การย่อยสลายฟอร์มัลดีไฮด์โดยใช้รังสียูวีร่วมกับไฮโดรเจนเปอร์ออกไซด์

นางสาวอาริศรา ทะริยะ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2546

ISBN : 974-17-4048-4

DEGRADATION OF FORMALDEHYDE BY UV/H_2O_2 PROCESS

Miss Arissara Tariya

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Environmental Management (Inter-Department)
Graduate School
Chulalongkorn University
Academic Year 2003

ISBN 974-17-4048-4

Thesis Title	Degradation of Formaldehyde by UV/H_2O_2 Process
By	Arissara Tariya
Field of Study	Environmental Management
Thesis Advisor	Puangrat Kajitvichyanukul, Ph.D.
Thesis Co-advisor	Professor Chih-Hsiang Liao, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master 's Degree

………………………………………………… Dean of Graduate School
(Professor Suchada Kiranandana, Ph.D.)

THESIS COMMITTEE

………………………………………………… Chairman
(Assistant Professor Sutha Khaodhiar, Ph.D.)

………………………………………………… Thesis Advisor
(Puangrat Kajitvichyanukul, Ph.D.)

………………………………………………… Thesis Co-advisor
(Professor Chih-Hsiang Liao, Ph.D.)

………………………………………………… Member
(Associate Professor Wanpen Wirojanagud)

………………………………………………… Member
(Assistant Professor Jarurat Voranisarakul)

นางสาวอาริศรา ทะริยะ : การย่อยสลายฟอร์มัลล์ดีไฮด์โดยใช้รังสียูวีร่วมกับไฮโดรเจนเปอร์ออกไซด์. (DEGRADATION OF FORMALDEHYDE BY UV/H_2O_2 PROCESS) อ. ที่ปรึกษา : ดร. พวงรัตน์ ขจิตวิชยานุกูล, อ.ที่ปรึกษาร่วม : Prof. Chin-Hsiang Liao, Ph. D. 99 หน้า. ISBN 974-17-4048-4.

ในงานวิจัยนี้ได้ศึกษาสภาวะที่เหมาะสมได้แก่ พีเอช อัตราส่วนโมล่าร์ของฟอร์มัลล์ดีไฮด์ต่อไฮโดรเจนเปอร์ออกไซด์ และความเข้มข้นเริ่มต้นของฟอร์มัลล์ดีไฮด์ เมื่อมีการย่อยสลายฟอร์มัลล์ดีไฮด์ในน้ำเสียสังเคราะห์ โดยวิธีใช้แสงยูวีร่วมกับไฮโดรเจนเปอร์ออกไซด์เพื่อประยุกต์ใช้เป็นกระบวนการเบื้องต้นในการบำบัดน้ำเสียฟอร์มาลีนจากโรงพยาบาล จากการทดลองนี้พบว่ารังสียูวีช่วยกระตุ้นการแตกตัวของไฮโดรเจนเปอร์ออกไซด์ให้เป็นไฮดรอกซิล-เรดิคอล (OH•) ซึ่งมีความสามารถสูงในการทำลายโมเลกุลของฟอร์มัลล์ดีไฮด์ โดยพบว่าสภาวะที่เหมาะสมที่สุดที่ให้ประสิทธิภาพสูงสุดในการย่อยสลายฟอร์มัลล์ดีไฮด์ ประกอบด้วยการทดลองที่พีเอช 7 อัตราส่วนโมลาร์ของฟอร์มัลล์ดีไฮด์ต่อไฮโดรเจนเปอร์ออกไซด์เป็น 1:2 และใช้เวลาในการย่อยสลาย 240 นาที เมื่อใช้อัตราส่วนโมลาร์ของฟอร์มัลล์ดีไฮด์ต่อไฮโดรเจนเปอร์ออกไซด์มากกว่าหรือน้อยกว่าสภาวะที่เหมาะสมทำให้ระบบมีประสิทธิภาพในการบำบัดลดลง โดยพบว่าที่อัตราส่วนโมลาร์น้อยกว่า 1:2 ไฮโดรเจนเปอร์ออกไซด์ที่เข้าทำลายโมเลกุลของฟอร์มัลล์ดีไฮด์มีปริมาณไม่เพียงพอ ในทางกลับกันเมื่อใช้อัตราส่วนโมลาร์มากกว่า 1:2 พบว่าไฮโดรเจนเปอร์ออกไซด์มีปริมาณมากเกินไปจนทำปฏิกิริยากับโมเลกุลไฮโดรเจนเปอร์ออกไซด์ด้วยกันเองส่งผลให้ประสิทธิภาพของระบบลดลง การย่อยสลายฟอร์มัลล์ดีไฮด์โดยวิธีการใช้แสงยูวีร่วมกับไฮโดรเจนเปอร์ออกไซด์ในสภาวะกรดให้ประสิทธิภาพสูงกว่าในสภาวะด่าง อย่างไรก็ตามพบว่าการบำบัดด้วยวิธีนี้ในสภาวะเป็นกลางให้ประสิทธิภาพสูงที่สุด นอกจากนี้ยังพบว่าการย่อยสลายฟอร์มัลล์ดีไฮด์ด้วยกระบวนการนี้ไม่สามารถย่อยสลายเป็นคาร์บอนไดออกไซด์และน้ำได้หมด โดยพบว่าฟอร์มัลล์ดีไฮด์ได้เปลี่ยนรูปเป็นกรดฟอร์มิค โดยที่ความเข้มข้นเริ่มต้นของฟอร์มัลล์ดีไฮด์ที่น้อยกว่า 5,000 มก./ล. น้ำที่ผ่านการบำบัดแล้วจะไม่มีความเป็นพิษต่อจุลินทรีย์ โดยวิธีการย่อยสลายฟอร์มัลล์ดีไฮด์นี้จึงเหมาะสมในการนำไปใช้เมื่อน้ำเสียมีฟอร์มัลล์ดีไฮด์ในช่วงค่าดังกล่าว

ภาควิชาการจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต...
สาขาวิชาการจัดการสิ่งแวดล้อม ลายมือชื่ออาจารย์ที่ปรึกษา......................................
ปีการศึกษา 2546 ลายมือชื่ออาจารย์ทีปรึกษาร่วม................................

4589487320 : MAJOR ENVIRONMENTAL MANAGEMENT

KEY WORDS: FORMALDEHYDE / PHOTOOXIDATION / ADVANCED OXIDATION PROCESSES/ ULTRAVIOLET IRRADIATION / HYDROGEN PEROXIDE

ARISSARA TARIYA: DEGRADATION OF FORMALDEHYDE BY UV/H_2O_2 PROCESS THESIS ADVISOR: ASST. PROF. PUANGRAT KAJITVICHYANUKUL, Ph.D., THESIS CO-ADVISOR: PROF. CHIH-HSIANG LIAO, Ph.D., 99 pp. ISBN 974-17-4048-4.

Degradation of the synthetic formaldehyde wastewater using advance oxidation process, UV/H_2O_2, was investigated in order to apply this system as a pre-treatment method for formalin solution used in the hospitals. The effects of solution pH, molar ratio of formaldehyde to hydrogen peroxide, and initial concentration of formaldehyde on process performance were systemically studied. It was revealed that UV photolysis had a little effect on degradation of formaldehyde. The highest efficiency of formaldehyde degradation was achieved with the molar ratio of formaldehyde to hydrogen peroxide at 1:2 at pH 7 within 240 min. At the molar ratio lower than the optimum condition, an inadequate amount of hydrogen peroxide was presented. On the contrary, the highest ratio than that causing the decomposition of hydrogen peroxide itself. Regarding the study of the pH effect, it was found that formaldehyde degradation in acidic solution gave a favorable oxidation rate than that in basic solution. However, the highest formaldehyde removal efficiency was observed at neutral pH. The toxicity and total organic carbon reductions were determined. The toxicity reduction below EC_{50} was attained when the initial concentration less than 5,000 mg/l. The formaldehyde degradation by UV/H_2O_2 did not accomplish the total mineralization since the by product of formaldehyde, formic acid, was identified in GC Chromatogram during the reaction period. Findings from this study can be potentially applied for formalin wastewater with the formaldehyde concentration less than 5,000 mg/l.

Field of study	Environmental Management	Student's signature……….……………….....
Academic year	2003	Advisor's signature………………………….
		Co-advisor's signature……………..………..

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my thesis advisor, Dr.Puangrat Kajitvichyanukul for her encouragement, invaluable support, and kindness guidance throughout my work. Her comments and suggestions not merely provide valuable knowledge but broaden perspective in practical applications as well. I am grateful to Prof. Chih-Hsiang Liao, my co-advisor, Asst. Prof. Sutha Khaodhiar, Chairman of the committee, Assoc. Prof. Wanpen Wirojanagud, and Asst. Prof. Jarurat Voranisarakul members of thesis committee for many valuable comments.

I am grateful to the Environmental Research Institute Center, Chulalongkorn University (ERIC), all staffs and students in the National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM) Program. Special thanks to all authorities in laboratory, Department of Environmental Engineering King’s Mongkut’s University of Technology Thonburi, for lab instrument supporting.

To my parents, I would like to extend my special appreciation for their constant support without them it will not be possible for me to complete my work.

This work was also supported by the Thailand Research Fund under grant no. MRG4680029 and National Research Center – Environmental Hazardous Waste Management (NRC-EHWM), Chulalongkorn University.

CONTENTS

Pages

CHAPTER 2 BACKGROUNDS AND LITERATURE REVIEW

CONTENTS (Cont.)

Pages

CONTENTS (Cont.)

LIST OF FIGURES

LIST OF FIGURES (Cont.)

LIST OF FIGURES (Cont.)

LIST OF TABLES

NOMENCLATURE

RELs = Reference Exposure Levels

STEL = Short-Term Exposure Limit

TWA = Time Weighted Average

OSHA = Occupational Safety and Health (Administration or Act)

PEL = Permissible Exposure Limit

HSDB = Hazardous Substances Data Bank

NO_x = nitrogen oxide

SO_x = sulfur oxide

VOC = Volatile Organic Compound

CERCLA = Comprehensive Environmental Response Compensation and Liability Act (Superfund)

HMIS = Hazardous Materials Inventory Statement

AOPs = Advanced Oxidation Processes

AOTs = Advanced Oxidation Technologies

UV = Ultraviolet

UV/H_2O_2 = Ultraviolet combined with hydrogen peroxide

UV/TiO_2 = Ultraviolet combined with titanium dioxide

$UV/Fe^{2+}/H_2O_2$ = Photo-Fenton

BETX = Benzene, Ethylene, Toluene, and Xylene

COD = Chemical Oxygen Demand

BOD = Biological Oxygen Demand

TOC = Total Organic Carbon

NOM = Natural Organic Matter

EDTA = ethylenediamine tetra acetic acid

Pollutant: H_2O_2 = Molar ratio of pollutant to hydrogen peroxide

CH_2O: H_2O_2 = Molar ratio of formaldehyde to hydrogen peroxide

CH_2O = formaldehyde

CO_2 = carbon dioxide

H_2O_2 = hydrogen peroxide

$[H_2O_2]$ = Concentration of hydrogen peroxide

$[H_2O_2]_o$= Initial concentration of hydrogen peroxide

$OH^{\bullet}$ = Hydroxyl radical

HO_2^- = Perhydroxyl ion

OH^- = Hydroxide ion

CO_3^{2-} = Carbonate ion

PO_4^{3-} = Phosphate ion

HCO_3^- = Bicarbonate ion

CHAPTER 1

INTRODUCTION

1.1 Motivations

Medical wastewater contains a variety of toxic organic contaminants in a wide range of concentrations. The toxic chemicals used in hospitals include formalin solution as 40% formaldehyde and other chemicals such as acetone chloroform, etc. According to studies from King Mongkut's University of Technology Thonburi (KMUTT) (Charuratana and Voranisarakul, 1993; Cheawchanthanakit and Sangphromma 1997), the failure of the wastewater treatment plant in many hospitals is the result of the direct discharge of these toxic chemicals to the wastewater treatment plant. The findings from these studies also indicated that formaldehyde is considered to be the most toxic organic contaminant in medical wastewater that causing this failure due to its relatively high concentration in the large volume of its. Formalin is commonly used as a preservative in hospital laboratories and an embalming agent in embalming rooms.

From our investigation, the used formalin is discharged to the wastewater treatment plant once a week with amount of 500 ml from laboratories and twice a year with amount of 67.5 m^3 from embalming rooms. From the analysis of wastewater in this study, the concentration of formaldehyde in used formalin solution from the laboratory and embalming room were about 5,000 mg/l and 40,000 mg/l, respectively. For the analysis of formaldehyde concentrations in influent and effluent of medical wastewater treatment plant, the detected amounts of formaldehyde were lower than 0.01mg/l because formalin waste was not discharged during the studied period (normally it is discharged twice a year).

The preliminary study in our research group on biodegradability of formaldehyde was conducted using sequencing batch reactor (SBR) biological treatment process (see Appendix B for more information on experimental procedure and results). The monitored parameters were chemical oxygen demand (COD) and suspended sludge (SS). The results showed that with initial concentration of formaldehyde as high as 10,000 mg/l (0.333 M) in influent, the SBR system has inability in COD removal as evidence on COD value of effluent was higher than that of influent. This result also indicated that there was COD accumulation in the system. With lower initial concentration of formaldehyde at 10 - 500 mg/l or 3.33×10^{-4} - 1.65×10^{-2} M, the results show that at first period COD can be removed then COD was accumulated to higher value while proceeding the experiment and finally the system had no longer capability to remove COD whereas 98% COD removal was achieved in control experiment. Another parameter, SS, was monitored to observe effect of formaldehyde on amount of microorganisms in the system. Each reactor had initial SS about 3,000 mg/l that rapidly decreased if containing high amount of formaldehyde in the system. For example, at 0.33 M of formaldehyde, SS was reduced to 2190 mg/l within 16 days while at 3.33×10^{-4} M of formaldehyde, SS was reduced to 1970 mg/l within 29 days. This finding points out the fact that formaldehyde toxicity affected the population of microorganism which leaded to lower the efficiency of the biological system on formaldehyde removal.

This study was focused on using chemical treatment method, a UV/H_2O_2 advance oxidation process as a pretreatment method for treating formaldehyde before further discharging this kind of waste to biological unit which poses high risk to environmental and human health of which the reasons are as follows:

1. UV/H_2O_2 process is a high efficiency technology to remove organic contaminants from wastewater and is not requiring a post-treatment process, for example, sludge handling.
2. UV/H_2O_2 process is considered as the economical method compare to advanced oxidation processes (AOPs) technology.

1.2 Objectives

The major objective of this study was to investigate formaldehyde removal efficiency in formalin solution using UV/H_2O_2 photooxidation process.

