0.0245 | | | |
| 5-15 | DCPMU | 0.18 mM | 6.0 | 0.0245 | | | |
| 5-16 | LNR | 0.29 mM | 6.0 | 0.0245 | 254 | $9.0 \times10^{-6}$ | |

| Experiment No. | Compound | Initial Concentration | Parameters | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | pH | $O_3$ (mM) | $Cl^-$ (M) | $SO_4^{2-}$ (M) | $CO_3^{2-}$ (M) | $HPO_4^{2-}$ (M) |
| 5-17 | LNR | 0.1 mM | 3.0 | 0.0171 | 0.01 | | | |
| 5-18 | LNR | 0.1 mM | 3.0 | 0.0171 | | 0.01 | | |
| 5-19 | LNR | 0.1 mM | 3.0 | 0.0171 | | | | 0.01 |
| 5-20 | LNR | 0.1 mM | 7.0 | 0.0245 | 0.01 | | | |
| 5-21 | LNR | 0.1 mM | 7.0 | 0.0245 | | 0.01 | | |
| 5-22 | LNR | 0.1 mM | 7.0 | 0.0245 | | | 0.01 | |
| 5-23 | LNR | 0.1 mM | 7.0 | 0.0245 | | | | 0.01 |
| 5-24 | LNR | 0.1 mM | 7.0 | 0.0245 | | | | |

| Experiment No. | Compound | Initial Concentration | Parameters | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | *pH* | *TiO₂* (g/L) | *WO₃* (g/L) | *ZnO* (g/L) | *Hg lamp* (nm) | *DO* mgL⁻¹ | *H₂O₂* (mM) |
| 6-1 | LNR | 0.1 mM | 6.0 | 0.6 | | | | | 10 |
| 6-2 | LNR | 0.1 mM | 6.0 | 0.6 | | | 419 | | |
| 6-3 | LNR | 0.1 mM | 6.0 | | | | 419 | | 10 |
| 6-4 | LNR | 0.1 mM | 6.0 | 0.6 | | | 419 | | 10 |
| 6-5 | LNR | 0.1 mM (with quencher) | 6.0 | 0.6 | | | 419 | | |
| 6-6 | LNR | 0.1 mM (with quencher) | 6.0 | 0.6 | | | 419 | | 10 |
| 6-7 | LNR | 0.1 mM | 6.0 | 0.6 | | | 419 | 31.2 | |
| 6-8 | LNR | 0.1 mM | 6.0 | | 0.6 | | 419 | | |
| 6-9 | LNR | 0.1 mM | 6.0 | | 0.6 | | 419 | 30.8 | |
| 6-10 | LNR | 0.1 mM | 6.0 | | 0.6 | | 419 | | 10 |
| 6-11 | LNR | 0.1 mM | 6.0 | | | 0.6 | 419 | | |
| 6-12 | LNR | 0.1 mM | 6.0 | | | 0.6 | 419 | 31.7 | |
| 6-13 | LNR | 0.1 mM | 6.0 | | | 0.6 | 419 | | 10 |
| 6-14 | LNR | 0.1 mM | 6.0 | 0.05 | | | 419 | | 10 |
| 6-15 | LNR | 0.1 mM | 6.0 | 0.1 | | | 419 | | 10 |
| 6-16 | LNR | 0.1 mM | 6.0 | 0.2 | | | 419 | | 10 |
| 6-17 | LNR | 0.1 mM | 6.0 | 0.4 | | | 419 | | 10 |
| 6-18 | LNR | 0.1 mM | 6.0 | 0.8 | | | 419 | | 10 |
| 6-19 | LNR | 0.1 mM | 6.0 | 1.0 | | | 419 | | 10 |
| 6-20 | LNR | 0.1 mM | 6.0 | 0.4 | | | 419 | | 1 |

| 6-21 | LNR | 0.1 mM | 6.0 | 0.4 | | | 419 | | 2 |
|------|-----|--------|-----|-----|---|---|-----|---|-----|
| 6-22 | LNR | 0.1 mM | 6.0 | 0.4 | | | 419 | | 5 |
| 6-23 | LNR | 0.1 mM | 6.0 | 0.4 | | | 419 | | 20 |
| 6-24 | LNR | 0.1 mM | 2.0 | 0.4 | | | 419 | | 5 |
| 6-25 | LNR | 0.1 mM | 4.0 | 0.4 | | | 419 | | 5 |
| 6-26 | LNR | 0.1 mM | 9.0 | 0.4 | | | 419 | | 5 |
| 6-27 | LNR | 0.1 mM | 11.0 | 0.4 | | | 419 | | 5 |
| 6-28 | LNR | 0.0125 mM | 6.0 | 0.4 | | | 419 | | 5 |
| 6-29 | LNR | 0.025 mM | 6.0 | 0.4 | | | 419 | | 5 |
| 6-30 | LNR | 0.05 mM | 6.0 | 0.4 | | | 419 | | 5 |
| 6-31 | LNR | 0.2 mM | 6.0 | 0.4 | | | 419 | | 5 |
| 6-32 | LNR | 0.3 mM | 6.0 | 0.4 | | | 419 | | 5 |

| Experiment. No | Compound | Initial Concentration | Parameters | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | pH | Rutile (g/L) | Anatase (g/L) | Hg lamp (nm) | DO mgL⁻¹ | H₂O₂ (mM) |
| 6-33 | LNR | 0.1 mM | 6.0 | 0.6 | | 419 | | |
| 6-34 | LNR | 0.1 mM | 6.0 | 0.6 | | 419 | | 10 |
| 6-35 | LNR | 0.1 mM | 6.0 | | 0.6 | 419 | | |
| 6-36 | LNR | 0.1 mM | 6.0 | | 0.6 | 419 | | 10 |

| Experiment. No | Compound | Initial Concentration | Parameters | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | pH | TiO$_2$ (g/L) | Hg lamp (*nm*) | Xe lamp (*nm*) | DO *mgL$^{-1}$* | H$_2$O$_2$ (*mM*) |
| 7-1 | LNR | 0.1 mM | 6.0 | 0.6 | | 420 | 6.1 | |
| 7-2 | LNR | 0.1 mM | 6.0 | | | 420 | 6.3 | 10 |
| 7-3 | LNR | 0.1 mM | 6.0 | 0.6 | | 420 | 39.3 | |
| 7-4 | LNR | 0.1 mM | 6.0 | 0.6 | | 420 | 5.9 | 10 |
| 7-5 | LNR | 0.1 mM | 6.0 | 0.6 | | 435 | 6.5 | 10 |
| 7-6 | LNR | 0.1 mM | 6.0 | 0.6 | | 450 | 6.4 | 10 |
| 7-7 | LNR | 0.1 mM | 6.0 | 0.6 | | 500 | 6.7 | 10 |
| 7-8 | LNR (100 mg/L NaN$_3$) | 0.1 mM | 6.0 | 0.6 | | 435 | 6.1 | 10 |
| 7-9 | LNR (100 mg/L HCO$_3$) | 0.1 mM | 6.0 | 0.6 | | 435 | 6.4 | 10 |
| 7-10 | LNR (100 mg/L t-butanol) | 0.1 mM | 6.0 | 0.6 | | 435 | 6.2 | 10 |
| 7-11 | LNR (3 g/L t-butanol) | 0.1 mM | 6.0 | 0.6 | | 435 | 6.1 | 10 |
| 7-12 | LNR | 0.29 mM | 6.0 | 0.6 | | 420 | 6.7 | 10 |
| 7-13 | LNR | 0.29 mM | 6.0 | 0.1 | 350 | | 6.5 | |
| 7-14 | DCPMU | 0.18 mM | 6.0 | 0.6 | | 420 | 6.4 | 10 |
| 7-15 | DCPU | 0.2 mM | 6.0 | 0.6 | | 420 | 6.3 | 10 |

| Experiment. No | Compound | Initial Concentration | Parameters | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | pH | Ga$_2$O$_3$ (g/L) | SiO$_2$ (g/L) | Al$_2$O$_3$ | Xe lamp (nm) | H$_2$O$_2$ (mM) |
| 7-16 | LNR | 0.1 mM | 6.0 | 0.6 | | | 420 | 10 |
| 7-17 | LNR | 0.1 mM | 6.0 | | 0.6 | | 420 | 10 |
| 7-18 | LNR | 0.1 mM | 6.0 | | | 0.6 | 420 | 10 |

# APPENDIX II: Mass spectrum of LNR and major intermediates

DCPMU-P25-H2O2-7hr02 #1849   RT: 18.60   AV: 1   NL: 3.04E6
T: - p ESI Full ms [ 55.00-400.00]

276.9

278.9

217.1

218.9

279.8
281.0

160.0

59.2
62.0  70.0

144.9  162.5  191.3  204.0  205.3  235.4  252.7  262.9  282.0  291.2  314.9  334.9  338.8  339.9  364.8  387.0  390.9  397.8

Relative Abundance

m/z
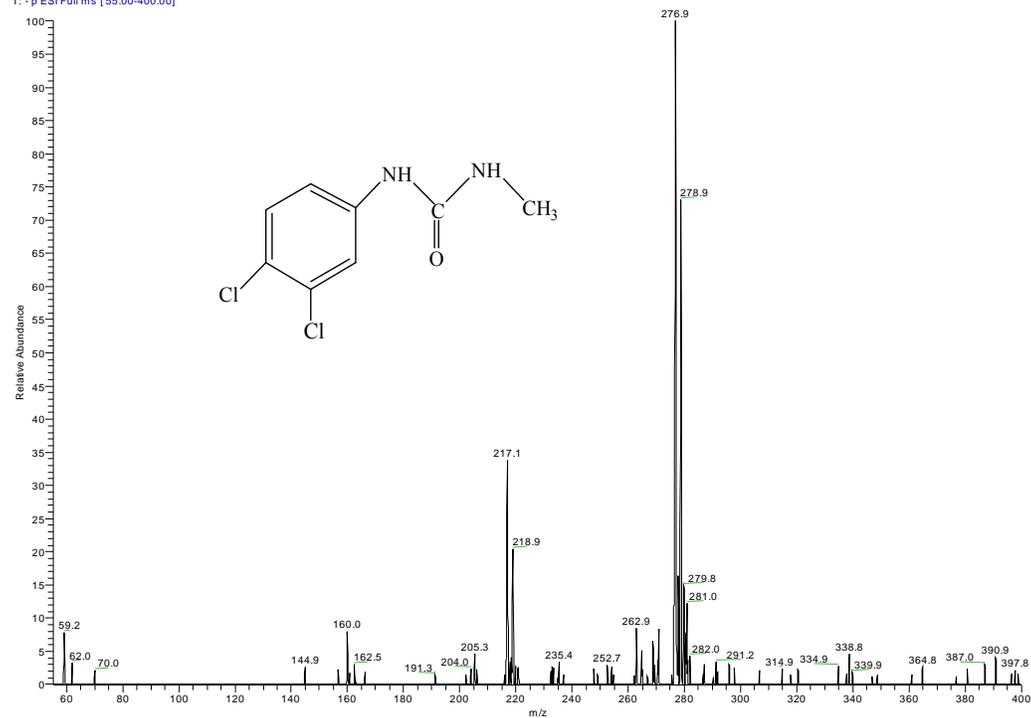
DCPMU-P25-H2O2-7hr02 #1770   RT: 17.91   AV: 1   NL: 2.66E6
T: - p ESI Full ms [ 55.00-400.00]

233.0

235.0

292.7

268.8

202.1

236.8

270.9

294.7

176.1

59.0

204.1

297.8

272.9

73.9  102.8  118.9  126.0  142.7  158.9  178.2  205.1  238.7  260.8  300.2  305.0  321.0  342.7  366.2  367.0  374.9  382.3  395.9