The two specific objectives were as follows:

1. To determine the optimum conditions for treating formaldehyde in synthetic formalin solution by UV/H_2O_2 process

2. To investigate the factors that influence UV/H_2O_2 process on its removal efficiency of formaldehyde.

1.3 Hypotheses

1. Formaldehyde degradation can be achieved by UV/H_2O_2 advanced oxidation process

2. The removal efficiency of the UV/H_2O_2 oxidation process for treating formaldehyde depends on pH, concentrations of H_2O_2 and the initial concentrations of formaldehyde.

1.4 Scopes of Work

Scopes of this work were as follows:

1. Synthetic wastewater with a concentration corresponding to the real wastewater, 10,000 mg/l, was used for all experiments unless otherwise specified.

2. Dependent variables included pH (e.g., acidic, neutral and basic), molar ratios of formaldehyde to hydrogen peroxide, and initial concentrations of formaldehyde.

3. Measured parameters were residual concentrations of formaldehyde and hydrogen peroxide concentrations in solution, total organic carbon (TOC), and toxicity.

1.5 Advantages of This Work

Results from this research can be beneficial for a treatment of medical wastewater containing formaldehyde. This UV/H_2O_2 technology can be transferred to be used on a bigger scale, pilot plant and to modify for a pretreatment method of formalin solution.

CHAPTER 2

BACKGROUNDS AND LITERATURE REVIEW

2.1 Properties of Formaldehyde

2.1.1 General Information

Formaldehyde is a colorless, organic chemical and a preservative and bonding agent. Formaldehyde is used as formalin which is a mixture containing 30-50% formaldehyde in water and a small amount of methanol (methyl alcohol) which is added to prevent polymerization. The chemical formula for formaldehyde is CH_2O and its molecular weight is 30.0262 g/mole (CRC Handbook of Chemistry and Physics, 1994). It is also known as methyl aldehyde, or methylene oxide. The structure of formaldehyde is shown in Figure 2.1.

In general purposes, it is used as an antiseptic, disinfectant, and preservative for biological materials. The use of formaldehyde as a preservative in medical laboratories and as an embalming agent in mortuaries for medical purposes is generally known. In industry manufacturing, formaldehyde is used as a sterile chemical, leather tanner, platter, preservative, and fumigant. It is also used to make commercial products such as resins, wrinkle-proof fabrics, rubber products, dyes, textiles, plastics, paper products, and cosmetics. Formaldehyde is also found in insulation materials, plywood, particleboard, and adhesives. Formaldehyde is also present in combustion products, such as fuel exhaust and tobacco smoke.

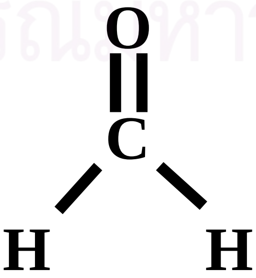


Figure 2.1 Th

2.1.2 Physical and Chemical Properties

Formaldehyde is a colorless, flammable gas with a strong, pungent, irritating odor. Its chemical properties (Hazardous Substances Data Bank, 1994; CRC Handbook of Chemistry and Physics, 1994) are as follows:

Molecular formula: CH_2O

Molecular weight: 30.03 g/mol

Density: 1.0800 g/L @ -20°C

Boiling point: -19°C

Melting point: -15°C

Vapor pressure: 220 kPa @ 0°C

Solubility: Soluble in water, ethanol, ether, acetone

Conversion factor: 1 ppm = 1.23-1.25 mg/m^3 @ 25°C

2.1.3 Formalin Solution

The solution of the gas in water (typically, 37-40 % of formaldehyde) are know as formalin and are commonly used as biological preserving agents (U.S. EPA 1985b). Formaldehyde in solution reacts with water to become hydrated. In this form, it becomes less volatile than water; thus, volatilization is not expected to be significant (U.S. EPA 1985b).

Normally, 37-40 % of formaldehyde contains about 10 % of methanol as stabilizing agent. The boiling point of formalin solution is 97 °C. For preparation of 1,000 ml of formalin solution for medical purposes, its composition is as follows:

37-40 % formaldehyde	100 ml
Distilled water	900 ml
Sodium acetate*	20 g

* being used in some hospital

2.1.4 Toxicology

Formaldehyde can cause adverse effects on human health such as skin irritation and respiratory tract disease (IPCS, 1989). It is also found to cause damage to DNA and mutation in microorganisms and mammalian cells (Grafstrom et al.

1985). Even low levels of formaldehyde can have health effects. Low levels of exposure, airborne concentrations above 0.1 ppm (per million parts of air), can irritate the eyes, nose and throat. The severity of irritation increases as concentrations increase. At 100 ppm it is immediately dangerous to life and health, by increasing a serious breathing problems and increasing people risk of certain kinds of cancer. Occupational Health and Safety Agency (OSHA) regulates formaldehyde as a cancer-causing substance.

Short-term exposure:

There is considerable individual variation when it comes to sensitivity to formaldehyde. Typical symptoms associated with over-exposure to formaldehyde are listed by route of entry:

Inhalation: Irritation of the nose and throat can occur after an exposure of 0.25 ppm to 0.45 ppm. Levels between 0.4 ppm and 0.8 ppm can give rise to coughing and wheezing, tightness of the chest and shortness of breath. Sudden exposures to concentrations of 4 ppm may lead to irritation of lung and throat severe enough to give rise to bronchitis and laryngitis. Breathing may be impaired at levels above 10 ppm and serious lung damage may occur at 50 ppm.

Skin: Direct contact with the liquid can lead to irritation, itching, burning and drying. It is also possible to develop an allergic reaction to the compound following exposure by any routine.

Eyes: Exposure to airborne levels of formaldehyde of 0.4 ppm can bring on tearing and irritation. Small amounts of liquid in the eye can cause damage to the cornea.

Ingestion: As little as 0.035 liquid gram has resulted in deaths to humans. Smaller amounts can damage the throat, stomach, and intestines, resulting in nausea, vomiting, abdominal pain, and diarrhea. Accidental exposure may also cause a loss of consciousness, lower blood pressure, kidney damage and if the victim is pregnant, the possibility of the fetus being aborted.

Long-term exposure:

Inhalation can result in respiratory congestion with associated coughing and shortness of breath. Daily skin contact can lead to drying and scaling. Some individuals may experience allergic reactions after initial contact with the chemical. Subsequent contact may cause skin rashes and asthma and reactions may become severe if exposure persists (chronic toxicity of formaldehyde).

Long-term inhalation of high levels of formaldehyde vapor (14 ppm) in rats has resulted in an elevated incidence of cancer of the nose. Genetic damage from exposure has been shown in bacteria and some insects. Whether it causes these effects in humans is uncertain.

Permisible Explosure Limit

The permissible exposure limit (PEL) for formaldehyde in all workplaces (including general industry, construction, and maritime, but not in agriculture) covered by the Occupational Safety Health Agency (OHSA) standard which is 0.75 ppm measured as an 8-hour time weighted average (TWA). The standard includes a 2 ppm short-term exposure limit (STEL) (i.e., maximum exposure allowed during a 15-minute period). The "action level" is 0.5 ppm measured over 8 hours.

Kerfoot and Mooney (1975) reported that estimated formaldehyde exposures of 0.25-1.39 ppm evoked numerous complaints of upper respiratory tract and eye irritation among 7 embalmers at 6 different funeral homes. Three of the 7 embalmers in this study reportedly had asthma. Levine et al. (1984) examined the death certificates of 1477 Ontario undertakers. Exposure measurements taken from a group of West Virginia embalmers were used as exposure estimates for the embalming process, ranging from 0.3-0.9 ppm (average 1-hour exposure) and 0.4-2.1 ppm (peak 30-minute exposure). Mortality due to non-malignant diseases was significantly elevated due to a two-fold excess of deaths related to the digestive system. The authors suggest increased alcoholism could have contributed to this increase.

Table 2.1 presents a summary of potential Reference Exposure Level, RELs, based on chronic and sub-chronic animal studies. The toxicological endpoint was nasal lesions, consisting principally of rhinitis, squamous metaplasia, and dyplasia of the respiratory epithelium.

Table 2.1. Summary of Chronic and Sub-chronic Formaldehyde Studies in Experimental Animals

Study	Animal	Exposure Duration	LOAEL/ NOAEL (mg/m^3)	HEC adj. (mg/m^3)	Cumulative UF	REL ($\mu g/m^3$)
Woutersen *et al*., 1989	rat	28 mo	9.8 / 1.0	0.06	30	2
Kerns *et al*., 1983	rat	24 mo	2.0 / NA	0.1	300	0.3
Monticello *et al*., 1996	rat	24 mo	6.01 / 2.05	0.1	30	4
Kamata *et al*., 1997	rat	24-28 mo	0.30 / NA	0.02	100	0.2
Appelman *et al*., 1988	rat	52 wk	9.4 / 1.0	0.06	30	2
Rusch *et al*., 1983	rat	26 wk	2.95 / 0.98	0.2	30	7
Kimbell *et al*., 1997	rat	26 wk	6 / 2	0.1	30	3
Wilmer *et al*., 1989	rat	13 wk	4 / 2	0.2	300	0.7
Woutersen *et al*., 1987	rat	13 wk	9.7 / 1.0	0.03	100	0.3
Zwart *et al*., 1988	rat	13 wk	2.98 / 1.01	0.2	300	0.7
Kerns *et al*., 1983	mouse	24 mo	2.0 / NA	0.05	100	0.5
Maronpot *et al*., 1986	mouse	13 wk	10.1 / 4.08	0.09	100	0.9
Rusch *et al*., 1983	monkey	26 wk	2.95 / 0.98	none	300	4

where: LOAEL = Lowest observed adverse effect level
NOAEL = No observed adverse effect level
Cumulative CF = Cumulative Uncertain Factor
HEC = High explosive concentration
RELs = Reference Exposure Levels

2.2 Properties of Hydrogen Peroxide

2.2.1 General Information

Hydrogen peroxide is a ubiquitous compound present in natural water, (for example: in sea water [H_2O_2] = 0.5 to 14 µg/l; in fresh water [H_2O_2] = 1 to 30 µg/l), in air [H_2O_2] = 0.1 to 1 ppb, in aerobic living cells (Offermanns et al. 2000) and in space on planetary surfaces (e.g. Carlson et al. 1999). Although pure hydrogen peroxide is fairly stable, it decomposes into water and oxygen when heated above about 80°C. It also decomposes in the presence of numerous catalysts, e.g., most metals, acids, or oxidizable organic materials. Highly concentrated solutions were first used in World War II by the military, e.g., in fuels for rockets and torpedoes. Hydrogen peroxide is prepared commercially by oxidation of alkylhydro-anthraquinones and by electrolysis of ammonium bisulfate. It can also be prepared by reaction of barium peroxide with sulfuric acid and is prepared (with acetone) by oxidation of isopropanol. Hydrogen peroxide was discovered by Thenard in 1818. Aqueous solution of hydrogen peroxide is mainly used for oxidation reactions, including bleaching process, chemical syntheses, and AOPs for water and wastewater treatment (Offermanns et al. 2000; Höppke and Hagel, 1991). In drinking water purification, hydrogen peroxide is used to pre-oxidize organics water constituents and to eliminate iron and manganese ions. In Germany, The residual concentration of hydrogen peroxide in drinking water must lie below 0.1 mg/l (Aurand et al. 1989)

2.2.2 Physical and Chemical Properties

An aqueous solution of hydrogen peroxide is clear, colorless, water-like in appearance and nonflammable. It is miscible with cold water and is soluble in alcohol and ether. At high concentration, it has a slightly pungent or acidic odor. The chemical formula for hydrogen peroxide is H_2O_2 and its molecular weight is 34.015 g/mole. The structure of hydrogen peroxide is shown in Figure 2.2.

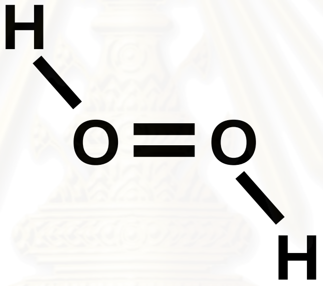


Figure 2.2 The structure of hydrogen peroxide

2.2.3 Environmental Applications of Hydrogen Peroxide

Hydrogen peroxide applications span the range of possible media: air, water, wastewater, soils and sludges. Depending on the objective, H_2O_2 may be used either alone or in combination with other processes to enhance their performance.

2.2.3.1 Stand-Alone Applications

Odor control - Hydrogen peroxide oxidizes hydrogen sulfide, mercaptans, amines and aldehydes. H_2O_2 may be applied directly to aqueous wastes containing these odorants, or to wet scrubbers used to remove them from air streams. If the odors are the result of biological activity, H_2O_2 may instead be added as a preventative to eliminate the anoxic conditions, which favor the generation of odors.

Corrosion control - Hydrogen peroxide destroys residual chlorine and reduced sulfur compounds (thiosulfates, sulfites, and sulfides) which form corrosive acids when condensed onto processing equipment and oxidized by air.

BOD/COD removal - Hydrogen peroxide oxidizes both organic and inorganic pollutants which contribute to BOD and COD -- catalytic, H_2O_2 may be needed to oxidize the more resistant substances. H_2O_2 may also affect BOD/COD removal by enhancing the performance of other processes (see below).

Inorganic oxidation - Hydrogen peroxide oxidizes cyanides, NO_x/SO_x, nitrites, hydrazine, carbonyl sulfide, and other reduced sulfur compounds mentioned above (odor/corrosion control).

Organic oxidation - Hydrogen peroxide hydrolyzes formaldehyde, carbon disulfide, carbohydrates, organophosphorus and nitrogen compounds, and various water-soluble polymers; and (with catalysis) destroys phenols, BTEX pesticides, solvents, plasticizers, chelants, and virtually any other organic requiring treatment.

Metals oxidation - Hydrogen peroxide oxidizes ferrous iron, manganese, arsenic, and selenium to improve their adsorption, filtration, or precipitation from process waters and wastewaters.

Toxicity reduction/Biodegradability improvement - With catalysis, Hydrogen peroxide chemically digests complex organics into smaller, less toxic and more biodegradable fragments.

Disinfection/Bio-control - Hydrogen peroxide excess bio-growth in water supplies and cooling circuits, and (with catalysis) disinfects process waters and biological effluents.

2.2.3.2 Enhancement (Combination) Applications

Flocculation/Precipitation - Hydrogen peroxide oxidizes metal complexes and improves the performance of inorganic flocculants.

Air Flotation - Hydrogen peroxide releases evenly dispersed microbubbles which entrain emulsified fats, oils and greases to enhance their removal in air flotation units and grease traps.

Biotreatment - As a pretreatment, hydrogen peroxide degrades toxic, refractory or bio-inhibitory organics, rendering them more amenable to biodegradation. Hydrogen peroxide provides a supplemental source of dissolved oxygen *in-situ* (penetrating both soil columns and bioflocs, eliminating the sludge bulking phenomenon). As a polishing step - Hydrogen peroxide destroys trace levels of organics that pass through biotreatment, providing the ancillary benefit of disinfection.

Filtration - Hydrogen peroxide controls biofouling of UF and RO membranes while eliminating foulodors from media filters.

Carbon adsorption - Hydrogen peroxide enhances the adsorption of many pollutants while providing dissolved oxygen to support biologically-active carbon beds (improving removal efficiencies even further).

Air scrubbers - Hydrogen peroxide replaces chlorine for deodorizing offgases and controlling VOC's. Depending on the target pollutant(s), a catalytic or Advanced Oxidation Processes may be required.

Incineration - Hydrogen peroxide provides supplemental oxygen to improve combustion efficiencies and lower operating temperatures.

Advanced Oxidation Processes (AOPs) - AOPs represent the newest development in H_2O_2 technology, and are defined as processes that generate highly reactive oxygen radicals without the addition of metal catalysts. Typically, this means combining H_2O_2 with ozone or ultraviolet light. The result is the on-site total destruction of even refractory organics without the generation of sludges or residues. This technology is being widely applied to treat contaminated groundwater, to purify and disinfect drinking waters and process waters, and to destroy trace organics in industrial effluents.

2.2.4 Toxicology

Significantly, no concentration of H_2O_2 is listed as a regulated substance (i.e., a persistent environmental hazard) under Comprehensive Environmental Response Compensation and Liability Act, CERCLA. If released to the environment, hydrogen peroxide will decompose to oxygen and water with concurrent generation of heat. Nor are the standard industrial strengths hydrogen peroxide (those < 52% wt.%) covered under the Federal Risk Management guidelines. However, a hazardous material permit - termed a Hazardous Materials Inventory Statement (HMIS) - may be required by local response agencies, depending on the concentration, volume, and location of hydrogen peroxide stored.

2.3 Ultraviolet Radiation

2.3.1 Electromagnetic Spectral Range of Interest in photochemical

The wavelength range generally utilized in photochemistry lies between 170 nm and 1,000 nm. This is mainly due to the fact that electromagnically excited states M* of organic or inorganic molecules M are usually generated by photoexcitation within this wavelength range. This bandwidth is determined by the absorption characteristics of inorganic and organic molecules in liquid or gaseous phase.

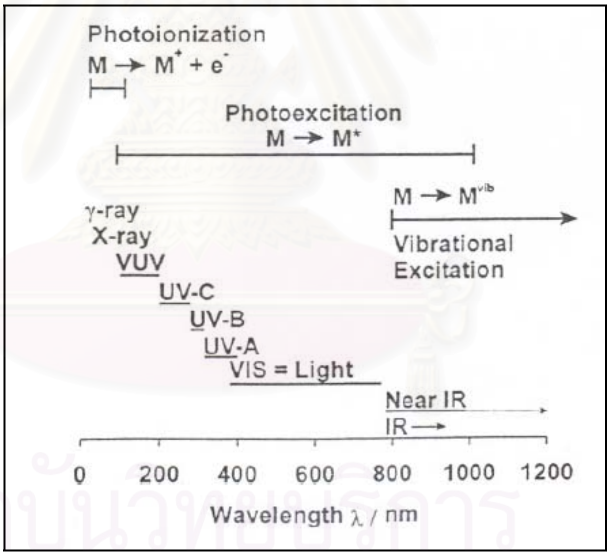


Figure 2.3 Classification of electromagnetic radiation in the wavelength range below A of 1200 nm as bands with specific names, and the interaction with molecules M (VUV: vacuumUV) (Oppenländer, 2002)

The photochemically active region of the electromagnetic spectrum has been divided into five sub bands: The vacuum-UV (VUV), UV-C, UV-B, UV-A and VIS (Figure 2.3). The UV-B region is usually defined between wavelength of 280 and 315 nm.

2.3.2 Sources and Their Characteristics

Ultraviolet light is an electromagnetic radiation spread between the wavelengths 100 nm and 400 nm. A mercury vapor lamp is the most common UV light source (Hanzon and Vigilia, 1999). The lamp is filled with mercury vapor at different pressures. Mercury atoms in the gas phase are electronically excited by an electronical discharge between two electrodes. These electrodes are in direct contact with the mercury vapor phase. The electronically excited mercury atoms deactivated to their ground state by emission of radiation according to the energy level diagram (Murov, 1973), thus generating an intense radiating arc with in the quartz envelope. Ultraviolet lamps are classified as either low, medium or high pressure units. The most common mercury arc lamp is the low pressure (LP) type, being extensively used in the field of UV disinfection. This lamp type is an effective converter of electrical into radiant energy, usually with a UV-C output in the range of 30 to 50 W (Altena et al. 2001). They provide almost monochromatic UV radiation at wavelength of 253.7 nm (usually refered to as 254 nm radiation in the technical literature) with an ordinary quartz envelope. The intensity is a function of the lamp array's geometry as well as the UV transmittance of the wastewater. The literature investigated for this study dealt with low, medium and high-pressure lamps. The UV chambers vary in size and were configured by either vertical or horizontal lamp placement. Other factors that limit the effectiveness of the system are the wattage and output. The UV lamps described in the literature varied from 14 watts to 35 watts for a low pressure lamp (Shu et al. 1994; Namboodri and Walsh, 1996; Liao et al. 2000) and 200 to 300 watts for a medium pressure lamps (Glaze 1993; Yang et al. 1998).

2.3.3 Adsorption of UV radiation by Molecules

The principles of photochemistry and photophysics related to the interaction of UV/VIS radiation with matter, however, some comments that are necessary for the understanding of the processes involved in photochemical advanced oxidation will be discussed briefly. Fundamentally, physical phenomena (reflection, refraction and scattering) have to be distinguished from photo physical (absorption, luminescence, etc.) and photochemical processes (formation of photoproducts) as is demonstrated schematically by Figure 3.3. The physical phenomena are of considerable interest in sophisticated photo reactor modeling, because many photoreactors used for water treatment possess an air/quartz/water interface that influences the influence rate distribution within a photoreactor. This is especially important for drinking water applications where the optical transmittance of water is usually very high (Bolton, 2000).The absorbed radiation is used to produce electronically excited states of the sample molecules initiating photophysical deactivation processes or the formation of photoproducts. The intensities of the incident and of the transmitted beam are correlated by the *Beer-Lambert* law, which quantitatively describes the attenuation of UV/VIS radiation by transmitting any absorbing medium.

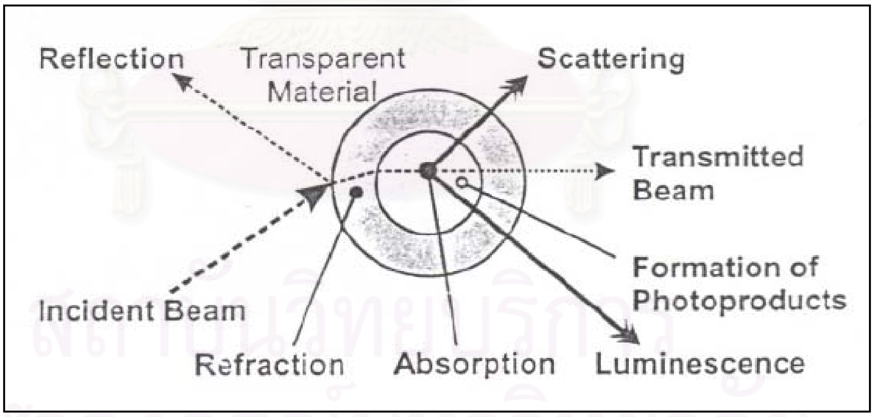


Figure 2.4 Schematic representation of physical, photo physical and photochemical phenomena and processes observed during interaction of UV/VIS radiation with matter. (Oppenländer, 2002.)

The light absorbance and photolytic properties of chlorophenols and hydrogen peroxide were found to be highly dependent on solution pH, the absorbance increased significantly when the solution pH were above the pK_a value of the respective compounds (Shen et al., 1995).

2.4 UV/H_2O_2 Process

2.4.1 Photochemistry of Hydrogen Peroxide

The thermal and photo induced decomposition of pure aqueous solution of hydrogen peroxide leads to the formation of water and oxygen. The effect of electromagnetic radiation on the decomposition of hydrogen peroxide can be explained by the so-called *Habere-Weiss* mechanism (Figure 2.5). The primary and principle step for The UV/H_2O_2 degradation has been postulated as the initial attack by photon of hydrogen peroxide and the formation of $OH^{\bullet}$ radicals (equation 2.1). Then, these radicals chain mechanism suggest that the hydroxyl radicals formed by hemolytic cleavage of the central HO-OH bond initiate a propagation cycle with the net reaction leading to water and molecular oxygen.

Photolysis of hydrogen peroxide may be affected by suspended particles and other absorbing species in the aqueous solution being treated (Glaze et al. 1987). The presence of other radical-reactive species in a water sample such as carbonate, bicarbonate, humic substances, or phosphate ions will affect the degradation rate of organic contaminants by consuming hydroxyl radicals (Glaze et al. 1995). Inorganic compounds present in water may also precipitate following UV exposure, coating lamp tubes and affecting the amount of UV light that is available for water treatment (Venkatadri and Peters, 1993).

Initiation: $H_2O_2 + h\nu \longrightarrow 2OH^{\bullet}$ (2.1)

Propagation: $H_2O_2 + OH^{\bullet} \longrightarrow H_2O + HO_2^{\bullet}$ (2.2)

$HO_2^{\bullet} + H_2O_2 \longrightarrow H_2O + O_2^{\bullet} + OH^{\bullet}$ (2.3)

Net Reaction: $2H_2O_2 \longrightarrow 2H_2O + O_2$ (2.4)

Termination: $OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2$ (2.5)

$OH^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O + O_2^{\bullet -}$ (2.6)

$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$ (2.7)

Figure 2.5 Radical chain mechanism of the photo-induced decomposition of hydrogen peroxide in pure water according to *Haber Weiss* (as cited in Gmelin, 1996)

2.4.2 Hydroxyl Radicals

Hydroxyl radicals are extremely reactive, short-lived and unselective transient species. The mean lifetime of $OH^{\bullet}$ depends on their chemical environment and was estimated to be in the order of 10 μs in the presence of dissolved natural organic matter, bicarbonate and carbonate (Hoigne, 1998). Pryor (1986) estimated the half-life of hydroxyl radicals in the presence of linoleate ($C_{18}H_{31}O_2^-$), the conjugate base of linoleic acid at T= 37°C to be in the order of nano seconds.

The hydroxyl radical is one of the most reactive free radicals and one of strongest oxidants (Buettner, 1985). It has a very high oxidizing capacity equalling 2.8 V. (Prengle et al. 1978; Masten and Divies, 1994; Himebaugh, 1994) and attacks the organic compounds relatively non-selective with rate constants ranging from $10^6 – 10^{10}$ M^{-1} s^{-1} (Buxton et al. 1988)

Hydroxyl radicals can oxidize organic and inorganic substrates by different types of reactions (equation 2.8 to 2.10) (Legrini et aI. 1993, Hoigne, 1998):

Electron Transfer Reaction:

$$OH^{\bullet} + M^{n} \longrightarrow M^{n+1} + (OH^{-})_{aq} \qquad (2.8)$$

Hydrogen Abstraction:

$$OH^{\bullet} + R\text{-}H \longrightarrow R^{\bullet} + H_2O \qquad (2.9)$$

Electrophilic addition:

$$OH^{\bullet} + R_2C{=}CR_2 \longrightarrow {}^{\bullet}CR_2\text{-}C(OH)R_2 \qquad (2.10)$$

In equation 2.9, the hydroxyl radical is capable of oxidizing organic compounds mostly by hydrogen abstraction. Electron transfer to hydroxyl radicals (equation 2.8) is interesting in the case where the hydrogen abstraction or electrophilic addition reaction may be disfavored by multiple halogen substitution or steric hindrance. Finally, electrophilic addition of hydroxyl radicals to organic π system, another mechanism of oxidative degradation presents in equation 2.10.

2.5 Oxidative Degradation of Organic Pollutants by UV/H_2O_2 Process

Advance Oxidation Processes or Technologies (AOPs or AOTs: Glaze, 1987; Glaze et al. 1987; Huang et al. 1993; Legrini et al. 1993; Bolton and Cater, 1994), have been defined as the chemical oxidation technologies that rely on a formation of the hydroxyl radical ($OH^{\bullet}$, E^0 = 2.8 V) to further oxidize organic and/or inorganic contaminants. Usually, AOPs are integrated with conventional chemical or biological processes as a pre-oxidation or polishing step to increase overall effectiveness of the treatment. There are several AOPs which are UV/H_2O_2, UV/TiO_2 and UV/Fe^{2+}/H_2O_2 Processes, etc.

These processes offer several advantages primarily that they do not produce sludge and are effective at short reaction time. Moreover, an advantage of AOPs over activated carbon and air stripping is that, if effective, the contaminant is degraded into other compounds, removing the contaminant from the environment, not just from the aqueous phase. A disadvantage of any chemical or biological degradative treatment method including AOPs is the potential for forming by-products with higher toxicity than the original contaminant. Ultimately these by-products will probably also be mineralized by the AOPs, but the rates may be economically unfavorable. An additional complication is that the by-product distribution may depend on the characteristics of the water being treated.

The UV/H_2O_2 is one of AOPs that has been proved very effective in treatment of various hazardous organic pollutants in water. For example, the UV/H_2O_2 treatment has been shown to degrade 99.9% of various contaminants found in water, including benzene (Weir et al. 1987), trichloroethene (Weir and Sundstrom, 1993), pesticides (Beltrán et al. 1993, 1996) and acetone (Stefan et al. 1996) although the rates of parent compound transformation differ widely. AOPs have also been proposed for color removal and degradation of dyes. Particularly, these techniques have been found suitable for azo-type dyes, which are the most used textile colorants (Ince et al., 1997; Chun and Yizhong, 1999; Fung et al., 1999; Rott and Minke, 1999; Stock et al., 2000).

The UV/hydrogen peroxide process has been investigated by Aleboyeh et al., (2003) using a continuous photochemical reactor with a 15 W low pressure mercury lamp. It was found that the rate of decolorization rises by increasing the initial dosage of H_2O_2 up to a ‘‘critical’’ value at which it is maximum and beyond which it is inhibited.

Rafael et al. (2002) reported that acetone (C_3H_6O) removal efficiency of 96% was achieved within 60 min at optimum concentration of hydrogen peroxide approximately 100 ppm (C_3H_6O: H_2O_2 =20).

The results of UV/H_2O_2 advance oxidation of reactive dyebath, proposed by Alaton et al. (2002) shows that complete color removal could be achieved after only 10 min of oxidation.