Relative Abundance

m/z
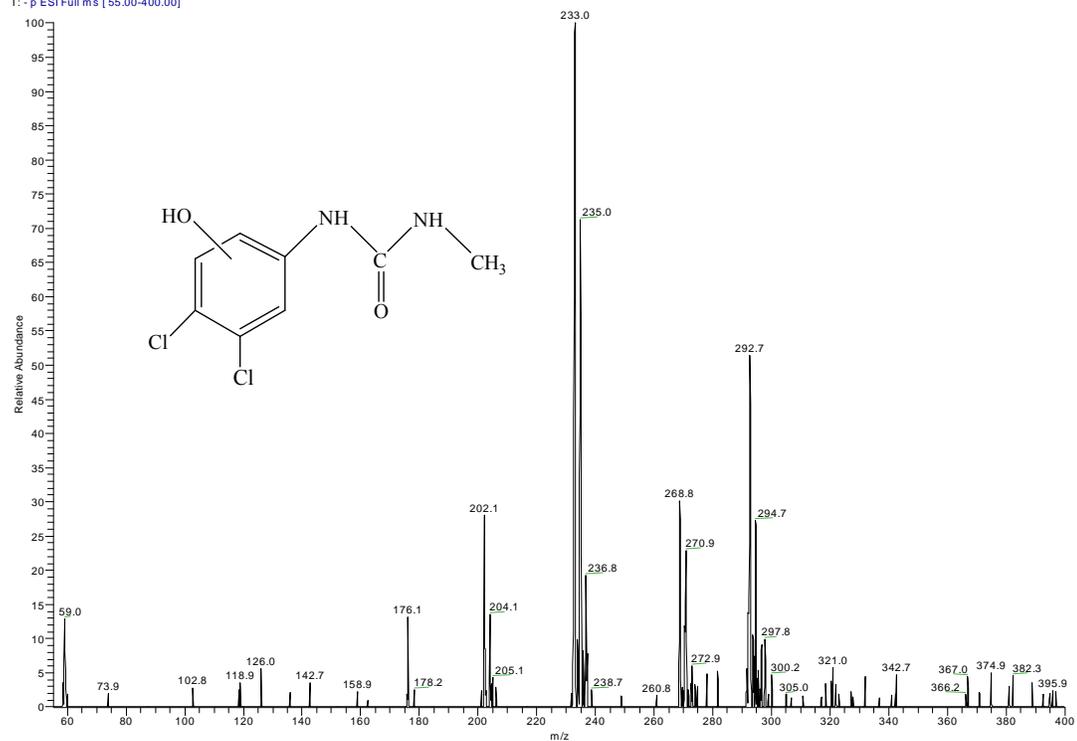
LNR-P25-H2O2-20hr #1678  RT: 16.71  AV: 1  NL: 3.15E5
T: - p ESI Full ms [ 55.00-400.00]
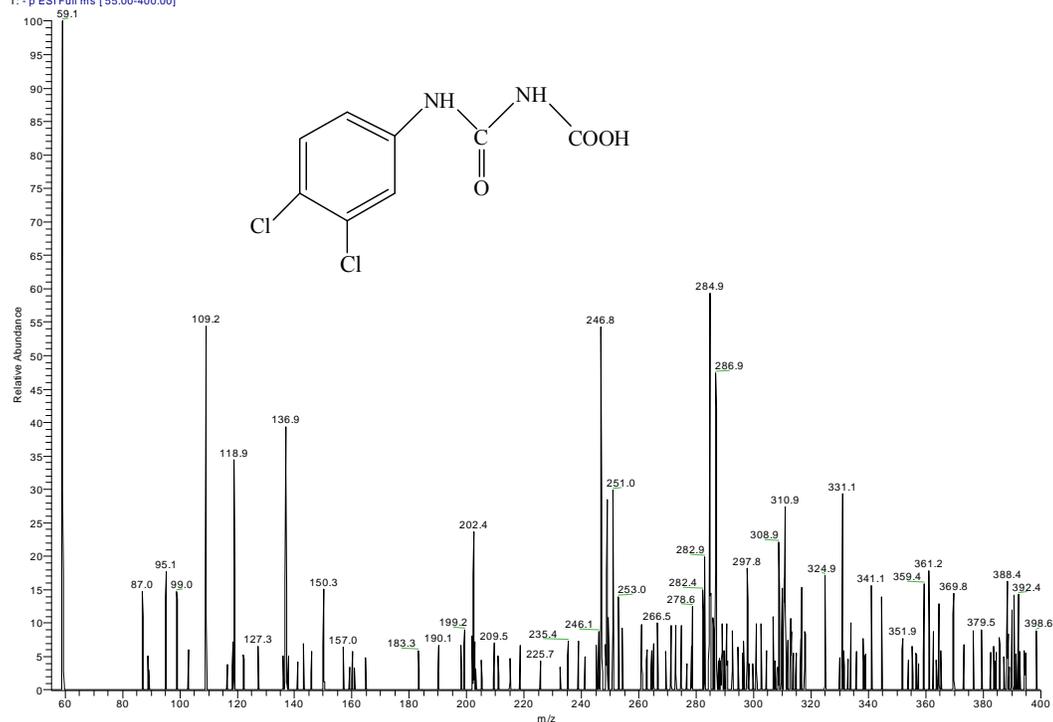


LNR-UV-1hr #1393  RT: 12.65  AV: 1  NL: 2.98E6
T: - p ESI Full ms [ 55.00-400.00]
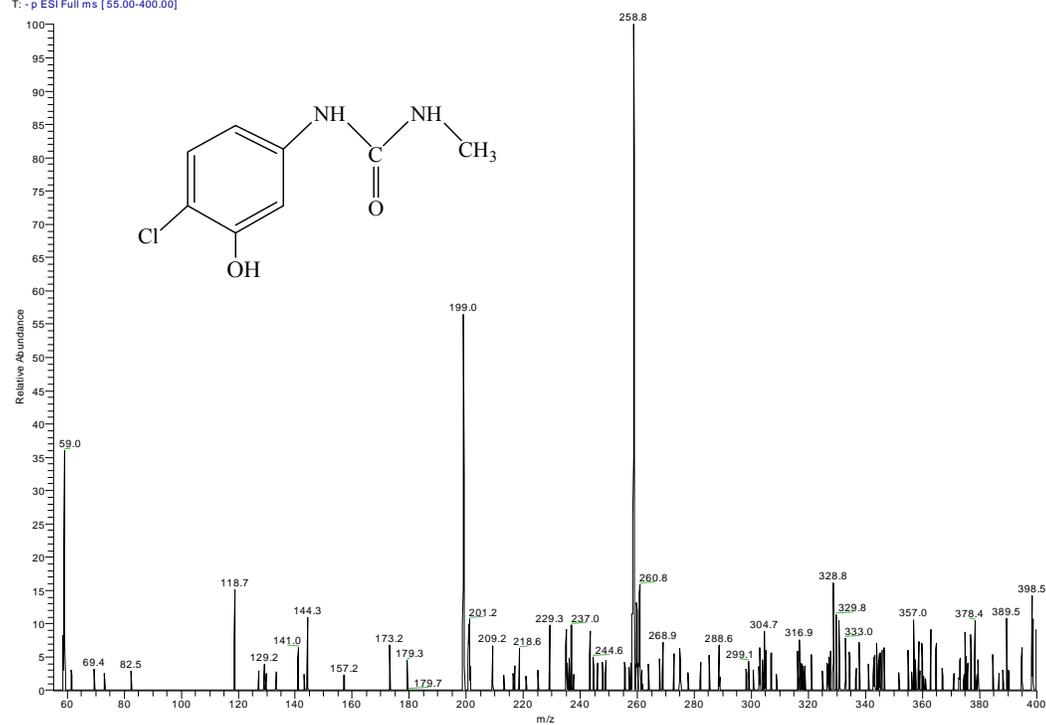
LNR-P25-H2O2-16hr #2028  RT: 19.83  AV: 1  NL: 2.52E6
T: - p ESI Full ms [ 55.00-400.00]
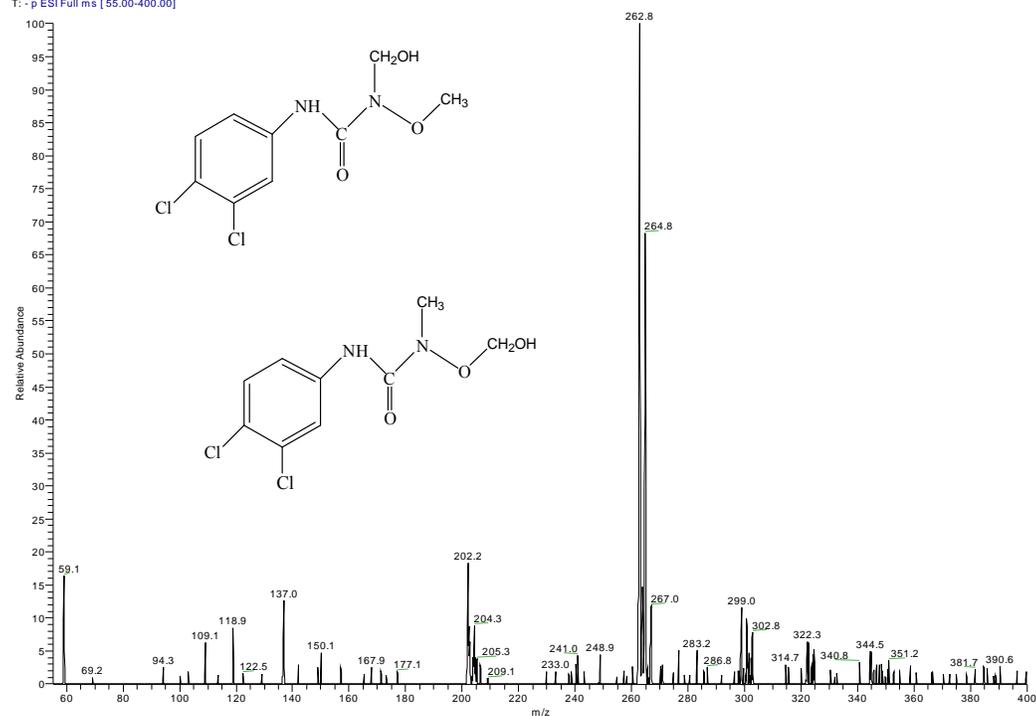


LNR-P25-H2O2-16hr #1915  RT: 18.83  AV: 1  NL: 5.35E5
T: - p ESI Full ms [ 55.00-400.00]
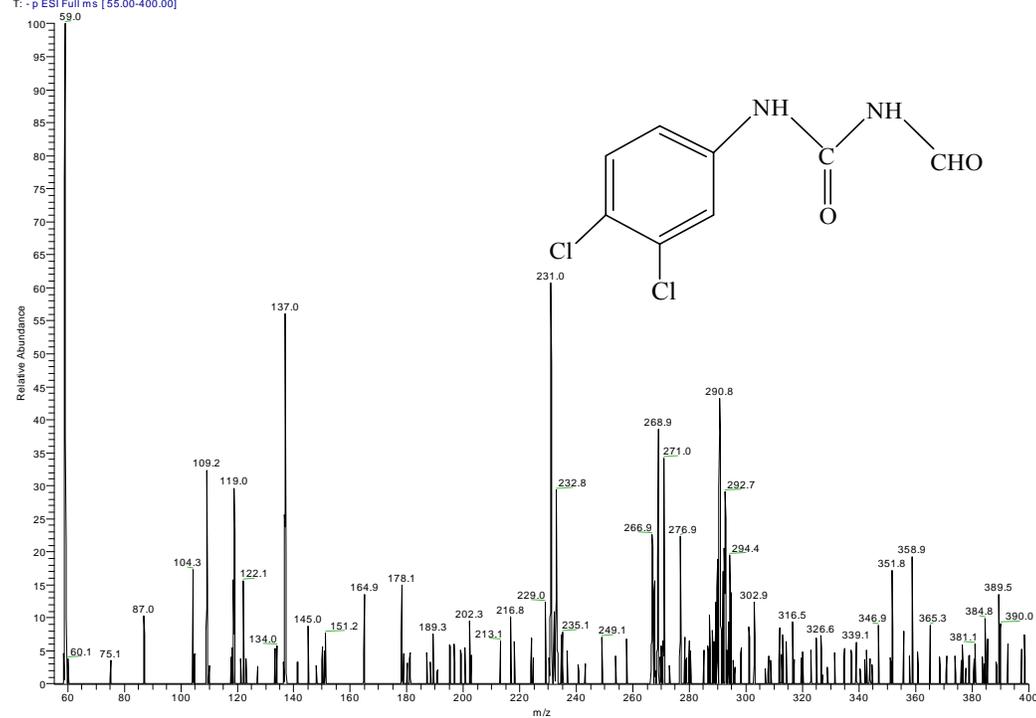
LNR-P25-H2O2-16hr #1570  RT: 15.75  AV: 1  NL: 1.07E6
T: - p ESI Full ms [ 55.00-400.00]
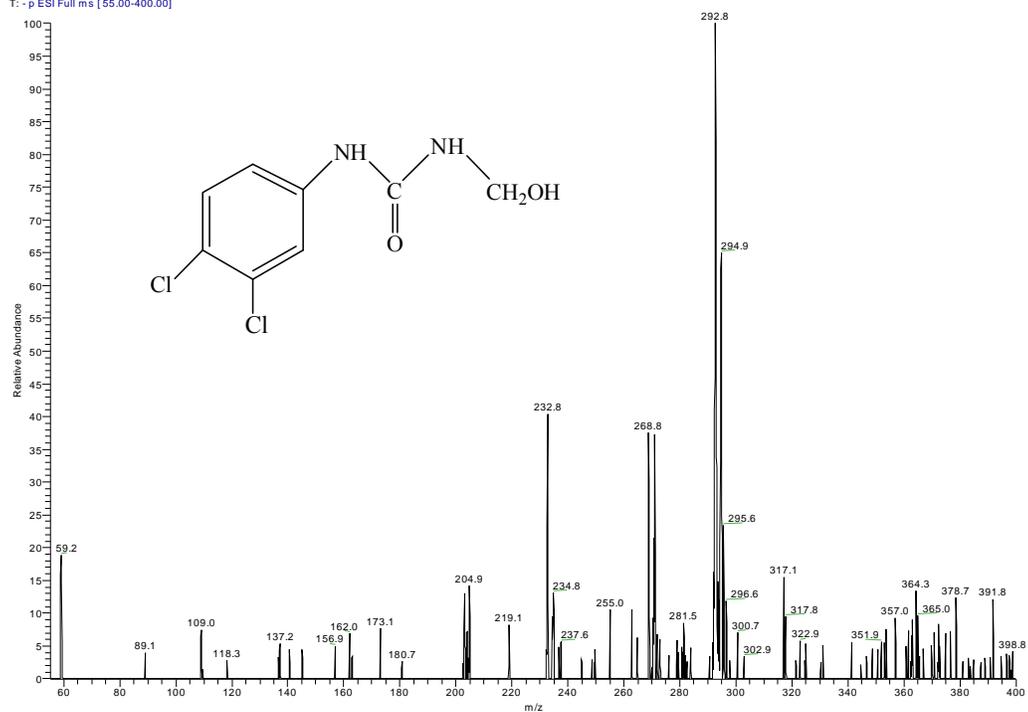


DCPMU-UV-20min #1040  RT: 10.41  AV: 1  NL: 6.27E5
T: - p ESI Full ms [ 55.00-400.00]
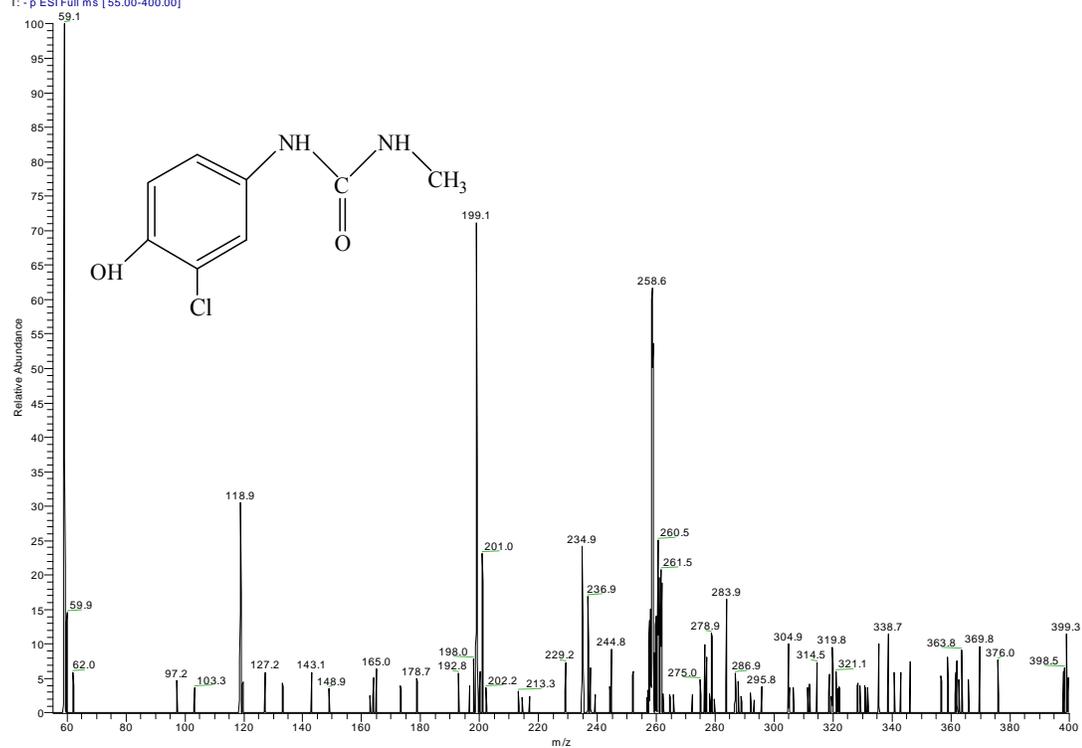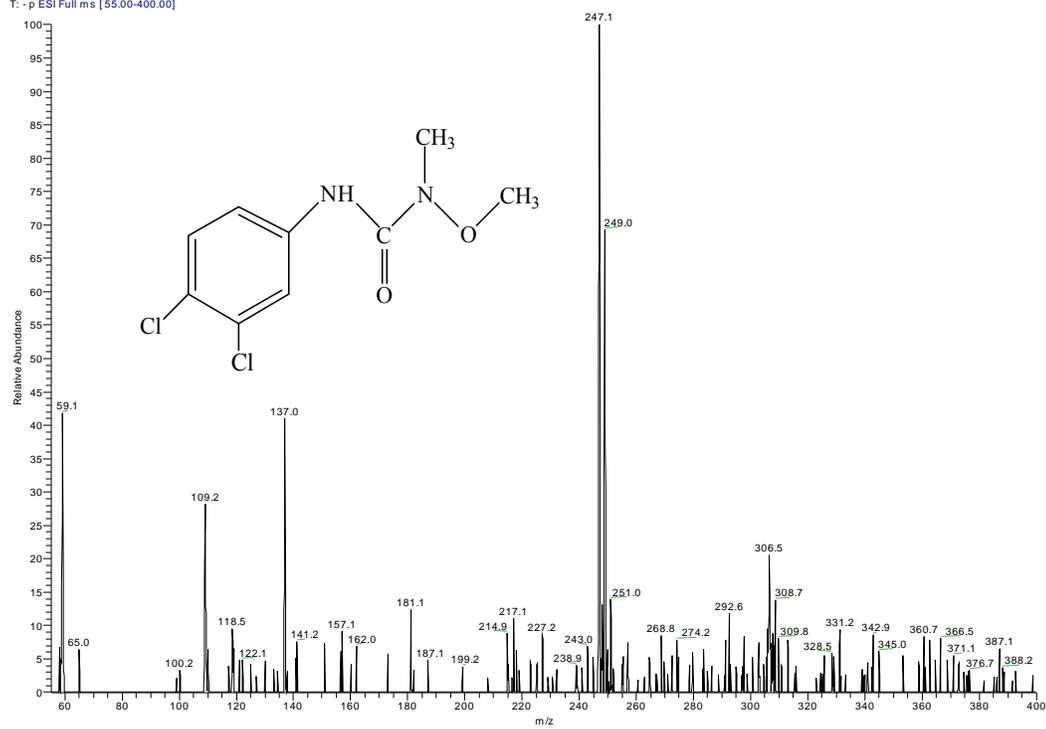
# APPENDIX III: Absorption spectrum of LNR
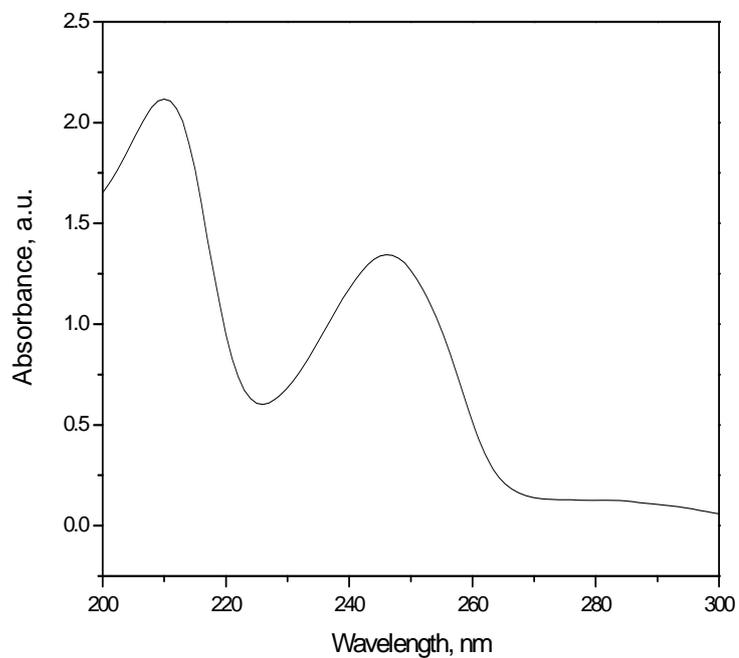


Figure A-1: Absorption spectrum of LNR at 0.295 mM

# APPENDIX IV: Experimental Results

Expt No: 4-1
Probe cpd: LNR
System: sole-UV with 2 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.298 | 1271214 | 0.0943 | 1 | 0 |
| 5 | 6.287 | 958668 | 0.0712 | 0.754136 | -0.28218 |
| 10 | 6.301 | 709240 | 0.0526 | 0.557923 | -0.58353 |
| 15 | 6.292 | 528882 | 0.0393 | 0.416045 | -0.87696 |
| 20 | 6.295 | 379576 | 0.0282 | 0.298593 | -1.20867 |
| 25 | 6.292 | 271125 | 0.0201 | 0.21328 | -1.54515 |
| 30 | 6.302 | 190592 | 0.0141 | 0.149929 | -1.89759 |

Expt No: 4-2
Probe cpd: LNR
System: sole-UV with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.275 | 1283471 | 0.0952 | 1 | 0 |
| 5 | 6.284 | 733668 | 0.0544 | 0.571628 | -0.55927 |
| 10 | 6.281 | 412276 | 0.0306 | 0.32122 | -1.13563 |
| 15 | 6.278 | 204317 | 0.0152 | 0.159191 | -1.83765 |
| 20 | 6.287 | 94622 | 0.00702 | 0.073724 | -2.60743 |
| 25 | 6.274 | 38846 | 0.00288 | 0.030267 | -3.4977 |
| 30 | 6.271 | 11623 | 0.000862 | 0.009056 | -4.70433 |

Expt No: 4-3
Probe cpd: LNR
System: sole-UV with 6 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.245 | 1295864 | 0.0962 | 1 | 0 |
| 5 | 6.241 | 558656 | 0.0415 | 0.431107 | -0.8414 |
| 10 | 6.243 | 211652 | 0.0157 | 0.163329 | -1.81199 |
| 15 | 6.236 | 65241 | 0.00484 | 0.050346 | -2.98884 |
| 20 | 6.248 | 13301 | 0.000987 | 0.010264 | -4.57909 |

Expt No: 4-4
Probe cpd: LNR
System: sole-UV with 8 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.330 | 1290147 | 0.0958 | 1 | 0 |
| 5 | 6.329 | 419101 | 0.0311 | 0.324848 | -1.1244 |
| 10 | 6.326 | 107406 | 0.00798 | 0.083251 | -2.4859 |
| 15 | 6.323 | 16688 | 0.00124 | 0.012935 | -4.34782 |

Expt No: 4-5
Probe cpd: LNR
pH: 3
System: sole-Ozone with [O$_3$] of 0.0171 mM

| T (Sec) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.256 | 1259883 | 0.0943 | 1 | 0 |
| 60 | 6.261 | 110211 | 0.0825 | 0.874772 | -0.13379 |
| 120 | 6.257 | 982067 | 0.0735 | 0.779491 | -0.24911 |
| 180 | 6.259 | 872436 | 0.0653 | 0.692474 | -0.36748 |
| 240 | 6.263 | 792169 | 0.0593 | 0.628764 | -0.464 |
| 300 | 6.260 | 721734 | 0.0540 | 0.572858 | -0.55712 |