An advanced oxidation treatment, UV/H_2O_2, was applied to an azo dye, Hispamin Black CA, and widely used in the Peruvian textile industry. Rates of color removal and degradation of the dye have been evaluated. A strongly absorbing solution was completely decolorized after 35 min of treatment, and after 60 min an 82% reduction of the total organic carbon (TOC) was obtained. It has been found that the degradation rate increased until an optimum value, beyond which the reagent exerted an inhibitory effect. The degradation rate was also a function of pH (Cisneros et. al. 2002).

The UV/H_2O_2 oxidation process for the removal of humic acids in water has been studied by Wang et al. (2001). UV photolysis alone play an important role in the degradation of humic acids. The presence of hydrogen peroxide was found to promote the degradation efficiency. However, an excessive dosage of H_2O_2 does not further improve the degradation of humic acids. On the contrary, the lower the H_2O_2 dosage the higher the amount of humic acids can be removed. Aeration with air does not favor the removal efficiency of humic acids as the oxidation lasts for a sufficiently long time. The presence of carbonate species deteriorates the humic acids’ removal, whereas it results in a larger amount of H_2O_2 decomposition.

The degradation rate of 4-nitrophenol was found to be slightly dependent of pH. The apparent first order rate constant of 4-nitrophenol degradation was $5.85x\ 10^{-4}$; $5.14x\ 10^{-4}$; $6.38 \times 10^{-4}\ s^{-1}$ at pH 3.0, 7.0 and 9.5 respectively. The degradation rate of 4-nitrophenol is definitely dependent on concentration of hydrogen peroxide (Trapido and Kallas, 2000).

The UV/H_2O_2 treatment resulted in >99.9% removal of MTBE after 75 min of reaction with the major purgable by-product identified as tert-butyl formate (TBF). The second order rate constant for the degradation of MTBE from the hydroxyl radical was estimated to be $3.9\ (\pm 0.73) \times 10^9\ M^{-1}s^{-1}$ (Paulette and Thomas, 2000).

Phenol degradation with a UV/H_2O_2 advanced oxidation process was studied in a completely mixed, batch photolytic reactor (Alnaizy and Akgerman, 2000). The experimental results indicated that there is an optimum H_2O_2:phenol molar ratiowas in the range of 100-250. At initial phenol concentrations of approximately 200 ppm, phenol completely disappeared in less than 1 h at 27°C by the UV/H_2O_2 process, however, only approximately 20% of phenol was mineralized to CO_2 and water and the rest was converted to the reaction intermediates. A sufficient amount of hydrogen peroxide was necessary, but a very high hydrogen peroxide concentration inhibited the photoxidation rate. No pH effect was observed in the pH range of 4-10. In addition, results showed that as the initial contaminant concentration increased, the efficiency of the UV/H_2O_2 AOPs decreased.

The oxidation of metol (N-methyl-p-aminophenol) in aqueous solution by means of a UV/H2O2 system has been studied (Andreozzi et al. 2000) in the pH range 3.0±9.0. The results of this investigation indicated that the pH, H_2O_2 and substrate concentration and oxygen presence significantly influence the system behavior.

The results showed that Natural Organic Matter (NOM) oxidation and H_2O_2 decomposition on UV/H_2O_2 system followed first-order and zero-order reaction kinetics, respectively. The optimum H_2O_2 dose was found to be 0.01% for the oxidation of humic acids in this study. Carbonate and bicarbonate ions inhibited the degradation of humic acids (Gen-Shuh Wang et al. 2000).

The results of the direct pre-treatment with UV/H_2O_2 process revealed that the recalcitrant compounds presented in petrochemical wastewater would be destroyed to small molecules and might reduce some degree of activity inhibition to bioculture (Lain-Chuen Juang et al. 1997).

2.6 UV/H_2O_2 Process and Factors that affect Efficiency

The production of hydrogen hydroxyl radicals within a UV/H_2O_2 system can be affected by variables such as temperature, pH, concentration of hydrogen peroxide (a molar ratio of pollutant to hydrogen peroxide, Pollutant: H_2O_2), initial concentration of pollutant and presence of hydroxyl radical scavenger species.

2.6.1 Influence of Hydrogen Peroxide Concentration

During the UV/H_2O_2 process the concentration of the organic compounds directly influence the optimum H_2O_2 dosage for oxidative performance. The two effects of hydrogen peroxide on UV/H_2O_2 photooxidation were clearly seen. Firstly, the positive influence on the process, when H_2O_2 is applied below the optimum dosage, increasing its dosage improves the oxidative performance. While if the H_2O_2 dosage is higher than optimum dosage it may result in lower oxidation efficiency (Benitez et al. 2001; Alnaizy and Akgerman, 2000; Ku et al. 1998; Sapach and Viraraghavan, 1997). In agreement with Wang, et al. (2001) who reported that the excessive dosage of H_2O_2 does not further improve the degradation of humic acids by photo degradation in the presence of H_2O_2. Secondly, the positive influence on the process, when high dosage of H_2O_2 was applied, it can act as scavenger (more detail in 2.7.4)

The effect of H_2O_2 concentration can be expressed in term of the ratio of pollutant: H_2O_2. This ratio is varied depending on types of organic pollutant. For example, an optimum batch added H_2O_2 concentration appears to be at the value of 100 ppm dose for removal of approximately 5 ppm of acetone (acetone: H_2O_2 is 1: 20) (Rafael et al. 2002). The same ratio was also reported by De Laat et al. (1999) using in the oxidation of acetone. The result of the oxidation experiment indicated that the removal efficiency of dissolved organic compound (DOC) by UV/H_2O_2 process was about 51 % under the concentration ratio of acetone:H_2O_2 as 1: 20 with incident photonic flux at 253.7 nm. In the ethylenediaminetetra acetic acid (EDTA) degradation by UV/H_2O_2 process at pH 2 the optimized experiment conditions of H_2O_2: EDTA molar ratio was 1: 10 with the mineralization ratio higher than 90 % at reaction time of 6 min.

However, the optimum concentration of hydrogen peroxide in the system will depend on the rate constant for the reaction of hydroxyl radical with the contaminant of interest (Rafael et al. 2002).

2.6.2 Influence of Initial Concentration of Pollutant

The efficiency of the UV/H_2O_2 process decreases drastically with increasing pollutant concentration. For heavily polluted effluents, high dose of H_2O_2 are required as stated in the advanced oxidation of synthetic dyehouse (Arslan et al. 1999).

Wang, et al. (2001) proposed that the higher the humic concentration the higher the residual H_2O_2. Two possible ways can lead to such a result. First, higher humic concentration can compete with H_2O_2 for more UV light photons and thus reduce light absorption by H_2O_2 to a greater degree. As a result, the residual H_2O_2 is relatively higher. Second, the higher H_2O_2 residue at higher humic concentration might be due to the generation of H_2O_2 over the reaction period. This was evidenced in some literature that H_2O_2 might form as a by-product of sunlight-induced reactions in natural waters (Cooper et al. 1989; Hoigne et al. 1989). In addition, as reported by Liao (1993), H_2O_2 was generated at a level proportional to the exposure time when the solution with the presence of Aldrich humic acids was irradiated by UV light; this can further lead to the photoproduction of $OH^{\bullet}$ Moreover, the UV-irradiated natural organic solute was also reported to result in the production of hydrated electrons, which can react with dioxygen and protons to form H_2O_2 (Zeppi et al. 1987).

2.6.3 Influence of pH

During the photo-oxidation processes pH of the reaction medium is decreased due to formation of acidic species (Andreozzi, et al. 1999; Crittenden, et al. 1999). The pH effect is due to the acid-base decomposition of hydrogen peroxide which is undesirable in UV/H_2O_2 system because it consumes hydrogen peroxide without generating hydroxyl radical. Furthermore, a reduction of $OH^{\bullet}$ production was present at pH 11 as a result of the base catalyzed reaction.

$$H_2O_2 + OH^- \longrightarrow HO_2^- + H_2O \quad pKa = 11.6 \qquad (2.11)$$

$$H_2O_2 + HO_2^- \longrightarrow H_2O + O_2 + OH^- \qquad (2.12)$$

This phenomenon was affected by the ionization of H_2O_2, whose pKa was 11.6. H_2O_2 molecular species was dissociated into the perhydroxyl ion, and plenty of dissolved oxygen was generated from H_2O_2 (reaction 2.11 and reaction 2.12). Without enough

$OH^{\bullet}$, the efficiency of UV/H_2O_2 process was reduced (Juang et al. 1997). Therefore, it is important to adjust the pH of the treated water at value which enables achieve the highest efficiency of pollutant abatement.

The degradation of organic pollutants by UV/H_2O_2 process was observed to be dependent of pH (Trapido and Kallas, 2000; Yung et al. 1995). As reported in several previous studies; the efficiencies of UV/H_2O_2 processes were observed to decrease for higher pH, while were not affected by pH below 8 (De Laat et al. 1994); the results of H_2O_2/UV-C oxidation of reactive dyebath showed that the process was strongly suppressed by increasing the reaction pH (Idil Arslan Alaton et al. 2002).

Beltran et al. (1996) and Stefan et al. (1996) observed that direct photolysis contributions decreased when pH increased from 2 to 7 and then efficiency increased to 60% at pH 12. In addition, they reported that the initial rate of acetone removal was independent of pH in the range of 2-7. At pH 10, the initial rate was inhibited. This was explained in terms of hydrogen peroxide dissociation in alkaline media. Also, the fast reaction of hydroxyl radicals with hydrogen peroxide was responsible for the observed decrease in phenol destruction in acidic media.

Lipczynska-Kochany (1993) studied phenol oxidation by the UV/H_2O_2 process and observed no significant effects in the pH range from 7.0 to 9.0. On the other hand, phenol degradation and catechol formation decreased rapidly at pH 7 and pH 9. This observed decrease was probably due to the fast decomposition of hydroxyl radicals and hydrogen peroxide at high pH (Christensen et al., 1982).

In the advanced oxidation of synthetic dyehouse effluent by UV/H_2O_2 process, the experiment was conducted at various pH values (2.5-11.5) and H_2O_2 concentrations (0.1-100 mM) for an hour reaction time. The control experiments were conducted by the application of UV irradiation alone and 10 mM H_2O_2 alone at pH 7 in the same reaction period. For all examined treatments, pH value did not change more than one digit during the experiments, since the reaction solution was buffered heavily by its high carbonate content (Arslan et al. 1999).

However, the effect of pH on the efficiency of hydroxyl radical production and its final degradation reaction depends on the nature of contaminant. It is found that degradation rate was pH dependent and it was varied form type to type of organic pollutants (Legrini et al. 1993; Chu et al. 2001). It is also reported that the decay of 2,4-D was pH dependent in UV/H_2O_2 process.

2.6.4 Influence of Hydroxyl radical Scavengers Presence

Hydroxyl radical scavengers (bicarbonate, carbonate, phosphate, and chloride) presented in many effluents can drastically reduce the efficiency of pollutant oxidation in direct proportion to their concentration via the reaction (Duguet et al. 1989) as;

$$OH^{\bullet} + HCO_3^{-} \longrightarrow OH^{-} + HCO_3^{\bullet} \qquad (2.13a)$$

$$OH^{\bullet} + CO_3^{2-} \longrightarrow OH^{-} + HCO_3^{-\bullet} \qquad (2.13b)$$

$$OH^{\bullet} + PO_4^{3-} \longrightarrow OH^{-} + HPO_4^{2-\bullet} \qquad (2.13c)$$

$$OH^{\bullet} + Cl^{-} \longrightarrow OH^{-} + Cl^{\bullet} \qquad (2.13d)$$

The bicarbonate specie was reported to consumed $OH^{\bullet}$ effectively, preventing contaminants from being attacked by $OH^{\bullet}$ in UV/H_2O_2 (Liao and Gural, 1995)

It was indicated that the hydroxyl radicals were scavenged by inorganic ions of alkalinity, such as CO_3^{2-}, and HCO_2^{-} ions. Additionally, low potential radicals e.g. $HO_2^{\bullet-}$, were produced at a large amount of hydrogen peroxide solution and HO_2^{-} formed resulting in the decreasing of the photodecomposition of organics (Schultei et al. 1991; Kochany and Bolton, 1992)

Since it is already well establish that H_2O_2 itself can act as an effective $OH^{\bullet}$ scavenger at the concentrations that are specific for the pollution in question (Walling, 1975). The excessive amount of H_2O_2 can serve as significant scavengers of the hydroxyl radical, resulting in the limitation of the rate of forming hydroxyl radical (see equation 2.5-2.7) (Arslan et al. 1999; Baxendale and Wilson, 1957; Hong et al. 1996; Zappi, 1995; Christensen H. et al. 1982). As presented in equation 2.5 – 2.7, hydrogen peroxide reacts with the hydroxyl radical with rate constant of 2.7×10^7 l/mol.s (Hong et al. 1996). The negative effect of this reaction will depend on the residual concentration of hydrogen peroxide in the system.

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Chemicals

Formaldehyde (CH_2O, 40% m/v) and Hydrogen peroxide (H_2O_2, 30% m/v) were purchased from Carlo erba chemical. Sodium sulfite (Na_2SO_3), sulfuric acid (H_2SO_4, 96%), sodium hydroxide (NaOH) were purchased form Merck chemical. All chemicals were used as received. Enzyme catalase was purchased from Sigma.