Expt No: 4-6
Probe cpd: LNR
pH: 6
System: sole-Ozone with [O$_3$] of 0.0171 mM

| T (Sec) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.266 | 1278354 | 0.0949 | 1 | 0 |
| 30 | 6.261 | 1137173 | 0.0844 | 0.889561 | -0.11703 |
| 60 | 6.267 | 1038597 | 0.0771 | 0.812449 | -0.2077 |
| 120 | 6.270 | 919229 | 0.0682 | 0.719073 | -0.32979 |
| 180 | 6.263 | 783383 | 0.0581 | 0.612806 | -0.48971 |

Expt No: 4-7
Probe cpd: LNR
pH: 9
System: sole-Ozone with [O$_3$] of 0.0171 mM

| T (Sec) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.310 | 1238976 | 0.0920 | 1 | 0 |
| 30 | 6.314 | 1065679 | 0.0791 | 0.860129 | -0.15067 |
| 60 | 6.296 | 962484 | 0.0715 | 0.776839 | -0.25252 |
| 90 | 6.318 | 857958 | 0.0637 | 0.692474 | -0.36544 |
| 120 | 6.320 | 779023 | 0.0578 | 0.628764 | -0.46623 |
| 180 | 6.294 | 709757 | 0.0527 | 0.572858 | -0.71470 |

Expt No: 4-8
Probe cpd: LNR
pH: 10
System: sole-Ozone with [O$_3$] of 0.0171 mM

| T (Sec) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.340 | 1348695 | 0.1002 | 1 | 0 |
| 15 | 6.391 | 1183251 | 0.0879 | 0.87733 | -0.13087 |
| 30 | 6.395 | 1050198 | 0.0780 | 0.778677 | -0.25016 |
| 45 | 6.397 | 990968 | 0.0736 | 0.734761 | -0.30821 |
| 60 | 6.392 | 947194 | 0.0704 | 0.702304 | -0.35339 |

Expt No: 4-9
Probe cpd: LNR
pH: 10.7
System: sole-Ozone with [O$_3$] of 0.0171 mM

| T (Sec) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.253 | 1298849 | 0.0964 | 1 | 0 |
| 15 | 6.249 | 1098767 | 0.0815 | 0.845954 | -0.16729 |
| 30 | 6.258 | 974902 | 0.0724 | 0.750589 | -0.2869 |

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| T (Sec) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 45 | 6.251 | 832157 | 0.0617 | 0.640688 | -0.44521 |
| 60 | 6.247 | 725760 | 0.0539 | 0.558772 | -0.58201 |

Expt No: 4-10
Probe cpd: LNR
pH: 11
System: sole-Ozone with [O$_3$] of 0.0171 mM

| T (Sec) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.281 | 1313231 | 0.0975 | 1 | 0 |
| 15 | 6.285 | 998820 | 0.0742 | 0.760582 | -0.27367 |
| 30 | 6.278 | 835310 | 0.0620 | 0.636072 | -0.45244 |
| 45 | 6.290 | 699084 | 0.0519 | 0.532339 | -0.63047 |
| 60 | 6.287 | 601564 | 0.0447 | 0.458079 | -0.78071 |

Expt No: 4-11
Probe cpd: LNR
pH: 9
System: sole-Ozone with $[O_3]$ of 0.00996 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.401 | 1248176 | 0.0927 | 1 | 0 |
| 60 | 6.396 | 1067541 | 0.0793 | 0.855281 | -0.15633 |
| 120 | 6.393 | 932871 | 0.0693 | 0.747387 | -0.29117 |
| 180 | 6.398 | 834165 | 0.0619 | 0.668307 | -0.40301 |
| 240 | 6.404 | 730953 | 0.0543 | 0.585617 | -0.53509 |

Expt No: 4-12
Probe cpd: LNR
pH: 10
System: sole-Ozone with $[O_3]$ of 0.00996 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.335 | 1301892 | 0.0967 | 1 | 0 |
| 60 | 6.330 | 1037650 | 0.0770 | 0.797032 | -0.22686 |
| 120 | 6.341 | 837124 | 0.0596 | 0.643006 | -0.4426 |
| 180 | 6.339 | 720136 | 0.0535 | 0.553146 | -0.59213 |
| 240 | 6.337 | 609842 | 0.0453 | 0.468427 | -0.75837 |

Expt No: 4-13
Probe cpd: LNR
pH: 10.7
System: sole-Ozone with $[O_3]$ of 0.00996 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.249 | 1286734 | 0.0955 | 1 | 0 |
| 60 | 6.254 | 936732 | 0.0695 | 0.727992 | -0.31747 |
| 120 | 6.257 | 691208 | 0.0513 | 0.53718 | -0.62142 |
| 180 | 6.246 | 547801 | 0.0406 | 0.42573 | -0.85395 |
| 240 | 6.251 | 419872 | 0.0312 | 0.326308 | -1.11991 |

Expt No: 4-14
Probe cpd: LNR
pH: 11
System: sole-Ozone with $[O_3]$ of 0.00996 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.284 | 1331958 | 0.0989 | 1 | 0 |
| | | | | *Cont'd* | |
| 15 | 6.290 | 1173124 | 0.0871 | 0.880751 | -0.12698 |
| 30 | 6.281 | 1049816 | 0.0779 | 0.788175 | -0.23804 |
| 45 | 6.287 | 968712 | 0.0719 | 0.727284 | -0.31844 |
| 60 | 6.295 | 880412 | 0.0654 | 0.660991 | -0.41402 |

Expt No: 4-15
Probe cpd: LNR
pH: 9
System: sole-Ozone with [$O_3$] of 0.0244 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---------|------|------|--------|---------|--------------|
| 0 | 6.312 | 1218721 | 0.0905 | 1 | 0 |
| 30 | 6.308 | 983793 | 0.0730 | 0.807234 | -0.21414 |
| 60 | 6.297 | 860479 | 0.0639 | 0.706051 | -0.34807 |
| 90 | 6.316 | 710575 | 0.0530 | 0.585305 | -0.53562 |
| 120 | 6.305 | 616364 | 0.0458 | 0.505747 | -0.68172 |

Expt No: 4-16
Probe cpd: LNR
pH: 10
System: sole-Ozone with [$O_3$] of 0.0244 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---------|------|------|--------|---------|--------------|
| 0 | 6.278 | 1346149 | 0.0999 | 1 | 0 |
| 30 | 6.271 | 961880 | 0.0658 | 0.714542 | -0.33611 |
| 60 | 6.275 | 844058 | 0.0471 | 0.627017 | -0.46678 |
| 90 | 6.269 | 703472 | 0.0360 | 0.522581 | -0.64898 |
| 120 | 6.273 | 605678 | 0.0308 | 0.449934 | -0.79865 |

Expt No: 4-17
Probe cpd: LNR
pH: 10.7
System: sole-Ozone with [$O_3$] of 0.0244 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---------|------|------|--------|---------|--------------|
| 0 | 6.267 | 1341142 | 0.0995 | 1 | 0 |
| 30 | 6.270 | 836128 | 0.0648 | 0.623445 | -0.4725 |
| 60 | 6.263 | 663415 | 0.0499 | 0.494664 | -0.70388 |
| 90 | 6.261 | 456137 | 0.0452 | 0.340111 | -1.07848 |
| 120 | 6.265 | 317965 | 0.0388 | 0.237085 | -1.43934 |

Expt No: 4-18
Probe cpd: LNR
pH: 11
System: sole-Ozone with [$O_3$] of 0.0244 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---------|------|------|--------|---------|--------------|
| 0 | 6.291 | 1325890 | 0.0984 | 1 | 0 |
| 15 | 6.287 | 956054 | 0.0710 | 0.721066 | -0.32702 |
| 30 | 6.284 | 749062 | 0.0556 | 0.56495 | -0.57102 |
| 45 | 6.281 | 623434 | 0.0463 | 0.47020 | -0.7546 |
| 60 | 6.285 | 512592 | 0.0380 | 0.386602 | -0.95036 |

Expt No: 4-19
Probe cpd: LNR
pH: 9
System: sole-Ozone with $[O_3]$ of 0.0309 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.310 | 1283732 | 0.0953 | 1 | 0 |
| 15 | 6.303 | 1026638 | 0.0762 | 0.799729 | -0.22348 |
| 30 | 6.308 | 930386 | 0.0691 | 0.724751 | -0.32193 |
| 45 | 6.298 | 858984 | 0.0638 | 0.66913 | -0.40178 |
| 60 | 6.304 | 709144 | 0.0526 | 0.552408 | -0.59347 |

Expt No: 4-20
Probe cpd: LNR
pH: 10
System: sole-Ozone with $[O_3]$ of 0.0309 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.275 | 1283732 | 0.0953 | 1 | 0 |
| 15 | 6.271 | 1004924 | 0.0746 | 0.782814 | -0.24486 |
| 30 | 6.280 | 883612 | 0.0656 | 0.688315 | -0.37351 |
| 45 | 6.278 | 790244 | 0.0587 | 0.615583 | -0.48518 |
| 60 | 6.273 | 660548 | 0.0490 | 0.514553 | -0.66446 |

Expt No: 4-21
Probe cpd: LNR
pH: 10.7
System: sole-Ozone with $[O_3]$ of 0.0309 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.312 | 1341918 | 0.0996 | 1 | 0 |
| 15 | 6.317 | 930796 | 0.0691 | 0.693631 | -0.36582 |
| 30 | 6.320 | 775541 | 0.0576 | 0.577935 | -0.54829 |
| 45 | 6.311 | 658433 | 0.0489 | 0.490666 | -0.71199 |
| 60 | 6.323 | 532770 | 0.0395 | 0.397021 | -0.92377 |

Expt No: 4-22
Probe cpd: LNR
pH: 11
System: sole-Ozone with $[O_3]$ of 0.0309 mM

| T (Sec) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.302 | 1324562 | 0.0983 | 1 | 0 |
| 15 | 6.308 | 840760 | 0.0624 | 0.634746 | -0.45453 |
| 30 | 6.305 | 669373 | 0.0497 | 0.505354 | -0.6825 |
| 45 | 6.310 | 533450 | 0.0396 | 0.402737 | -0.90947 |
| 60 | 6.307 | 435708 | 0.0323 | 0.328945 | -1.11187 |

Expt No: 4-23
Probe cpd: LNR
pH: 6
System: UV/$H_2O_2$ with UV of 254 nm

| T (Sec) | R.T. | Area | C (μM) | $C_0/C$ | $\ln(C_0/C)$ |
|---|---|---|---|---|---|
| 0 | 6.262 | 133648 | 9.92 | 1 | 0 |
| 5 | 6.265 | 131222 | 9.74 | 1.018488 | 0.018319 |

*Cont'd*

| | | | | | |
|---|---|---|---|---|---|
| 10 | 6.267 | 122318 | 9.08 | 1.092627 | 0.088585 |
| 15 | 6.270 | 121197 | 8.99 | 1.102734 | 0.097792 |
| 20 | 6.263 | 117582 | 8.73 | 1.136637 | 0.128074 |
| 30 | 6.272 | 116879 | 8.68 | 1.143473 | 0.13407 |

Expt No: 4-23
Probe cpd: Atrazine (ATZ)
pH: 6
System: $UV/H_2O_2$ with UV of 254 nm

| T (Sec) | R.T. | Area | C (μM) | $C_0/C$ | $\ln(C_0/C)$ |
|---|---|---|---|---|---|
| 0 | | 208841 | 9.98 | 1 | 0 |
| 5 | | 204362 | 9.76 | 1.021917 | 0.02168 |
| 10 | | 191344 | 9.14 | 1.091443 | 0.0875 |
| 15 | | 188876 | 9.02 | 1.105704 | 0.100482 |
| 20 | | 184859 | 8.83 | 1.129731 | 0.12198 |
| 30 | | 179327 | 8.57 | 1.164582 | 0.152362 |

Expt No: 4-24
Probe cpd: LNR
pH: 6
System: $UV/O_3$ with $[O_3]$ of 0.0171 mM and 2 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.308 | 1265710 | 0.0939 | 1 | 0 |
| 2 | 6.302 | 700180 | 0.0519 | 0.553192 | -0.59205 |
| 4 | 6.311 | 454226 | 0.0337 | 0.358871 | -1.02479 |
| 6 | 6.298 | 269483 | 0.0199 | 0.212911 | -1.54688 |
| 8 | 6.305 | 124652 | 0.0092 | 0.098484 | -2.31786 |
| 10 | 6.301 | 32263 | 0.0024 | 0.02549 | -3.66947 |

Expt No: 4-25
Probe cpd: LNR
pH: 6
System: $UV/O_3$ with $[O_3]$ of 0.0171 mM and 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.324 | 1216178 | 0.0902 | 1 | 0 |
| 2 | 6.328 | 634652 | 0.0471 | 0.521841 | -0.65039 |
| 4 | 6.320 | 331446 | 0.0246 | 0.272531 | -1.3 |
| 6 | 6.329 | 146630 | 0.0108 | 0.120566 | -2.11556 |
| 8 | 6.318 | 47378 | 0.0035 | 0.038956 | -3.24531 |

Expt No: 4-26
Probe cpd: LNR
pH: 6
System: $UV/O_3$ with $[O_3]$ of 0.0171 mM and 6 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.290 | 1278120 | 0.0948 | 1 | 0 |
| 2 | 6.295 | 623285 | 0.0462 | 0.487658 | -0.71814 |
| 4 | 6.302 | 231118 | 0.0171 | 0.180827 | -1.71021 |
| 6 | 6.293 | 65954 | 0.00489 | 0.051603 | -2.96418 |
| 8 | 6.297 | 14749 | 0.00109 | 0.01154 | -4.46196 |

Expt No: 4-27
Probe cpd: LNR
pH: 6
System: UV/O$_3$ with [O$_3$] of 0.0171 mM and 8 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.268 | 1283426 | 0.0952 | 1 | 0 |
| 1 | 6.271 | 629328 | 0.0467 | 0.490358 | -0.71265 |
| 2 | 6.265 | 314670 | 0.0233 | 0.245180 | -1.40578 |
| 3 | 6.263 | 167399 | 0.0124 | 0.130432 | -2.0369 |
| 4 | 6.274 | 88243 | 0.0065 | 0.068756 | -2.67719 |

Expt No: 5-1
Probe cpd: LNR
pH: 3
System: sole-UV with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.261 | 1261024 | 0.0935 | 1 | 0 |
| 5 | 6.258 | 654179 | 0.0485 | 0.518768 | -0.6563 |
| 10 | 6.267 | 351539 | 0.0260 | 0.278773 | -1.27736 |
| 15 | 6.263 | 180782 | 0.0134 | 0.143361 | -1.94239 |
| 20 | 6.269 | 85235 | 0.00632 | 0.067592 | -2.69427 |
| 25 | 6.271 | 29397 | 0.00218 | 0.023312 | -3.75879 |
| 30 | 6.265 | 9971 | 0.000739 | 0.007907 | -4.84 |

Expt No: 5-2
Probe cpd: LNR
pH: 9
System: sole-UV with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.312 | 1298647 | 0.0963 | 1 | 0 |
| 5 | 6.307 | 725502 | 0.0538 | 0.55866 | -0.58221 |
| 10 | 6.303 | 378521 | 0.0281 | 0.291474 | -1.23281 |
| 15 | 6.305 | 178339 | 0.0132 | 0.137327 | -1.98539 |
| 20 | 6.297 | 86591 | 0.00642 | 0.066678 | -2.70789 |
| 25 | 6.301 | 32669 | 0.00242 | 0.025156 | -3.68266 |
| 30 | 6.311 | 7665 | 0.00057 | 0.005902 | -5.13238 |

Expt No: 5-3
Probe cpd: LNR
pH: 10
System: sole-UV with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | C/C$_0$ | ln(C/C$_0$) |
|---|---|---|---|---|---|
| 0 | 6.283 | 1259608 | 0.0934 | 1 | 0 |
| 5 | 6.289 | 673934 | 0.0499 | 0.535035 | -0.62542 |
| 10 | 6.293 | 351145 | 0.0260 | 0.278773 | -1.27736 |
| 15 | 6.287 | 163909 | 0.0121 | 0.130127 | -2.03925 |
| 20 | 6.281 | 74629 | 0.0055 | 0.059248 | -2.82602 |
| 25 | 6.285 | 27681 | 0.0020 | 0.021976 | -3.81782 |
| 30 | 6.290 | 6118 | 0.00045 | 0.004857 | -5.3273 |

Expt No: 5-4
Probe cpd: LNR
pH: 11
System: sole-UV with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.267 | 1309359 | 0.0971 | 1 | 0 |
| 5 | 6.278 | 767481 | 0.0569 | 0.58615 | -0.53418 |
| 10 | 6.269 | 433230 | 0.0321 | 0.330872 | -1.10602 |
| 15 | 6.273 | 244565 | 0.0181 | 0.186782 | -1.67781 |
| 20 | 6.270 | 127017 | 0.0094 | 0.097007 | -2.33297 |
| 25 | 6.269 | 61502 | 0.0045 | 0.046971 | -3.05822 |
| 30 | 6.274 | 25643 | 0.0019 | 0.019584 | -5.30549 |

Expt No: 5-5
Probe cpd: LNR
pH: 3
System: UV/$O_3$ with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.350 | 1249870 | 0.0927 | 1 | 0 |
| 2.5 | 6.347 | 751688 | 0.0558 | 0.601413 | -0.50847 |
| 5 | 6.352 | 575033 | 0.0426 | 0.460074 | -0.77637 |
| 7.5 | 6.358 | 413557 | 0.0307 | 0.33088 | -1.106 |
| 10 | 6.354 | 264614 | 0.0196 | 0.211713 | -1.55252 |

Expt No: 5-6
Probe cpd: LNR
pH: 6
System: UV/$O_3$ with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.281 | 1230198 | 0.0912 | 1 | 0 |
| 2 | 6.278 | 610157 | 0.0448 | 0.491395 | -0.71051 |
| 4 | 6.285 | 301762 | 0.0224 | 0.245295 | -1.40529 |
| 6 | 6.287 | 134612 | 0.0096 | 0.105816 | -2.24605 |
| 8 | 6.283 | 35712 | 0.0026 | 0.029029 | -3.53944 |

Expt No: 5-7
Probe cpd: LNR
pH: 9
System: UV/$O_3$ with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.265 | 1274158 | 0.0945 | 1 | 0 |
| 0.5 | 6.269 | 910091 | 0.0675 | 0.714269 | -0.3365 |
| 1 | 6.258 | 750550 | 0.0557 | 0.589056 | -0.52923 |
| 1.5 | 6.261 | 556212 | 0.0412 | 0.436533 | -0.82889 |
| 2 | 6.267 | 458106 | 0.0340 | 0.359536 | -1.02294 |

Expt No: 5-8
Probe cpd: LNR
pH: 10
System: UV/$O_3$ with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.313 | 1241701 | 0.0921 | 1 | 0 |

| | | | | | |
|---|---|---|---|---|---|
| 0.5 | 6.309 | 841205 | 0.0624 | 0.677462 | -0.3894 |
| 1 | 6.315 | 618401 | 0.0459 | 0.498027 | -0.6971 |
| 1.5 | 6.311 | 412735 | 0.0306 | 0.332395 | -1.10143 |
| 2 | 6.307 | 310928 | 0.0231 | 0.250405 | -1.38468 |

Expt No: 5-9
Probe cpd: LNR
pH: 11
System: UV/$O_3$ with 4 lamps at 254 nm

| T (min) | R.T. | Area | C (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.330 | 1254389 | 0.0930 | 1 | 0 |
| 0.5 | 6.337 | 654841 | 0.0485 | 0.52204 | -0.65001 |
| 1 | 6.331 | 367632 | 0.0272 | 0.293077 | -1.22732 |
| 1.5 | 6.328 | 209075 | 0.0155 | 0.166675 | -1.79171 |
| 2 | 6.335 | 128548 | 0.0095 | 0.102479 | -2.2781 |

Expt No: 5-17
Probe cpd: LNR
pH: 3
System: sole-Ozone with $[O_3]$ at 0.0171 mM and $[Cl^-]$ at 0.01 M

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.401 | 1354245 | 0.100 | 1 | / |
| 5 | 6.406 | 1163132 | 0.0859 | 0.858879 | / |
| 10 | 6.397 | 1105614 | 0.0816 | 0.816406 | / |
| 15 | 6.402 | 1045246 | 0.772 | 0.771829 | / |
| 20 | 6.398 | 940884 | 0.0695 | 0.694766 | / |
| 25 | 6.395 | 915244 | 0.0676 | 0.675833 | / |
| 30 | 6.403 | 882242 | 0.0651 | 0.651464 | / |

Expt No: 5-18
Probe cpd: LNR
pH: 3
System: sole-Ozone with $[O_3]$ at 0.0171 mM and $[SO_4^{2-}]$ at 0.01 M

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.287 | 1242150 | 0.0921 | 1 | / |
| 5 | 6.282 | 775998 | 0.0575 | 0.624722 | / |
| 10 | 6.285 | 510958 | 0.0379 | 0.41135 | / |
| 15 | 6.290 | 374404 | 0.0278 | 0.301416 | / |
| 20 | 6.293 | 221116 | 0.0164 | 0.178011 | / |
| 25 | 6.284 | 135588 | 0.01 | 0.109156 | / |
| 30 | 6.291 | 96614 | 0.00716 | 0.07778 | / |

Expt No: 5-19
Probe cpd: LNR
pH: 3
System: sole-Ozone with $[O_3]$ at 0.0171 mM and $[HPO_4^{2-}]$ at 0.01 M

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.271 | 1242150 | 0.0921 | 1 | / |
| 5 | 6.264 | 761076 | 0.0564 | 0.612709 | / |
| 10 | 6.267 | 451710 | 0.0335 | 0.363652 | / |
| 15 | 6.275 | 281400 | 0.0209 | 0.226543 | / |

| | | | | | |
|---|---|---|---|---|---|
| 20 | 6.278 | 187556 | 0.0139 | 0.150993 | / |
| 25 | 6.269 | 115958 | 0.0085 | 0.093353 | / |
| 30 | 6.271 | 107592 | 0.0079 | 0.086618 | / |

Expt No: 5-20
Probe cpd: LNR
pH: 7
System: sole-Ozone with $[O_3]$ at 0.0245 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.271 | 1267251 | 0.0940 | 1 | / |
| 4 | 6.265 | 479336 | 0.0356 | 0.378249 | / |
| 8 | 6.261 | 169516 | 0.0126 | 0.133767 | / |
| 12 | 6.259 | 53463 | 0.0039 | 0.042188 | / |
| 16 | 6.273 | 25544 | 0.0019 | 0.020157 | / |
| 20 | 6.268 | 12059 | 0.00089 | 0.009516 | / |

Expt No: 5-21
Probe cpd: LNR
pH: 7
System: sole-Ozone with $[O_3]$ at 0.0245 mM and $[Cl^-]$ at 0.01 M

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.312 | 1278465 | 0.0948 | 1 | / |
| 4 | 6.307 | 556456 | 0.0413 | 0.435253 | / |
| 8 | 6.305 | 246994 | 0.0183 | 0.193196 | / |
| 12 | 6.311 | 135754 | 0.0101 | 0.106185 | / |
| 16 | 6.308 | 82878 | 0.0061 | 0.064826 | / |
| 20 | 6.302 | 56027 | 0.0042 | 0.043824 | / |

Expt No: 5-22
Probe cpd: LNR
pH: 7
System: sole-Ozone with $[O_3]$ at 0.0245 mM and $[SO_4^{2-}]$ at 0.01 M

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.285 | 1267891 | 0.0940 | 1 | / |
| 4 | 6.289 | 534301 | 0.0396 | 0.421409 | / |
| 8 | 6.281 | 206395 | 0.0153 | 0.162786 | / |
| 12 | 6.277 | 73465 | 0.00545 | 0.057943 | / |
| 16 | 6.279 | 39404 | 0.0029 | 0.031078 | / |
| 20 | 6.283 | 16995 | 0.00126 | 0.013404 | / |