3.1.2 Photochemical reactor

A 1-litre photochemical batch reactor was used in all performed experiments. The photoreactor consists of outer and inner compartments. The inner part is an angular quartz vessel for 254 nm low pressure mercury lamp with 10 watts. This inner well is jacketed to permit a water flow for cooling purpose. The outer quartz compartment is the solution receiving well with two sampling ports. This system is well agitated by stirrer bar. The picture of photochemical reactor is provide in Figure 3.1

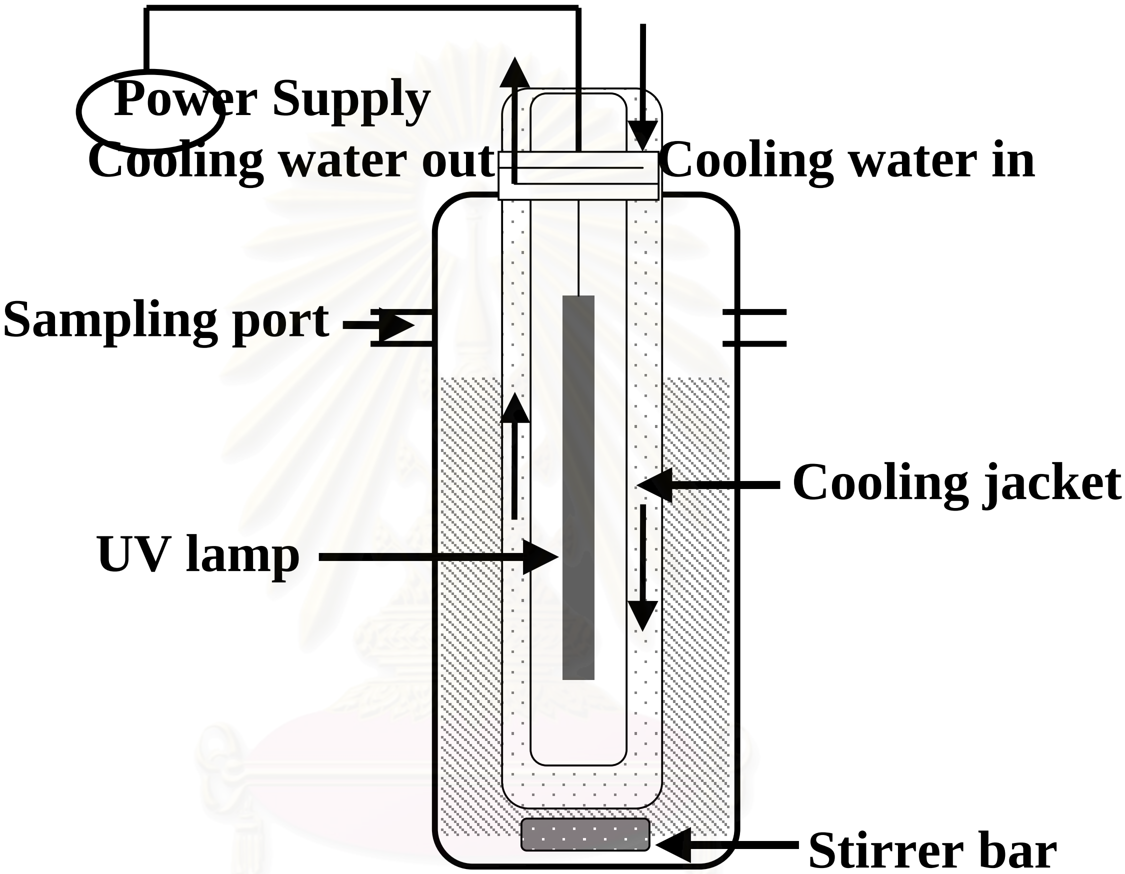


Figure 3.1 Photochemical reactor used in this study

3.2 Experimental Procedure

The experiment divided into 2 parts:

Part 1. Investigation on optimum conditions for formaldehyde degradation:

1.1 Optimum conditions for acidic pH

1.2 Optimum conditions for neutral pH

1.3 Optimum conditions for basic pH

Part 2. Investigation on effect of initial concentrations of formaldehyde on removal efficiency

Part 1: Investigation on optimum conditions for formaldehyde degradation

To study the degradation of formaldehyde in synthetic formalin solution, the optimum molar ratio of pollutant to hydrogen peroxide concentration at each studied pH had to be investigated. Amounts of H_2O_2 were varied as the ratio of formaldehyde: hydrogen peroxide at the values of 1:0.1, 1:0.5, 1:1, 1:2 and 1:3 mol/l, respectively, to investigate the effect of H_2O_2 concentration on pollutant removal efficiency. At each pH, the effect of molar ratio was investigated. The studied pH included acidic (at pH of 3 and 5), neutral (at pH of 7), and basic conditions (at pH of 9). From these studies, the optimum conditions for treating formaldehyde in synthetic formalin solution in each pH solution were obtained. The experimental details of this part were as followed:

(1) Filled the 1 liter-reactor with synthetic formalin solution containing 10,000 mg/l of formaldehyde.
(2) Adjusted pH value of solution to a desire pH value (3, 5, 7 or 9).
(3) Added the calculated amount of H_2O_2 to the solution. The added hydrogen peroxide was varied corresponding to 10,000 mg/l (0.33 M) of formaldehyde where the molar ratios of formaldehyde to hydrogen peroxide were 1:0.1, 1:0.5, 1:1, 1:2 and 1:3 mol/l, respectively.
(4) Turned on the UV lamp to irradiate the solution.
(5) Taken the sample for analysis at 0, 5, 10, 15, 30, 60, 90, 120, 150, 180, 240 and 300 min of reaction period.

Note that the experiments were conducted by varying the molar ratio of formaldehyde to hydrogen peroxide at each ratio at acidic pH solution first, then at neutral and basic pH solution. The acidic pH solutions were 3 and 5. The neutral pH solution was 7 and basic pH solution was 9. In this research the wide range of conducted pH from 3-9 was correspondent the pH of real wastewater that might occurred.

The analysis parameters of this study included pH, hydrogen peroxide residual, total organic carbon, and toxicity, which were conducted as explained in the sample analysis section. The condition that provided the best performance of formaldehyde degradation, which were molar ratio of formaldehyde to hydrogen peroxide, initial pH, the profile of formaldehyde residual with time and the profile of hydrogen peroxide residual with time, were reported from these studies.

Part 2: Investigation on the effect of initial concentration of formaldehyde on removal efficiencies

The initial concentrations of formaldehyde were varied to correspond to the concentrations that might found from real wastewater, which were 1,000, 3,000, 5,000, 10,000 and 30,000 mg/l. The condition that provide the best performance in formaldehyde degradation such as optimum pH and the molar ratio of formaldehyde to hydrogen peroxide from the earlier experiment set was applied for this set of experiments. The experimental details were as shown below.

(1) Filled the 1 liter-reactor with synthetic formalin solution containing the interested amount of formaldehyde: 1,000, 3,000, 5,000, 10,000, and 30,000 mg/l.
(2) Adjusted pH value of solution to the optimum value obtained from the first part
(3) Added the calculated hydrogen peroxide to the solution by using the optimum ratio of formaldehyde to hydrogen peroxide remove obtaining previous study
(4) Turned on the UV lamp to irradiate the solution.
(5) Taken the sample to analyze at 0, 5, 10, 15, 30, 60, 90, 120, 150, 180, 240 and 300 min of reaction period.

The parameter analysis was conducted as stated earlier in part 1. From this experiment set, the effect of initial concentration of formaldehyde was obtained. The profiles of formaldehyde removal efficiency with time were reported and the rates of formaldehyde removal correspondence with initial concentration of formaldehyde were calculated.

3.3 Analytical Measurement

At appropriate time intervals, samples were taken from the reactor into glass vials. The samples were immediately analyzed to avoid further reaction. Enzyme catalase was also added to each sample to decompose hydrogen peroxide residue, preventing hydrogen peroxide from reacting with organic substrates during the analysis. The standard iodometric method was performed to determine the hydrogen peroxide residual concentrations. The concentrations of formaldehyde residue were determined by gas chromatography equipped with flame ionization detector (GC-17A Shimadzu with AT^{TM}-Aquawax glass capillary column 30m. x 0.25 mm. x 0.25 µm film thickness). The analytical conditions were set as follows: the injector and detector temperatures were 170°C and 250 °C, respectively; the column temperature programming was 35°C for one min, 40°C for 3 min with the ramp temperature rate at 0.8°C/min, and 110°C for 5 minutes with ramp temperature rate at 16 °C/min. The elution time of 1.85 minute was used for identifying formaldehyde peak. Helium was used as carrier gas. The injection sample volume was 2 µl with 20% split mode. The concentrations of formaldehyde were calculated from corresponding peak area. An initial and treated TOC were analyzed with Shimadzu 700 TOC ANALYZER 0-1 Analytical. Toxicity of samples were carried out by LUMIStox 300 according to ISO 1134 part 1, 2, 3 (1998).Toxicity was measured using freeze-dried luminescent bacteria (*Vibrio fisheri.*) The natural light emission of these bacteria was measured. The inhibition of the light emission in the presence of the sample was determined against a non-toxic control.

3.4 Experimental Chart

The experimental activity chart is provided in Figure 3.**2**

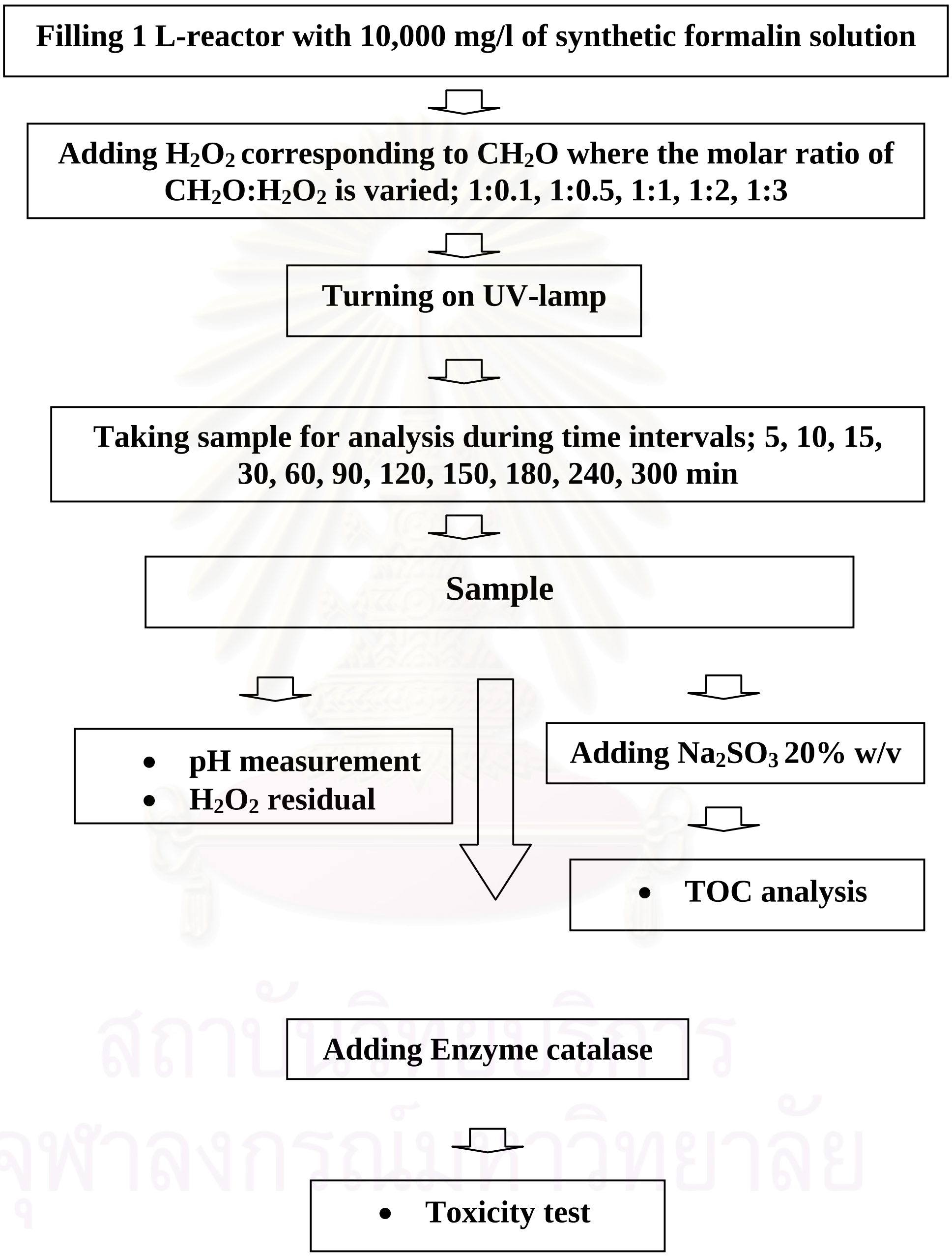


Figure 3.2 Experimental activities Chart

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Degradation of Formaldehyde by Photolysis Process

Formaldehyde is known as volatile organic compound, its boiling point and vapor pressure are 97˚C and 220 kPa at 0˚C (Hazardous Substances Data Bank, 1994; CRC Handbook of Chemistry and Physics, 1994). In addition, formaldehyde volatilization tends to be promoted due to well agitation of UV/H_2O_2 system. Thus, in order to quantify possible losses of formaldehyde to the UV reactor system via volatilization, a dark reaction experiment was conducted in absence of UV radiation and hydrogen peroxide. Another experiment was conducted to quantify amount of formaldehyde loss as a result of interaction between formaldehyde itself and hydrogen peroxide. In addition, it is known that organic contaminant can well adsorbed light in the ultraviolet wavelength, thus, the photolysis of organic contaminant is expected. In this study the first set of experiment was conducted to investigate the amounts of disappearing formaldehyde by volatilization, interaction between formaldehyde itself and hydrogen peroxide reaction, and photolysis processes. In comparison, one experiment of formaldehyde degradation by UV/H_2O_2 was performed to show the different among these four obtaining results.

Role of hydroxyl radicals in the decomposition of formaldehyde was clearly demonstrated in this first experimental set, with a group of experiments carried out by hydrogen peroxide alone (H_2O_2), UV radiation alone (photolysis) and by the combination of UV and hydrogen peroxide (UV/H_2O_2 process). This set of experiment was conducted in the same initial condition with 10,000 mg/l (0.333 M) of formaldehyde concentration at pH 5. From Figure 4.1, only 3.2% of formaldehyde was volatilized at the end of reaction. About 43% and 38% of formaldehyde removal was observed after 300 min of reaction by photolysis and reaction of hydrogen peroxide (0.666 M), respectively. The destruction rate of formaldehyde by UV/H_2O_2, with formaldehyde to hydrogen peroxide molar ratio of 1:2 which is same amount of hydrogen peroxide in the earlier cases were employed, shows remarkably decreasing formaldehyde concentrations in comparison to those by photolysis or by hydrogen peroxide alone. Since completely decomposition was achieved after 300 min of reaction, the formaldehyde reduction by volatilization was negligible (96.8% of formaldehyde removal while taking volatilization into account). It was clearly indicated that the presence of hydrogen peroxide in UV radiation enhances the degradation rate significantly compared to photolysis which was directly applied only UV light and interaction of hydrogen peroxide and formaldehyde. This was due to the formation of highly reactive species, hydroxyl radical, via UV/H_2O_2 process that further oxidized the molecules of pollutant. However, in the results and discussions of all experiments from now on, volatilization of formaldehyde will not taken into account.