Expt No: 5-23
Probe cpd: LNR
pH: 7
System: sole-Ozone with $[O_3]$ at 0.0245 mM and $[HPO_4^{2-}]$ at 0.01 M

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.323 | 1287106 | 0.0954 | 1 | / |
| 4 | 6.327 | 294155 | 0.0218 | 0.22854 | / |
| 8 | 6.321 | 69892 | 0.0052 | 0.054302 | / |
| 12 | 6.319 | 10508 | 0.00078 | 0.008164 | / |
| 16 | 6.328 | 0 | 0 | 0 | / |

Expt No: 5-24
Probe cpd: LNR
pH: 7
System: sole-Ozone with $[O_3]$ at 0.0245 mM and $[CO_3^{2-}]$ at 0.01 M

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.278 | 1291817 | 0.0957 | 1 | / |
| 4 | 6.288 | 497665 | 0.0369 | 0.385244 | / |
| 8 | 6.281 | 227899 | 0.0169 | 0.176418 | / |
| 12 | 6.287 | 123784 | 0.0092 | 0.095822 | / |
| 16 | 6.276 | 50925 | 0.0038 | 0.039421 | / |
| 20 | 6.283 | 2618 | 0.0019 | 0.020165 | / |

**The evolution of TOC, varied ions and pH during the decay process of LNR in sole-UV, sole-Ozone and UV/O$_3$ processes.**

Expt No: 5-10
Probe cpd: LNR
pH: 6
System: sole-UV with 6 lamps at 254 nm

| T (hr) | TOC (mg/L) | $Cl^-$ (mg/L) | $NO_3^-$ (mg/L) | $NH_4^+$ (mg/L) | pH |
|---|---|---|---|---|---|
| 0 | 31.025 | 0.0782 | 0 | 0 | 6 |
| 0.5 | 30.563 | 4.716 | 0 | 0.0326 | 4.28 |
| 1 | 30.971 | 9.89 | 0 | 0.0484 | 3.97 |
| 1.5 | 31.235 | 14.43 | 0.0627 | 0.0652 | 3.74 |
| 2 | 30.671 | 16.94 | 0.0913 | 0.105 | 3.65 |
| 2.5 | 31.174 | 18.57 | 0.0475 | 0.139 | 3.62 |
| 3 | 30.712 | 19.52 | 0.0808 | 0.154 | 3.6 |
| 3.5 | 30.456 | 19.7 | 0.0627 | 0.186 | 3.58 |
| 4 | 31.302 | 19.79 | 0.0694 | 0.187 | 3.59 |

Expt No: 5-14
Probe cpd: LNR
pH: 6
System: sole-Ozone with $[O_3]$ at 0.0245 mM

| T (min) | TOC (mg/L) | $Cl^-$ (mg/L) | $NO_3^-$ (mg/L) | $NH_4^+$ (mg/L) | pH |
|---|---|---|---|---|---|
| 0 | 30.986 | 0 | 0 | 0 | 6.03 |
| 20 | 27.936 | 11.036 | 0.8317 | 0.545 | 3.45 |
| 40 | 25.856 | 14.186 | 1.347 | 0.934 | 3.36 |
| 60 | 25.056 | 15.050 | 1.467 | 0.846 | 3.34 |
| 80 | 24.646 | 15.678 | 1.645 | 0.923 | 3.32 |
| 100 | 23.976 | 15.922 | 1.774 | 0.756 | 3.30 |
| 120 | 23.170 | 16.109 | 1.872 | 0.743 | 3.30 |

Expt No: 5-16
Probe cpd: LNR
pH: 6
System: UV/O$_3$ with $[O_3]$ at 0.0245 mM and six lamps at 254 nm

| T (min) | TOC (mg/L) | $Cl^-$ (mg/L) | $NO_3^-$ (mg/L) | $NH_4^+$ (mg/L) | pH |
|---|---|---|---|---|---|
| 0 | 31.2 | 0.1 | 0 | 0 | 6.0 |
| 20 | 29.5 | 16.84 | 1.278 | 0.488 | 3.14 |
| 40 | 23.86 | 19.64 | 2.124 | 0.628 | 3.06 |
| 60 | 16.11 | 19.76 | 4.830 | 0.734 | 3.09 |

| | | | | | |
|---|---|---|---|---|---|
| 80 | 8.763 | 20.31 | 9.497 | 0.931 | 3.11 |
| 100 | 5.943 | 20.48 | 15.49 | 1.005 | 3.08 |
| 120 | 4.313 | 20.41 | 15.92 | 1.120 | 3.05 |

Expt No: 6-1
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$ in dark

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.450 | 1260079 | 0.0933 | 1 | / |
| 30 | 6.447 | 1229409 | 0.0910 | 0.97566 | / |
| 60 | 6.453 | 1202339 | 0.0890 | 0.954177 | / |
| 90 | 6.458 | 1186452 | 0.0878 | 0.94157 | / |
| 120 | 6.446 | 1165358 | 0.0863 | 0.924829 | / |
| 150 | 6.451 | 1161629 | 0.0860 | 0.92187 | / |
| 180 | 6.449 | 1158779 | 0.0858 | 0.919608 | / |

Expt No: 6-2
Probe cpd: LNR
pH: 6
System: $TiO_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.401 | 1270871 | 0.0941 | 1 | / |
| 30 | 6.397 | 1187512 | 0.0879 | 0.934408 | / |
| 60 | 6.394 | 1161027 | 0.0860 | 0.913568 | / |
| 90 | 6.402 | 1155530 | 0.0855 | 0.909243 | / |
| 120 | 6.407 | 1142112 | 0.0846 | 0.898685 | / |
| 150 | 6.398 | 1131911 | 0.0838 | 0.890658 | / |
| 180 | 6.403 | 1132563 | 0.0839 | 0.891171 | / |

Expt No: 6-3
Probe cpd: LNR
pH: 6
System: $H_2O_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.387 | 1260986 | 0.0934 | 1 | / |
| 30 | 6.381 | 1222732 | 0.0906 | 0.969663 | / |
| 60 | 6.385 | 1199610 | 0.0888 | 0.951327 | / |
| 90 | 6.390 | 1185675 | 0.0878 | 0.940276 | / |
| 120 | 6.384 | 1175093 | 0.0870 | 0.931884 | / |
| 150 | 6.381 | 1161098 | 0.0860 | 0.920786 | / |
| 180 | 6.385 | 1152873 | 0.0854 | 0.914263 | / |

Expt No: 6-4
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.397 | 1225617 | 0.0908 | 1 | / |
| 30 | 6.394 | 564596 | 0.0418 | 0.460663 | / |
| 60 | 6.402 | 340863 | 0.0252 | 0.278115 | / |

| | | | | | |
|---|---|---|---|---|---|
| 90 | 6.393 | 184365 | 0.0137 | 0.150426 | / |
| 120 | 6.405 | 104228 | 0.0077 | 0.085041 | / |
| | | | | | *Cont'd* |
| 150 | 6.401 | 49488 | 0.0036 | 0.040378 | / |
| 180 | 6.395 | 19761 | 0.0015 | 0.016123 | / |

Expt No: 6-5
Probe cpd: LNR
pH: 6
System: $TiO_2$/visible light at 420 nm (Hg lamps) with the addition of 1 M MeOH

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.387 | 1271203 | 0.0942 | 1 | / |
| 1 | 6.381 | 1267219 | 0.0939 | 0.996866 | / |
| 2 | 6.390 | 1272020 | 0.0943 | 1.000643 | / |
| 3 | 6.385 | 1272730 | 0.0943 | 1.001201 | / |

Expt No: 6-6
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with the addition of 1 M
MeOH

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.378 | 1280145 | 0.0949 | 1 | / |
| 0.5 | 6.371 | 1251096 | 0.0927 | 0.977308 | / |
| 1 | 6.374 | 1250299 | 0.0927 | 0.976686 | / |
| 1.5 | 6.382 | 1235490 | 0.0916 | 0.965117 | / |
| 2 | 6.379 | 1234108 | 0.0915 | 0.964038 | / |
| 2.5 | 6.384 | 1235531 | 0.0916 | 0.965149 | / |
| 3 | 6.380 | 1230164 | 0.0912 | 0.960957 | / |

Expt No: 6-7
Probe cpd: LNR
pH: 6
System: $TiO_2$/visible light at 420 nm (Hg lamps) with the purge of $O_2$

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.290 | 1249873 | 0.0926 | 1 | / |
| 0.5 | 6.287 | 923787 | 0.0684 | 0.739105 | / |
| 1 | 6.293 | 868554 | 0.0643 | 0.694914 | / |
| 1.5 | 6.295 | 782862 | 0.0580 | 0.626353 | / |
| 2 | 6.285 | 731343 | 0.0542 | 0.585134 | / |
| 2.5 | 6.289 | 665062 | 0.0493 | 0.532104 | / |
| 3 | 6.296 | 599453 | 0.0444 | 0.479611 | / |

Expt No: 6-8
Probe cpd: LNR
pH: 6
System: $WO_3$/visible light at 420 nm (Hg lamps)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.305 | 1270659 | 0.0941 | 1 | / |
| 1 | 6.309 | 1165833 | 0.0863 | 0.917503 | / |
| 2 | 6.313 | 1118633 | 0.0828 | 0.880357 | / |
| 3 | 6.304 | 1078960 | 0.0799 | 0.849134 | / |

Expt No: 6-9
Probe cpd: LNR
pH: 6
System: $WO_3$/visible light at 420 nm (Hg lamps) with the purge of $O_2$

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|--------|------|------|--------|---------|--------------|
| 0 | 6.324 | 1261721 | 0.0934 | 1 | / |
| 1 | 6.327 | 918077 | 0.0680 | 0.727639 | / |
| 2 | 6.329 | 735073 | 0.0544 | 0.582596 | / |
| 3 | 6.321 | 633415 | 0.0469 | 0.502025 | / |

Expt No: 6-10
Probe cpd: LNR
pH: 6
System: $WO_3/H_2O_2$/visible light at 420 nm (Hg lamps)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|--------|------|------|--------|---------|--------------|
| 0 | 6.316 | 1285019 | 0.0951 | 1 | / |
| 0.5 | 6.311 | 929283 | 0.0688 | 0.723167 | / |
| 1 | 6.319 | 713703 | 0.0528 | 0.555403 | / |
| 1.5 | 6.308 | 546032 | 0.0404 | 0.424921 | / |
| 2 | 6.312 | 422521 | 0.0313 | 0.328805 | / |
| 2.5 | 6.305 | 340903 | 0.0252 | 0.26529 | / |
| 3 | 6.309 | 250219 | 0.0185 | 0.19472 | / |

Expt No: 6-11
Probe cpd: LNR
pH: 6
System: ZnO/visible light at 420 nm (Hg lamps)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|--------|------|------|--------|---------|--------------|
| 0 | 6.296 | 1275087 | 0.0944 | 1 | / |
| 1 | 6.291 | 1041614 | 0.0771 | 0.816896 | / |
| 2 | 6.287 | 886906 | 0.0657 | 0.695565 | / |
| 3 | 6.293 | 769894 | 0.0570 | 0.603797 | / |

Expt No: 6-12
Probe cpd: LNR
pH: 6
System: ZnO/visible light at 420 nm (Hg lamps) with the purge of $O_2$

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|--------|------|------|--------|---------|--------------|
| 0 | 6.330 | 1237474 | 0.0916 | 1 | / |
| 1 | 6.337 | 805727 | 0.0596 | 0.651106 | / |
| 2 | 6.328 | 585078 | 0.0433 | 0.472800 | / |
| 3 | 6.332 | 463443 | 0.0343 | 0.374507 | / |

Expt No: 6-13
Probe cpd: LNR
pH: 6
System: $ZnO/H_2O_2$/visible light at 420 nm (Hg lamps)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|--------|------|------|--------|---------|--------------|
| 0 | 6.321 | 1261549 | 0.0934 | 1 | / |
| 1 | 6.326 | 1039443 | 0.0770 | 0.823942 | / |
| 2 | 6.325 | 865096 | 0.0640 | 0.685741 | / |
| 3 | 6.329 | 769502 | 0.0570 | 0.609966 | / |

Expt No: 6-14
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $TiO_2$ dosage of 0.05 g/L

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.287 | 1231360 | 0.0912 | 1 | 0 |
| 30 | 6.281 | 1043715 | 0.0773 | 0.847612 | -0.16533 |
| 60 | 6.285 | 983049 | 0.0728 | 0.798344 | -0.22522 |
| 90 | 6.290 | 890814 | 0.0660 | 0.723439 | -0.32374 |
| 120 | 6.293 | 840361 | 0.0622 | 0.682466 | -0.38204 |
| 150 | 6.288 | 798880 | 0.0592 | 0.648779 | -0.43266 |
| 180 | 6.291 | 767769 | 0.0569 | 0.623513 | -0.47239 |

Expt No: 6-15
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $TiO_2$ dosage of 0.1 g/L

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.303 | 1244935 | 0.0922 | 1 | 0 |
| 30 | 6.298 | 993990 | 0.0736 | 0.798427 | -0.22511 |
| 60 | 6.301 | 885585 | 0.0656 | 0.71135 | -0.34059 |
| 90 | 6.307 | 775105 | 0.0574 | 0.622607 | -0.47384 |
| 120 | 6.295 | 708608 | 0.0525 | 0.569193 | -0.56354 |
| 150 | 6.302 | 639186 | 0.0473 | 0.513429 | -0.66664 |
| 180 | 6.306 | 577657 | 0.0428 | 0.464006 | -0.76786 |

Expt No: 6-16
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $TiO_2$ dosage of 0.2 g/L

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.275 | 1268821 | 0.0940 | 1 | 0 |
| 30 | 6.271 | 843234 | 0.0625 | 0.664581 | -0.4086 |
| 60 | 6.268 | 671211 | 0.0497 | 0.529004 | -0.63676 |
| 90 | 6.276 | 531313 | 0.0394 | 0.418745 | -0.87049 |
| 120 | 6.279 | 419260 | 0.0311 | 0.330433 | -1.10735 |
| 150 | 6.267 | 361633 | 0.0268 | 0.285015 | -1.25521 |
| 180 | 6.270 | 293336 | 0.0217 | 0.231188 | -1.46452 |

Expt No: 6-17
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $TiO_2$ dosage of 0.4 g/L

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.292 | 1237803 | 0.0917 | 1 | 0 |
| 30 | 6.297 | 618862 | 0.0458 | 0.499968 | -0.69321 |
| 60 | 6.291 | 366623 | 0.0272 | 0.296188 | -1.21676 |
| 90 | 6.287 | 225272 | 0.0167 | 0.181993 | -1.70378 |
| 120 | 6.290 | 132016 | 0.00978 | 0.106653 | -2.23817 |
| 150 | 6.285 | 68726 | 0.00509 | 0.055523 | -2.89097 |
| 180 | 6.289 | 30174 | 0.00224 | 0.024377 | -3.71411 |

Expt No: 6-18
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $TiO_2$ dosage of 0.8 g/L

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.279 | 1288889 | 0.0955 | 1 | 0 |
| 30 | 6.274 | 659509 | 0.0489 | 0.511688 | -0.67004 |
| 60 | 6.271 | 356634 | 0.0264 | 0.276699 | -1.28483 |
| 90 | 6.278 | 180337 | 0.0133 | 0.139917 | -1.9667 |
| 120 | 6.269 | 85208 | 0.00631 | 0.06611 | -2.71643 |
| 150 | 6.273 | 35069 | 0.00259 | 0.027209 | -3.60419 |
| 180 | 6.275 | 11036 | 0.00082 | 0.008563 | -4.76025 |

Expt No: 6-19
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $TiO_2$ dosage of 1.0 g/L

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.268 | 1271565 | 0.0942 | 1 | 0 |
| 30 | 6.265 | 523961 | 0.0388 | 0.41206 | -0.88659 |
| 60 | 6.261 | 257541 | 0.0191 | 0.202539 | -1.59682 |
| 90 | 6.271 | 123976 | 0.0092 | 0.097499 | -2.32792 |
| 120 | 6.269 | 41944 | 0.0031 | 0.032986 | -3.41167 |
| 150 | 6.273 | 11958 | 0.00088 | 0.009404 | -4.66664 |

Expt No: 6-20
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $H_2O_2$ at 1 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.283 | 1294377 | 0.0959 | 1 | 0 |
| 30 | 6.279 | 798456 | 0.0592 | 0.616865 | -0.48311 |
| 60 | 6.285 | 550740 | 0.0408 | 0.425487 | -0.85452 |
| 90 | 6.281 | 469742 | 0.0348 | 0.36291 | -1.0136 |
| 120 | 6.276 | 439437 | 0.0326 | 0.339497 | -1.08029 |
| 150 | 6.279 | 409984 | 0.0304 | 0.316743 | -1.14967 |
| 180 | 6.280 | 380696 | 0.0282 | 0.294115 | -1.22378 |

Expt No: 6-21
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $H_2O_2$ at 2 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.312 | 1312462 | 0.0972 | 1 | 0 |
| 30 | 6.309 | 757285 | 0.0561 | 0.576996 | -0.54992 |
| 60 | 6.307 | 519924 | 0.0385 | 0.396144 | -0.92598 |
| 90 | 6.311 | 383032 | 0.0284 | 0.291842 | -1.23154 |
| 120 | 6.315 | 311572 | 0.0231 | 0.237395 | -1.43803 |
| 150 | 6.308 | 219692 | 0.0163 | 0.167389 | -1.78743 |
| 180 | 6.324 | 205883 | 0.0152 | 0.156868 | -1.85235 |

Expt No: 6-22
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $H_2O_2$ at 5 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.263 | 1216492 | 0.0901 | 1 | 0 |
| 30 | 6.267 | 668490 | 0.0495 | 0.549523 | -0.59871 |
| 60 | 6.261 | 473384 | 0.0351 | 0.389139 | -0.94382 |
| 90 | 6.269 | 329960 | 0.0244 | 0.271239 | -1.30476 |
| 120 | 6.265 | 225545 | 0.0167 | 0.185406 | -1.68521 |
| 150 | 6.259 | 142732 | 0.0106 | 0.117331 | -2.14276 |
| 180 | 6.262 | 76583 | 0.00567 | 0.062954 | -2.76535 |

Expt No: 6-23
Probe cpd: LNR
pH: 6
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with $H_2O_2$ at 20 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.281 | 1300561 | 0.0963 | 1 | 0 |
| 30 | 6.285 | 646460 | 0.0479 | 0.497062 | -0.69904 |
| 60 | 6.279 | 410909 | 0.0304 | 0.315948 | -1.15218 |
| 90 | 6.275 | 271322 | 0.0201 | 0.208619 | -1.56724 |
| 120 | 6.280 | 191455 | 0.0142 | 0.14721 | -1.9159 |
| 150 | 6.286 | 103663 | 0.00767 | 0.079706 | -2.52941 |
| 180 | 6.276 | 59635 | 0.00442 | 0.045853 | -3.08231 |

Expt No: 6-24
Probe cpd: LNR
pH: 2.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.401 | 1218117 | 0.0902 | 1 | 0 |
| 30 | 6.397 | 1108853 | 0.0821 | 0.910301 | -0.09398 |
| 60 | 6.392 | 1024753 | 0.0759 | 0.84126 | -0.17285 |
| 90 | 6.395 | 937128 | 0.0694 | 0.769325 | -0.26224 |
| 120 | 6.393 | 817074 | 0.0605 | 0.670768 | -0.39933 |
| 150 | 6.398 | 781874 | 0.0579 | 0.641871 | -0.44337 |
| 180 | 6.402 | 714553 | 0.0529 | 0.586605 | -0.5334 |

Expt No: 6-25
Probe cpd: LNR
pH: 4.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.374 | 1242736 | 0.0920 | 1 | 0 |
| 30 | 6.371 | 703704 | 0.0521 | 0.566254 | -0.56871 |
| 60 | 6.375 | 472868 | 0.0350 | 0.380506 | -0.96625 |
| 90 | 6.380 | 302410 | 0.0224 | 0.243342 | -1.41329 |
| 120 | 6.379 | 218716 | 0.0162 | 0.175996 | -1.7373 |
| 150 | 6.372 | 156143 | 0.0116 | 0.125645 | -2.0743 |
| 180 | 6.377 | 112286 | 0.0083 | 0.090354 | -2.40402 |

Expt No: 6-26
Probe cpd: LNR
pH: 9.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.354 | 1253686 | 0.0928 | 1 | 0 |
| 30 | 6.357 | 971510 | 0.0719 | 0.774923 | -0.25499 |
| 60 | 6.351 | 774305 | 0.0573 | 0.617623 | -0.48188 |
| 90 | 6.358 | 645316 | 0.0478 | 0.514735 | -0.66410 |
| 120 | 6.352 | 520149 | 0.0385 | 0.414896 | -0.87973 |
| 150 | 6.360 | 441777 | 0.0327 | 0.352382 | -1.04304 |
| 180 | 6.358 | 358713 | 0.0266 | 0.286127 | -1.25132 |

Expt No: 6-27
Probe cpd: LNR
pH: 11.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.368 | 1211125 | 0.0896 | 1 | 0 |
| 30 | 6.361 | 1160797 | 0.0859 | 0.958445 | -0.04244 |
| 60 | 6.370 | 1120696 | 0.0829 | 0.925335 | -0.0776 |
| 90 | 6.373 | 1038921 | 0.0769 | 0.857815 | -0.15337 |
| 120 | 6.365 | 983031 | 0.0727 | 0.811668 | -0.20866 |
| 150 | 6.368 | 953499 | 0.0705 | 0.787284 | -0.23917 |
| 180 | 6.364 | 944997 | 0.0699 | 0.780264 | -0.24812 |

Expt No: 6-28
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with LNR at 0.0125 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.303 | 136536 | 0.0106 | 1 | 0 |
| 15 | 6.307 | 44414 | 0.00328 | 0.325291 | -1.12303 |
| 30 | 6.304 | 17082 | 0.00126 | 0.12511 | -2.07856 |
| 45 | 6.301 | 5436 | 0.000402 | 0.039814 | -3.22354 |

Expt No: 6-29
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with LNR at 0.025 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.325 | 270356 | 0.021 | 1 | 0 |
| 15 | 6.321 | 81627 | 0.0063 | 0.301924 | -1.19758 |
| 30 | 6.327 | 34601 | 0.00269 | 0.127983 | -2.05586 |
| 45 | 6.320 | 13407 | 0.00104 | 0.04959 | -3.00396 |
| 60 | 6.330 | 7339 | 0.00057 | 0.027146 | -3.60654 |

Expt No: 6-30
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with LNR at 0.05 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|

| T (min) | R.T. | Area | c (mM) | C/C₀ | ln(C/C₀) |
|---|---|---|---|---|---|
| 0 | 6.307 | 567024 | 0.0441 | 1 | 0 |
| 30 | 6.311 | 226381 | 0.0176 | 0.399244 | -0.91818 |
| 60 | 6.306 | 126381 | 0.00986 | 0.223521 | -1.49825 |
| 90 | 6.303 | 58368 | 0.00454 | 0.102937 | -2.27363 |
| 120 | 6.309 | 26729 | 0.00208 | 0.047139 | -3.05465 |
| 150 | 6.305 | 10364 | 0.00081 | 0.018278 | -4.00206 |
| 180 | 6.312 | 2889 | 0.000224 | 0.005095 | -5.27949 |

Expt No: 6-31
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with LNR at 0.2 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.334 | 2121586 | 0.165 | 1 | 0 |
| 30 | 6.337 | 1164476 | 0.0906 | 0.548871 | -0.59989 |
| 60 | 6.329 | 928857 | 0.0724 | 0.438871 | -0.82596 |
| 90 | 6.327 | 697305 | 0.0542 | 0.328672 | -1.1127 |
| 120 | 6.336 | 553833 | 0.0431 | 0.261047 | -1.34306 |
| 150 | 6.331 | 453176 | 0.0352 | 0.213602 | -1.54363 |
| 180 | 6.332 | 333008 | 0.0259 | 0.156962 | -1.85175 |

Expt No: 6-32
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 420 nm (Hg lamps) with LNR at 0.3 mM