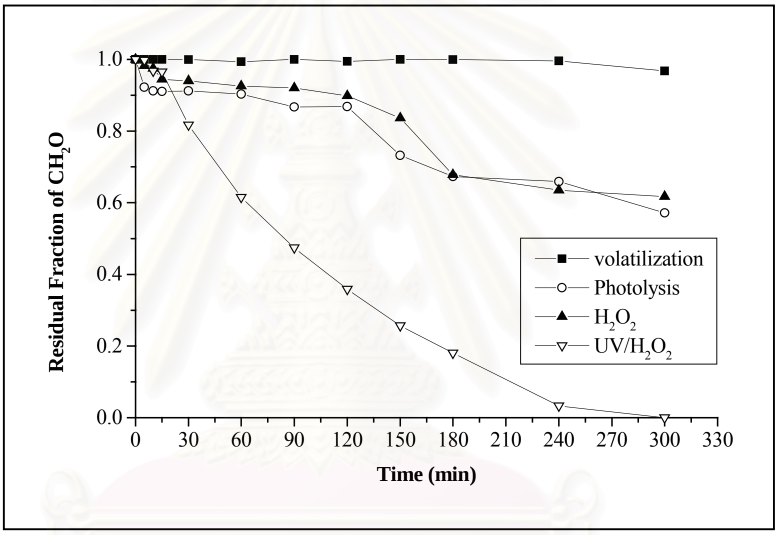


Figure 4.1 Degradation of formaldehyde by volatilization, UV, UV/H_2O_2 and H_2O_2 ($[CH_2O]_0$ = 0.333 M, CH_2O:H_2O_2 = 1:2, initial pH = 5)

4.2 Degradation of Formaldehyde by UV/H_2O_2 in Acidic Aqueous Solution

To stimulate the real wastewater characteristics that might occur, various initial pH values was varied from acidic region to neutral and finally to the basic region at pH of 3, 5, 7 and 9, respectively. In this part, all experiments were performed under UV/H_2O_2 system with initial concentration formaldehyde of 0.333 M by employing the varied amount of hydrogen peroxide in accordance with the ratio of formaldehyde to hydrogen peroxide at the values of 1:0.1, 1:0.5, 1:1, 1:2 and 1:3, respectively. The initial pH levels of 3 and 5 were selected to study formaldehyde removal efficiency of UV/H_2O_2 in acidic aqueous solution

4.2.1 Degradation of Formaldehyde at pH 3

Results of the formaldehyde degradation by UV/H_2O_2 in acidic aqueous solution at pH 3 are shown in Figure 4.2 (a) for profile of the residual fraction of formaldehyde, (b) for profile of the residual hydrogen peroxide, (c) profile of the residual total organic carbon, and (d) for profile of pH in UV/H_2O_2 system.

Figure 4.2 (a) illustrates the residual fractions of formaldehyde as a function of the irradiation times at different doses of added hydrogen peroxide. The lowest formaldehyde degradation was observed at 1:0.1 of formaldehyde to hydrogen peroxide molar ratio. The efficiency of formaldehyde degradation was reflected by the value of the residual fraction of formaldehyde. The degradation efficiency was increasing with the increasing of hydrogen peroxide concentration (small value of formaldehyde to hydrogen peroxide molar ratio). This improvement of formaldehyde degradation was continually increased until the formaldehyde to hydrogen peroxide molar ratio reaches the value of 1:2. Beyond this value the degradation was reduced. From graph, the highest efficiency was achieved with the ratio of formaldehyde to hydrogen peroxide ratio with the value of almost 100% removal efficiency.

(a)

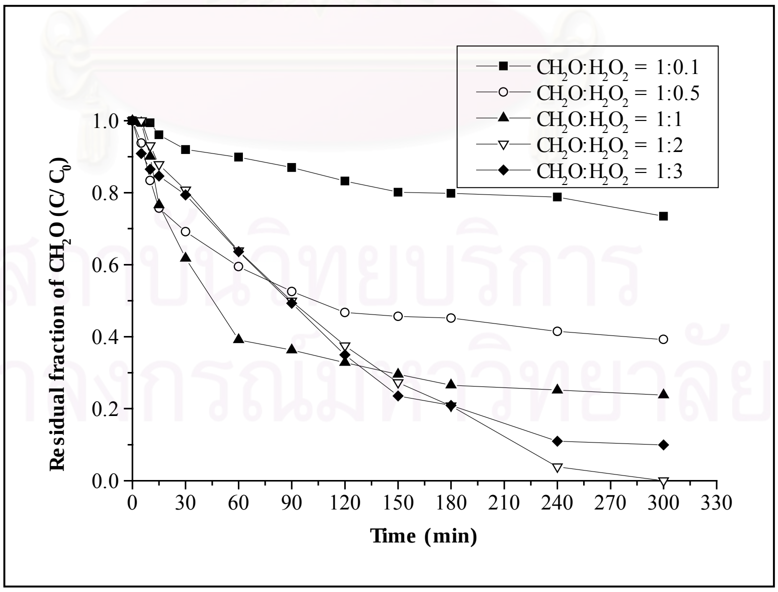


Figure 4.2 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 3). **(a)** Residual fraction of formaldehyde

The different of formaldehyde decreasing pattern was subject to reflected amount of hydrogen peroxide as seen from Figure 4.2 (b). The profile of residual fraction of hydrogen peroxide for each ratio of formaldehyde to hydrogen peroxide molar ratio is also presented. Insufficient hydrogen peroxide concentrations were observed in conditions of 1:0.1, 1:0.5 and 1:1 formaldehyde to hydrogen peroxide molar ratio, hydrogen peroxide was completely consumed by formaldehyde at these ratios within 120 min of the irradiation period. Whereas at the molar ratios of 1:2 and 1:3 formaldehyde to hydrogen peroxide, the excess amounts of hydrogen peroxide were seen, approximately 65% and 20% residual hydrogen peroxide presented in solution. This finding indicated that with the excess amounts of added hydrogen peroxide, the drastically reduced of formaldehyde degradations were seen. It was clearly showed that, hydrogen peroxide can act as hydroxyl radical scavenger at the concentrations (as molar ratio of formaldehyde to hydrogen peroxide) higher than optimum concentration which was 1:2 molar ratio of formaldehyde to hydrogen peroxide.

(b)

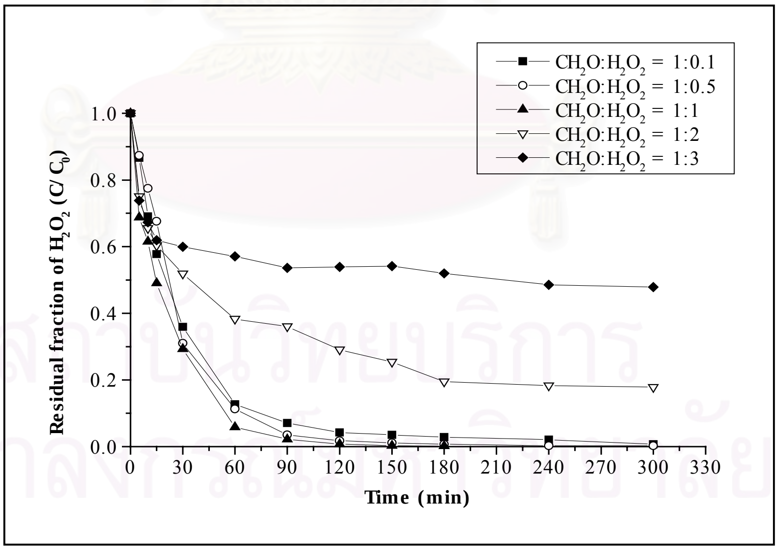


Figure 4.2 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 3). **(b)** Residual fraction of hydrogen peroxide

The slight reduction of total organic carbon was observed for all experiments and it was not an exception for the best condition that achieved the highest removal efficiency in this acidic solution pH (at the molar ratio of 1:2 formaldehyde to hydrogen peroxide). As it was indicated in Figure 4.2 (c), roughly about 80% of TOC still remained in solution for all experiment studied.

(c)

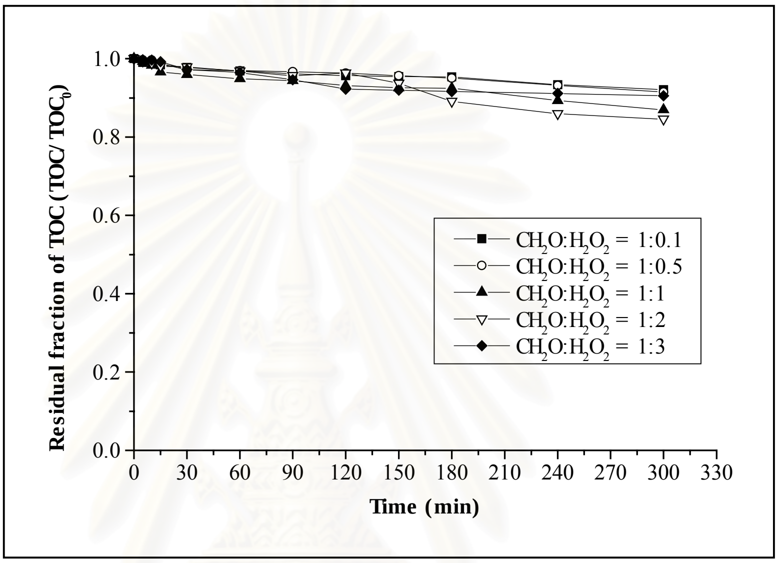


Figure 4.2 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 3).**(c)** Residual fraction of TOC

Finally, in Figure 4.2 (d), profiles of pH were monitored during formaldehyde degradation by UV/H_2O_2 at initial pH 3 for all conditions. During the experiment, it was observed that the pH values continuously declined and then remained constant, 2.00 ± 0.07, after 30 min of reaction at each molar ratio of formaldehyde to hydrogen peroxide excepted as 1:0.1 and 1:0.5 where the final pH value were 2.52 and 2.20, respectively.

(d)

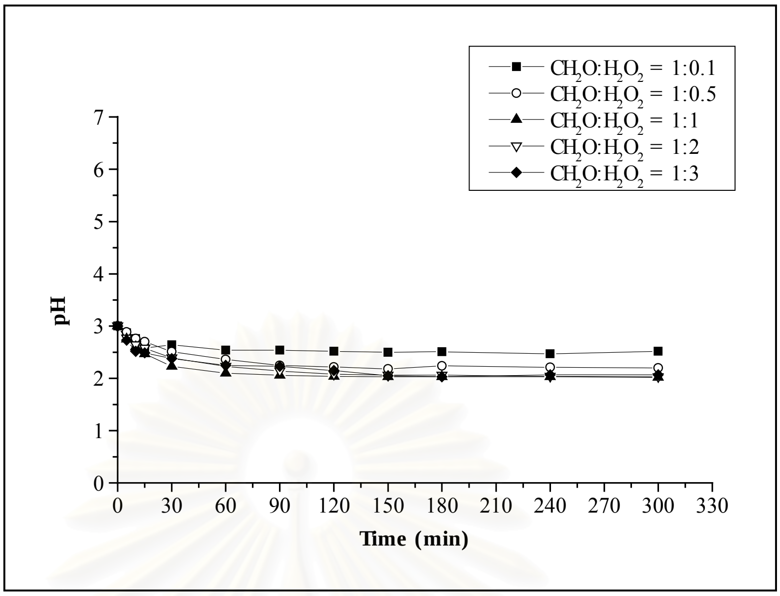


Figure 4.2 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 3). **(d)** pH profile

4.2.2 Degradation of Formaldehyde at pH 5

Another group of formaldehyde degradation experiments by UV/H_2O_2 in acidic aqueous solution was done at initial pH 5. The experiments were performed at five different molar ratios of formaldehyde to hydrogen peroxide as follows: 1:0.1, 1:0.5, 1:1, 1:2 and 1:3. As can be seen in Figure 4.3 (a) the percentage of formaldehyde residuals about 75, 60, 30 and 10 was observed at 1:0.1, 1:0.5, 1:1 and 1:3 molar ratios of formaldehyde to hydrogen peroxide, respectively. All results are given in Figure 4.3. Apparently, none of formaldehyde residual appeared at the end of reaction when 1:2 molar ratio of formaldehyde to hydrogen peroxide was employed.

(a)

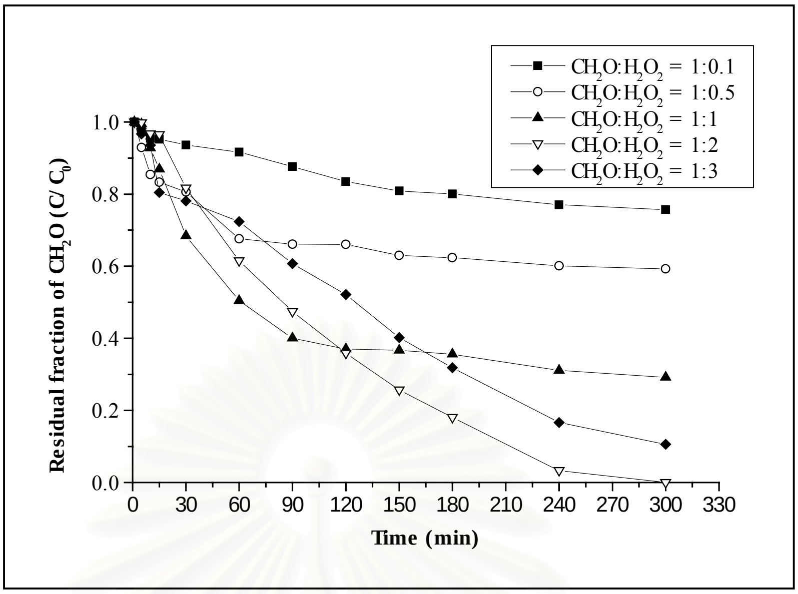


Figure 4.3 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 5). **(a)** Residual fraction of formaldehyde

(b)

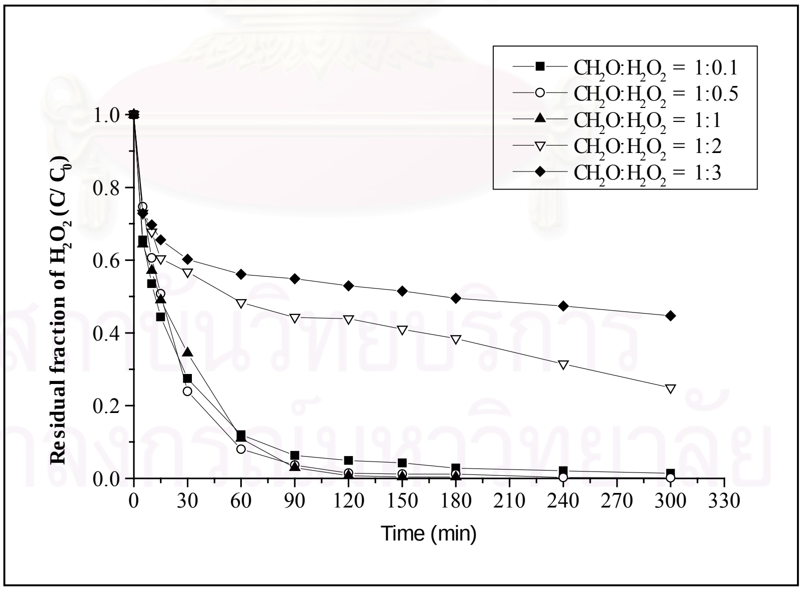


Figure 4.3 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 5). **(b)** Residual fraction of hydrogen peroxide

In view of hydrogen decomposition, Figure 4.3 (b) shows hydrogen peroxide residual as a function of irradiation time. It was indicated that by using 1:2 and 1:3 molar ratios of formaldehyde to hydrogen peroxide, approximately 25% and 45% of hydrogen peroxide remained in solution after 300 min of reaction time. At these ratios, the first 15 min of reaction gave the high dissociation rate of hydrogen peroxide to hydroxyl radical, after that it remained constant in the first ratio and gradually decreased in the latter. On the other hand, by using 1:0.1, 1:0.5 and 1:1 molar ratio of formaldehyde to hydrogen peroxide, nearly completed disappearance of hydrogen peroxide were found at 120 min after high dissociation rate in first 60 min of reaction time.

(c)

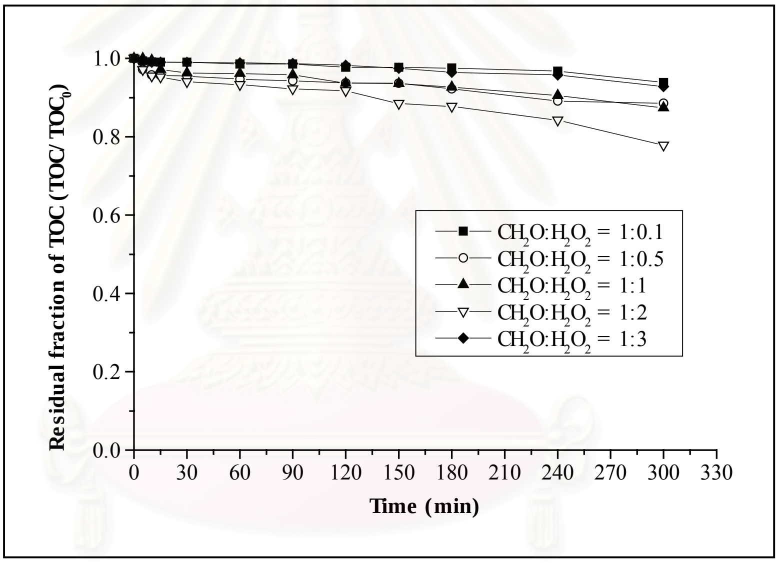


Figure 4.3 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 5). **(c)** Residual fraction of TOC

Total organic carbon (TOC) degradation rate with time at different molar ratios of formaldehyde to hydrogen peroxide in Figure 4.3 (c) presented only a small amount of TOC reduction. The highest TOC reduction rate, 20%, could be expected where there was a high reduction rate on formaldehyde removal (a molar ratio of 1: 2 formaldehyde to hydrogen peroxide).

(d)

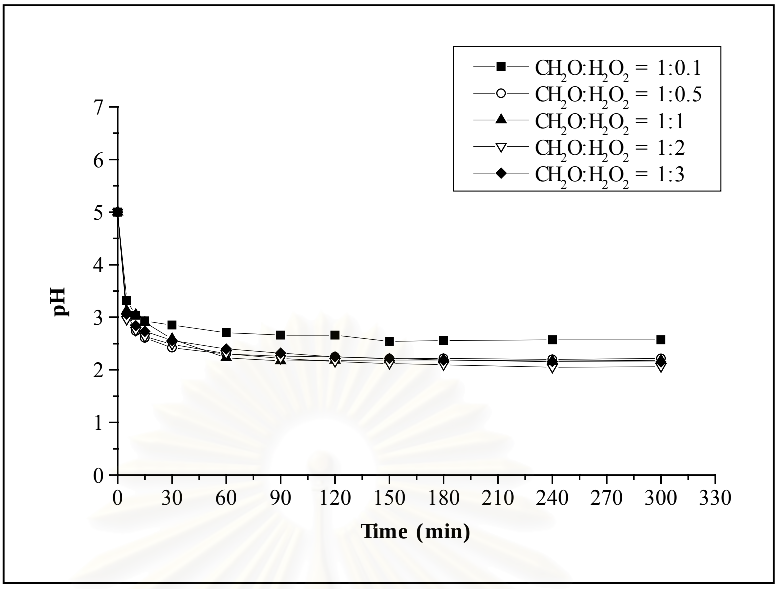


Figure 4.3 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 5). **(d)** pH profile

The pH monitoring during a photooxidation on formaldehyde degradation was investigated. It was found that the pH values of UV/H_2O_2 process on formaldehyde decomposition was rapidly reduced from 5.00 ± 0.02 to 3.00 ± 0.20 in the first 5 min at every molar ratio of formaldehyde to hydrogen peroxide (Figure 4.3 (d)). Since the point of 60 min, the pH remained constant at 2.00 ± 0.20 until the end of the reaction except at a molar ratio of 1:0.1 formaldehyde to hydrogen peroxide whose had a final pH at 2.57.

The results from this experiment set also presented the same findings as pH 3 experiment set that an amount of hydrogen peroxide in the system is the key factor in formaldehyde degradation.

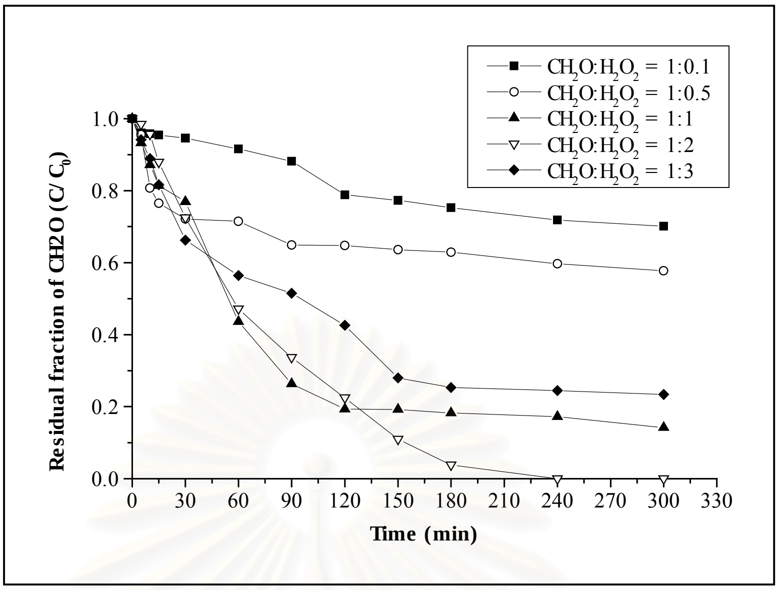
In summary, for formaldehyde degradation using UV/H_2O_2 in acidic pH, both pH 3 and 5 yields almost 100% formaldehyde removal efficiency at an optimum condition 1:2 mole ratio of formaldehyde to hydrogen peroxide within 300 min.

4.3 Degradation of Formaldehyde by UV/H_2O_2 in Neutral Aqueous Solution

The same formaldehyde initial concentration of 10,000 mg/l with earlier experiments was used to investigate formaldehyde degradation at different hydrogen peroxide concentrations in neutral aqueous solution pH 7. Figure 4.4 depicted the results obtained in this group of experiments on formaldehyde degradation by UV/H_2O_2 at pH 7. From Figure 4.4 (a), it can be observed that the best oxidation level was reached in 240 min of the irradiation time at 1:2 molar ratio of formaldehyde to hydrogen peroxide. At this ratio applied, the formaldehyde residuals could not be detected at the end of reaction period. Higher formaldehyde residual can be observed at others conditions as well for example 1:3, 1:1, 1:0.5, 1:0.1 molar ratio of formaldehyde to hydrogen peroxide.

Figure 4.4 (b) depicted the residual fraction of hydrogen peroxide at pH7.With the molar ratio of 1:2 and 1:3 formaldehyde to hydrogen peroxide, the excess amounts of added hydrogen peroxide were seen in UV/H_2O_2 system. On the contrary, the insufficient amounts of hydrogen peroxide were appeared in three conditions, 1:0.1, 1:0.5 and 1:1 molar ratio of formaldehyde to hydrogen peroxide. There was very slight amount of hydrogen peroxide residual about 3 % found at a ratio of 1:0.1 of formaldehyde to hydrogen peroxide, while no amount of hydrogen peroxide was observed at ratio of 0.05 and 1:1of formaldehyde to hydrogen peroxide during the last 180 min.

(a)



(b)

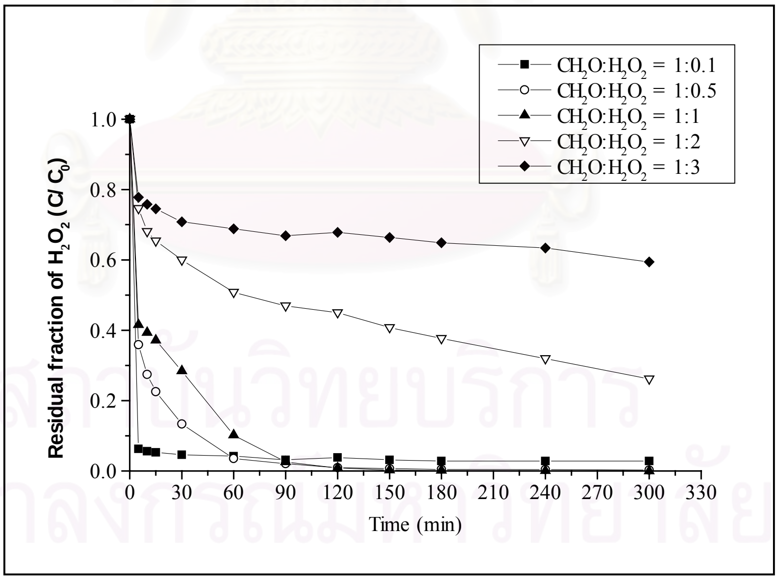


Figure 4.4 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 7).**(a)** Residual fraction of formaldehyde **(b)** Residual fraction of hydrogen peroxide

(c)

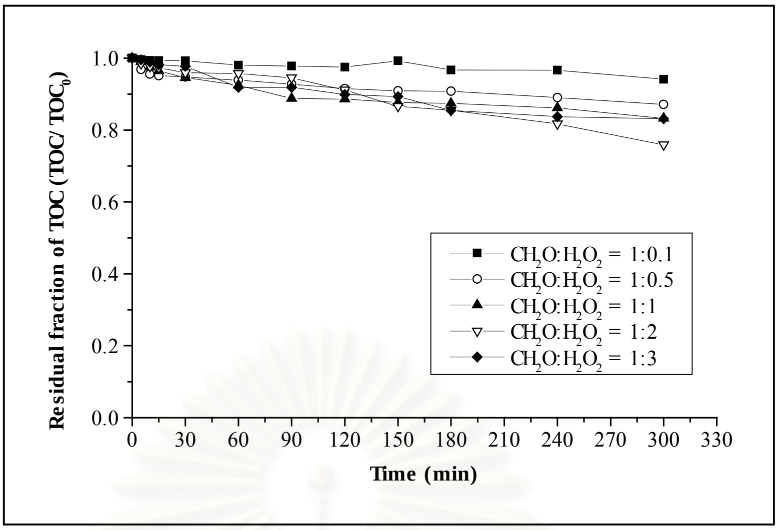


Figure 4.4 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 7). **(c)** Residual fraction of TOC

Figure 4.4 (c) shows the results of TOC removal as a function of reaction time. It was found that the total mineralization was not accomplished since there were rather high amounts of TOC residuals that remained in the treated solution. Even in the employed condition that produced the highest rate of TOC removal, 1:2 of formaldehyde to hydrogen peroxide 76% of TOC residual was left in solution.

In pH measurements performed during the experiment, it was observed time required to drop the pH down from the initial value of 7.00 ± 0.02 to 3.00 ± 0.35 (Figure 4.4 (d)) was only 5 min. Beyond that, pH was unchanged from the 60 min mark to the end of reaction time at the value of 2.00 ± 0.22 in most cases of the molar ratio of formaldehyde to hydrogen peroxide applied, except for 1:0.1 whose had the final pH at value of 2.62.

(d)

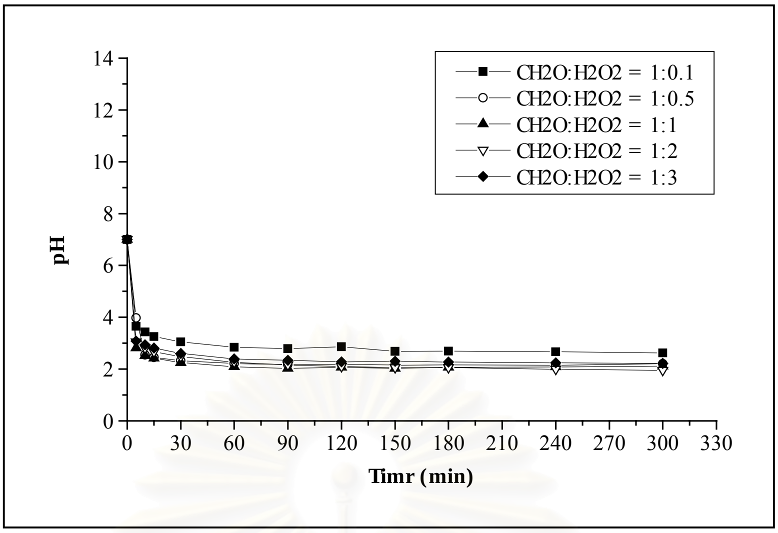


Figure 4.4 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ([CH_2O]$_0$ = 0.333 M, initial pH = 7). **(d)** pH profile

In summary, formaldehyde degradation using UV/H_2O_2 in neutral pH 7 yielded almost 100% formaldehyde removal efficiency at an optimum condition of 1:2 mole ratio of formaldehyde to hydrogen peroxide within 240 min of the reaction period.

4.4 Degradation of Formaldehyde by UV/H_2O_2 in Basic Aqueous Solution

The initial condition of pH 9 was selected to represent the degradation of formaldehyde by UV/H_2O_2 process in basic aqueous solution, due to the fact that a higher in real wastewater scarcely occurs. As depicted in Figure 4.5 (a), a complete formaldehyde removal did not occur in every molar ratio of formaldehyde to hydrogen peroxide used. The greater to the lower disappearance of formaldehyde residual is sequenced with molar ratios of formaldehyde to hydrogen peroxide employed as 1:2, 1:3, 1:1, 1:0.5 and 1:0.1, respectively.

Figure 4.5 (b) shows the results of hydrogen peroxide residual investigated in alkaline pH; the results of this experiment were almost similar to those appearing in acidic and neutral pH. The only difference in formalin is that high the hydrogen peroxide dissociation rates in the first 5 min of the reaction period were markedly seen in neutral pH region. Especially when 1:0.1, 1:0.5 and 1:1 molar ratio of formaldehyde to hydrogen peroxide was applied; 96%, 78% and 40% of hydrogen peroxide were consumed.