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.401 | 2905111 | 0.226 | 1 | 0 |
| 30 | 6.405 | 1970198 | 0.153 | 0.678183 | -0.38834 |
| 60 | 6.407 | 1605858 | 0.125 | 0.55277 | -0.59281 |
| 90 | 6.411 | 1552800 | 0.121 | 0.534506 | -0.62641 |
| 120 | 6.413 | 1379451 | 0.107 | 0.474836 | -0.74479 |
| 150 | 6.408 | 1107886 | 0.0862 | 0.381358 | -0.96402 |
| 180 | 6.415 | 977555 | 0.0760 | 0.336495 | -1.08917 |

Expt No: 6-33
Probe cpd: LNR
pH: 6.0
System: $TiO_2$-Rutile/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.361 | 1289595 | 0.0954 | 1 | / |
| 60 | 6.367 | 1277282 | 0.0945 | 0.990452 | / |
| 120 | 6.362 | 1293499 | 0.0957 | 1.003027 | / |
| 180 | 6.369 | 1297954 | 0.0960 | 1.006482 | / |

Expt No: 6-34
Probe cpd: LNR
pH: 6.0
System: $TiO_2$-Rutile/$H_2O_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.351 | 1297705 | 0.0960 | 1 | / |
| 30 | 6.347 | 770063 | 0.0570 | 0.593404 | / |
| 60 | 6.342 | 526076 | 0.0389 | 0.40539 | / |

*Cont'd*

| | | | | | |
|---|---|---|---|---|---|
| 90 | 6.345 | 394854 | 0.0292 | 0.304271 | / |
| 120 | 6.350 | 289458 | 0.0214 | 0.223054 | / |
| 150 | 6.348 | 182800 | 0.0135 | 0.140864 | / |
| 180 | 6.346 | 108328 | 0.0080 | 0.083477 | / |

Expt No: 6-35
Probe cpd: LNR
pH: 6.0
System: $TiO_2$-Anatase/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.341 | 1276360 | 0.0944 | 1 | / |
| 60 | 6.337 | 1224667 | 0.0906 | 0.95950 | / |
| 120 | 6.335 | 1103951 | 0.0816 | 0.864921 | / |
| 180 | 6.338 | 1033800 | 0.0765 | 0.80996 | / |

Expt No: 6-36
Probe cpd: LNR
pH: 6.0
System: $TiO_2$-Anatase/$H_2O_2$/visible light at 420 nm (Hg lamps)

| T (min) | R.T. | Area | c (mM) | $C/C_0$ | $\ln(C/C_0)$ |
|---|---|---|---|---|---|
| 0 | 6.325 | 1289886 | 0.0954 | 1 | / |
| 30 | 6.330 | 1138572 | 0.0842 | 0.882692 | / |
| 60 | 6.334 | 1029422 | 0.0761 | 0.798072 | / |
| 90 | 6.328 | 930395 | 0.0688 | 0.72130 | / |
| 120 | 6.323 | 841231 | 0.0622 | 0.652175 | / |
| 150 | 6.327 | 797858 | 0.0590 | 0.618549 | / |
| 180 | 6.329 | 700657 | 0.0518 | 0.543193 | / |

Expt No: 7-1
Probe cpd: LNR
pH: 6.0
System: $TiO_2$/visible light at 420 nm (Xe lamp)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.297 | 1256883 | 0.0929 | 1 |
| 1 | 6.291 | 1236006 | 0.0914 | 0.98339 |
| 2 | 6.295 | 1260618 | 0.0932 | 1.002972 |
| 3 | 6.298 | 1229645 | 0.0909 | 0.978329 |
| 4 | 6.302 | 1219304 | 0.0901 | 0.970102 |
| 5 | 6.305 | 1242436 | 0.0918 | 0.988506 |

Expt No: 7-2
Probe cpd: LNR
pH: 6.0
System: $H_2O_2$/visible light at 420 nm (Xe lamp)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.287 | 1272421 | 0.0940 | 1 |
| 1 | 6.285 | 1287253 | 0.0951 | 1.011657 |
| 2 | 6.282 | 1271037 | 0.0939 | 0.998912 |
| 3 | 6.290 | 1278273 | 0.0944 | 1.004599 |
| 4 | 6.287 | 1275998 | 0.0942 | 1.002811 |
| 5 | 6.281 | 1280966 | 0.0946 | 1.006716 |

Expt No: 7-3
Probe cpd: LNR
pH: 6.0
System: $TiO_2$/visible light at 420 nm (Xe lamp) with the purge of $O_2$

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.271 | 1299544 | 0.0960 | 1 |
| 1 | 6.268 | 1259369 | 0.0930 | 0.969086 |
| 2 | 6.277 | 1294599 | 0.0956 | 0.996195 |
| 3 | 6.273 | 1278221 | 0.0944 | 0.983592 |
| 4 | 6.269 | 1297487 | 0.0958 | 0.998417 |
| 5 | 6.272 | 1279827 | 0.0945 | 0.984828 |

Expt No: 7-4
Probe cpd: LNR
pH: 6.0
System: $TiO_2$/$H_2O_2$/visible light at 420 nm (Xe lamp)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.287 | 1241190 | 0.0917 | 1 |
| 1 | 6.285 | 722468 | 0.0534 | 0.582077 |
| 2 | 6.281 | 589626 | 0.0435 | 0.475049 |
| 3 | 6.288 | 520714 | 0.0385 | 0.419525 |
| 4 | 6.279 | 451617 | 0.0334 | 0.363858 |
| 5 | 6.284 | 364837 | 0.0270 | 0.293941 |
| 6 | 6.289 | 279840 | 0.0207 | 0.225461 |

Expt No: 7-5
Probe cpd: LNR
pH: 6.0
System: $TiO_2$/$H_2O_2$/visible light at 435 nm (Xe lamp)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.263 | 1230891 | 0.0909 | 1 |
| 1 | 6.259 | 867777 | 0.0641 | 0.704999 |
| 2 | 6.267 | 671621 | 0.0496 | 0.545638 |
| 3 | 6.261 | 605064 | 0.0447 | 0.491566 |
| 4 | 6.268 | 535182 | 0.0395 | 0.434792 |
| 5 | 6.259 | 457703 | 0.0338 | 0.371847 |
| 6 | 6.264 | 384167 | 0.0284 | 0.312105 |

Expt No: 7-6
Probe cpd: LNR
pH: 6.0
System: $TiO_2$/$H_2O_2$/visible light at 450 nm (Xe lamp)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.279 | 1200510 | 0.0887 | 1 |
| 1 | 6.283 | 1007824 | 0.0745 | 0.839497 |
| 2 | 6.277 | 928834 | 0.0686 | 0.77370 |
| 3 | 6.281 | 871266 | 0.0644 | 0.725747 |
| 4 | 6.284 | 846020 | 0.0625 | 0.704717 |
| 5 | 6.276 | 802134 | 0.0593 | 0.668161 |
| 6 | 6.271 | 740152 | 0.0547 | 0.616531 |

Expt No: 7-7
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 500 nm (Xe lamp)

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.312 | 1245609 | 0.0920 | 1 |
| 1 | 6.315 | 1197814 | 0.0885 | 0.96163 |
| 2 | 6.317 | 1187476 | 0.0877 | 0.95333 |
| 3 | 6.325 | 1177657 | 0.0870 | 0.945447 |
| 4 | 6.311 | 1137605 | 0.0840 | 0.913292 |
| 5 | 6.313 | 1123529 | 0.0829 | 0.901992 |
| 6 | 6.320 | 1104071 | 0.0815 | 0.886371 |

Expt No: 7-8
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 435 nm (Xe lamp) with the addition of 100 mg/L $NaN_3$

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.338 | 1252449 | 0.0925 | 1 |
| 1 | 6.342 | 1223521 | 0.0904 | 0.976903 |
| 2 | 6.345 | 1218288 | 0.0900 | 0.972725 |
| 3 | 6.337 | 1209783 | 0.0893 | 0.965934 |
| 4 | 6.340 | 1196017 | 0.0883 | 0.954943 |

Expt No: 7-9
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 435 nm (Xe lamp) with the addition of 100 mg/L $HCO_3$

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.321 | 1232914 | 0.0911 | 1 |
| 1 | 6.325 | 1224112 | 0.0904 | 0.992861 |
| 2 | 6.328 | 1230054 | 0.0909 | 0.99768 |
| 3 | 6.319 | 1214110 | 0.0897 | 0.984749 |
| 4 | 6.326 | 1205188 | 0.0890 | 0.977512 |

Expt No: 7-10
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 435 nm (Xe lamp) with the addition of 100 mg/L tert-Butanol

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.313 | 1241078 | 0.0917 | 1 |
| 1 | 6.315 | 1103941 | 0.0816 | 0.889502 |
| 2 | 6.320 | 1033978 | 0.0764 | 0.833129 |
| 3 | 6.311 | 977550 | 0.0722 | 0.787662 |
| 4 | 6.318 | 894539 | 0.0661 | 0.720776 |

Expt No: 7-11
Probe cpd: LNR
pH: 6.0
System: $TiO_2/H_2O_2$/visible light at 435 nm (Xe lamp) with the addition of 3 g/L tert-Butanol

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.309 | 1295706 | 0.0957 | 1 |
| 1 | 6.315 | 1280635 | 0.0946 | 0.988369 |
| 2 | 6.307 | 1278933 | 0.0945 | 0.987055 |
| 3 | 6.301 | 1265241 | 0.0934 | 0.976488 |
| 4 | 6.308 | 1256049 | 0.0928 | 0.969394 |

Expt No: 7-16
Probe cpd: LNR
pH: 6.0
System: $Ga_2O_3/H_2O_2$/visible light at 420 nm

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.331 | 1303676 | 0.0963 | 1 |
| 1 | 6.337 | 1305454 | 0.0964 | 1.001364 |
| 2 | 6.335 | 1298796 | 0.0959 | 0.996257 |
| 3 | 6.330 | 1296231 | 0.0957 | 0.994289 |
| 4 | 6.327 | 1302947 | 0.0962 | 0.999441 |

Expt No: 7-17
Probe cpd: LNR
pH: 6.0
System: $SiO_2/H_2O_2$/visible light at 420 nm

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.312 | 1297498 | 0.0958 | 1 |
| 1 | 6.309 | 1297399 | 0.0958 | 0.999924 |
| 2 | 6.305 | 1299132 | 0.0959 | 1.001259 |
| 3 | 6.301 | 1289854 | 0.0952 | 0.994109 |
| 4 | 6.308 | 1290321 | 0.0953 | 0.994469 |

Expt No: 7-18
Probe cpd: LNR
pH: 6.0
System: $Al_2O_3/H_2O_2$/visible light at 420 nm

| T (hr) | R.T. | Area | c (mM) | $C/C_0$ |
|---|---|---|---|---|
| 0 | 6.328 | 1321100 | 0.0975 | 1 |
| 1 | 6.321 | 1307728 | 0.0966 | 0.989878 |
| 2 | 6.324 | 1300218 | 0.0959 | 0.984193 |
| 3 | 6.327 | 1315768 | 0.0971 | 0.995964 |
| 4 | 6.320 | 1306894 | 0.0964 | 0.989247 |

**The evolution of TOC, varied ions and pH during the decay process of LNR in TiO$_2$/H$_2$O$_2$/Visible system.**

Expt No: 7-12
Probe cpd: LNR
Ph: 6.0
System: TiO$_2$/H$_2$O$_2$/Visible light at 420 nm (Xe lamp)

| T (hr) | TOC (mg/L) | Cl$^-$ (mg/L) | NO$_3^-$ (mg/L) | NH$_4^+$ (mg/L) | pH |
|--------|-----------|--------------|----------------|----------------|------|
| 0 | 27.514 | 0 | 0 | 0 | 6.00 |
| 2 | / | 1.2 | 0.0352 | 0.004 | 5.01 |
| 4 | / | 1.98 | 0.0485 | 0.023 | 4.23 |
| 8 | 26.0175 | 3.52 | 0.0798 | 0.0378 | 3.92 |
| 16 | 25.6565 | 6.43 | 0.186 | 0.109 | 3.68 |
| 24 | 23.9846 | 8.34 | 0.356 | 0.2036 | 3.56 |
| 32 | 22.9015 | 10.15 | 0.612 | 0.399 | 3.34 |
| 40 | 21.885 | 11.04 | 0.785 | 0.526 | 3.20 |
| 48 | 20.097 | 11.88 | 1.05 | 0.677 | 3.12 |
| 56 | 18.693 | 12.56 | 1.61 | 1.02 | 3.07 |