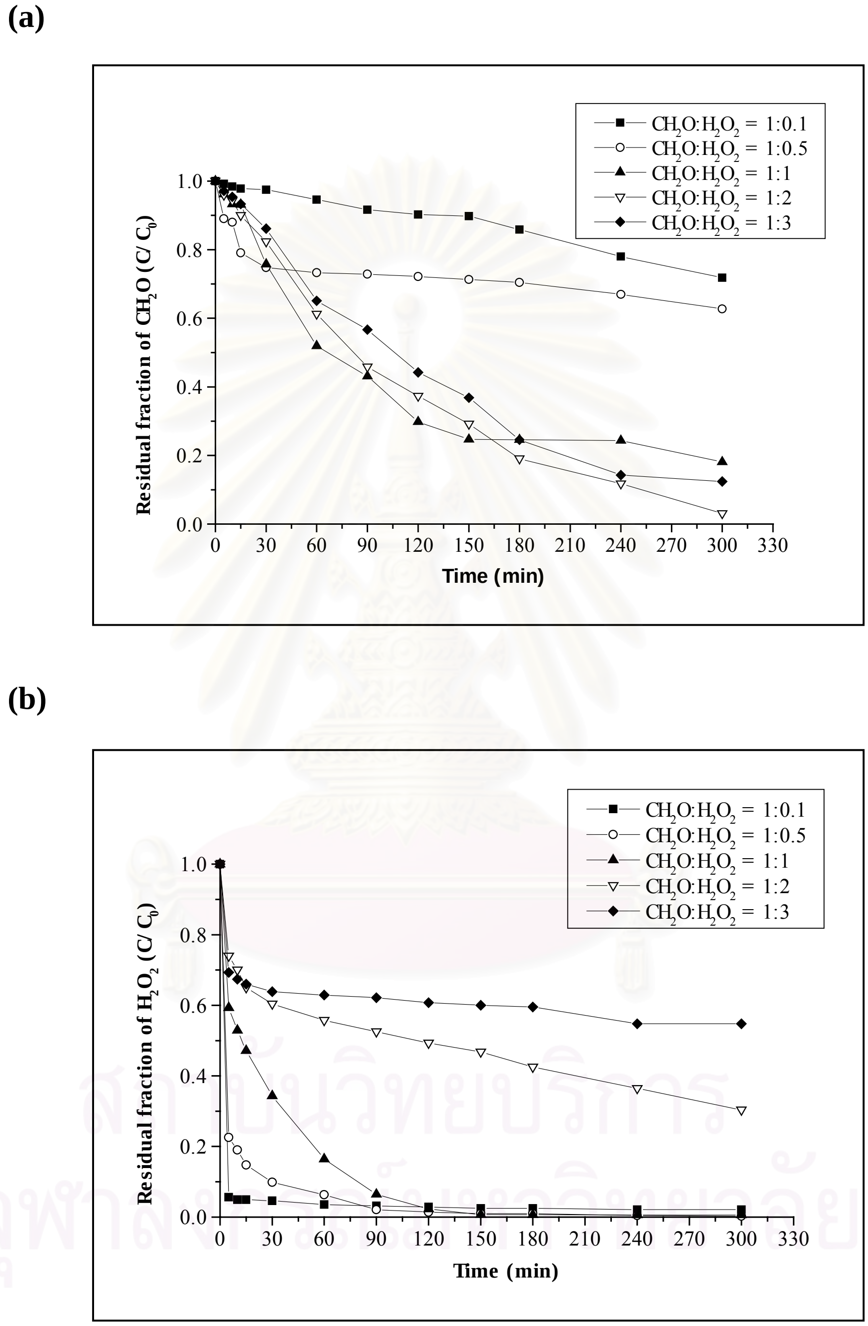


Figure 4.5 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 9).**(a)** Residual fraction of formaldehyde **(b)** Residual fraction of hydrogen peroxide

The efficiency of UV/H_2O_2 on TOC removal was investigated at 10,000 mg/l initial concentration of formaldehyde at five different ratios of formaldehyde to hydrogen peroxide. TOC removal were not distinguish in all experiments only about 10% TOC removals were achieved in the molar ratios of 1:2 and 1: 3 formaldehyde to hydrogen peroxide used while in the other ratios less than 10% of TOC removal was achieved, as can be seen in Figure 4.5 (c).

(c)

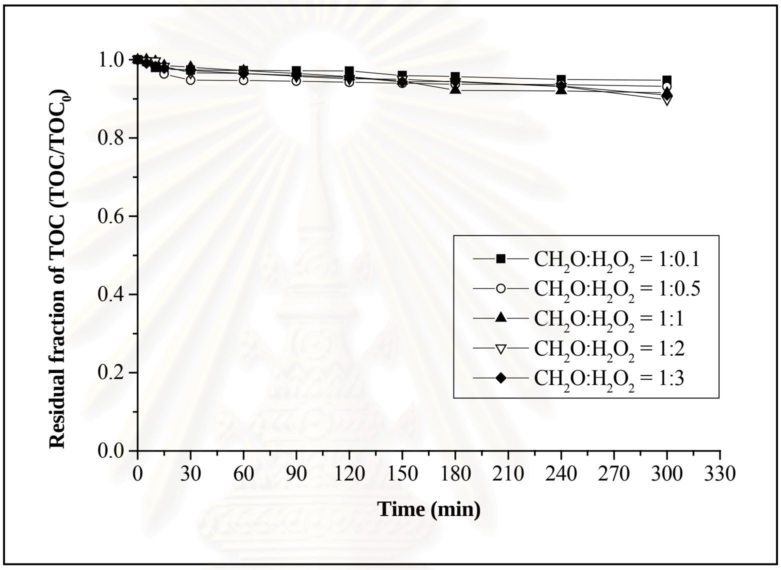


Figure 4.5 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ([CH_2O]$_0$ = 0.333 M, initial pH = 9). **(c)** Residual fraction of TOC

The pH was monitored during formaldehyde degradation using the UV/H_2O_2 process in alkaline pH 9. The profile of pH as a function of reaction period was demonstrated in Figure 4.5 (d). From this finding it took only 5 min to drop the pH down from the initial value of 9.00 ± 0.02 to 3.00 ± 0.3. After this point pH remained rather unchanged from the 60 min mark until the end of the reaction time at values of 2.00 ± 0.30 in most cases of the molar ratio of formaldehyde to hydrogen peroxide applied. The experiment at 1:0.1 molar ratio of formaldehyde to hydrogen peroxide had a pH at 5 min and 300 min at values 4.3 and 2.64, respectively.

In summary, formaldehyde degradation using UV/H_2O_2 in basic pH 9 yielded 97% formaldehyde removal efficiency at an optimum condition of 1:2 mole ratio of formaldehyde to hydrogen peroxide at the 300 min.

(d)

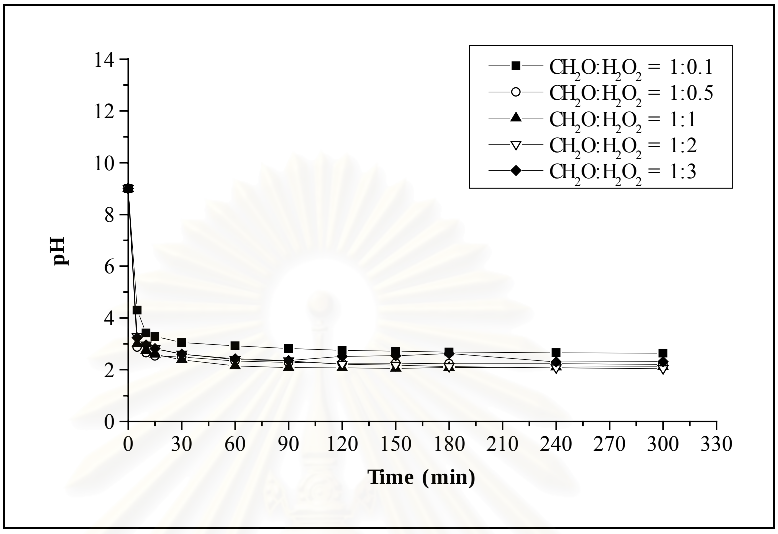


Figure 4.5 Degradation of formaldehyde by UV/H_2O_2 process with different molar ratios of CH_2O: H_2O_2**.** ($[CH_2O]_0$ = 0.333 M, initial pH = 9). **(d)** pH profile

From all results observed, formaldehyde degradation using UV/H_2O_2 in pH ranging from acidic to neutral and finally basic shown that the highest formaldehyde removal efficiency for each pH region was achieved at an optimum condition of 1:2 mole ratio of formaldehyde to hydrogen peroxide. Among these pH ranges, the fastest formaldehyde degradation was observed in the neutral aqueous solution. Thus, 1:2 mole ratio of formaldehyde to hydrogen peroxide at pH 7 is considered the best conditions that provide highest efficiency in shortest time for formaldehyde degradation using the UV/H_2O_2 process.

4.5 Degradation of Formaldehyde as a Function of Initial Concentration

In reality, a wide range of formaldehyde concentrations can be expected to be found in wastewater, therefore, in this set of experiments, degradation of formaldehyde as a function of the initial concentration was performed to observe formaldehyde degradation. In order to investigate the effect of initial concentration on formaldehyde removal efficiency, this experiment set was conducted at a 1:2 molar ratio of formaldehyde to hydrogen peroxide, at initial pH 7, which is the best condition providing the best performance in formaldehyde removal that obtained from earlier section. A wide range from a low to high concentration of formaldehyde: 1,000, 3,000, 5,000, 10,000 and 30,000 mg/l, (or 0.033, 0.099, 0.165, 0.333 and 0.999 M) were the variable initial concentrations applied. The results from this experiment set were shown in Figure 4.6. (a) is the residual fraction of formaldehyde, (b) is the residual fraction of hydrogen peroxide, (c) is the residual fraction of total organic carbon in supernatant and finally, (d) is the measurement of pH through the system.

The results showed that with an initial concentration of 0.033 M, it took only 5 min of the reaction period to complete the formaldehyde destruction. As it was depicted in Figure 4.6 (a), the higher the initial formaldehyde concentration, the longer period was required to attain complete formaldehyde removal. At initial formaldehyde concentrations of 0.033, 0.165 and 0.333 M the required reactions time were 90, 150, 240 min, respectively. The oxidation rate by UV/H_2O_2 was decreased significantly when the initial concentration formaldehyde concentration increased.

(a)

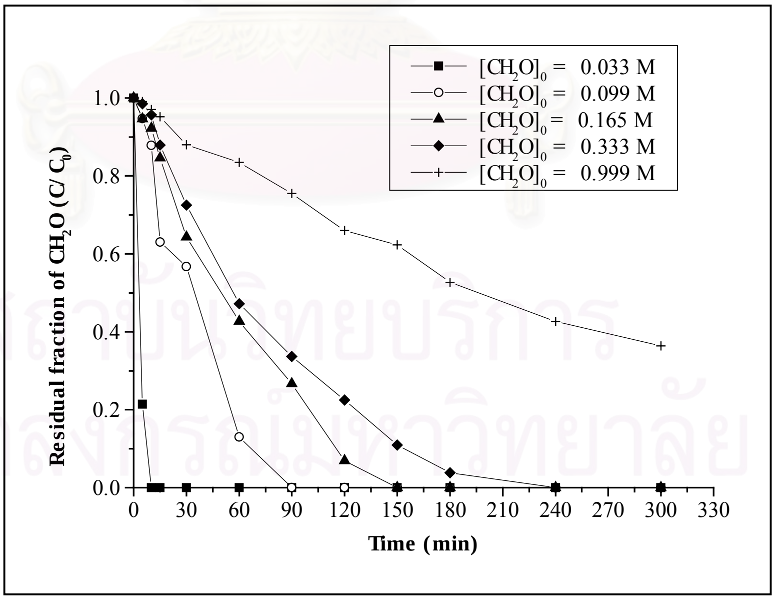


Figure 4.6 Degradation of formaldehyde by UV/H_2O_2 process with different initial concentrations of formaldehyde**.** (CH_2O:H_2O_2 = 1:2, initial pH = 7). **(a)** Residual fraction of formaldehyde

The hydrogen peroxide decompositions were also studied as the residual fraction versus time was presented in Figure 4.6 (b). The absence of hydrogen peroxide residuals were observed when the initial concentration of formaldehyde of 0.033, 0.099 and 0.165 M were applied at 180, 240 and 300 min, respectively. Nevertheless, large amounts of hydrogen peroxide residual, 5,928 and 24,450 mg/l where the initial concentration of formaldehyde of 0.330 and 0.999 M used, were found at the end of reaction.

(b)

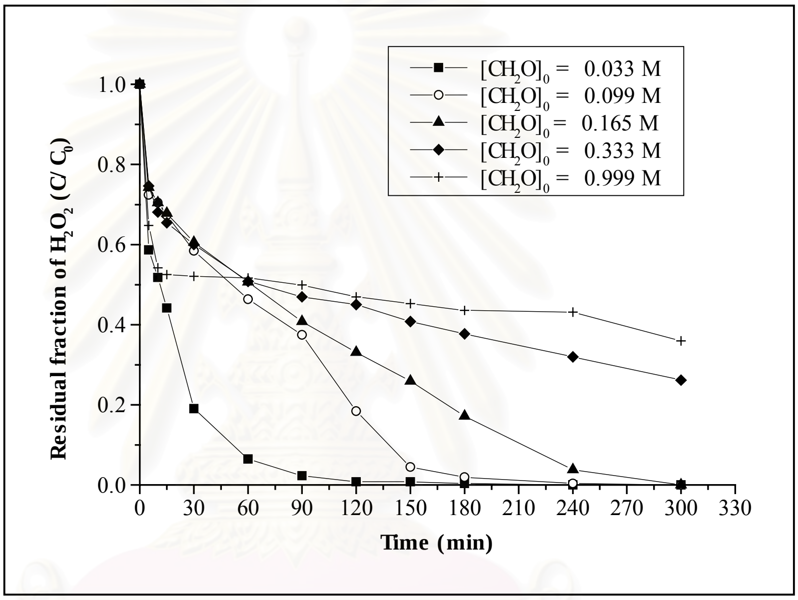


Figure 4.6 Degradation of formaldehyde by UV/H_2O_2 process with different initial concentrations of formaldehyde**.** (CH_2O:H_2O_2 = 1:2, initial pH = 7**)** **(b)** Residual fraction of hydrogen peroxide

The degree of formaldehyde mineralization by UV/H_2O_2 process was achieved at constant initial conditions of a 1:2 molar ratio of formaldehyde to hydrogen peroxide, at pH 7 and variable initial concentrations of formaldehyde from 0.033 to 0.999 M. Figure 4.6 (c) shows the results of TOC removal as a function of reaction time. Complete mineralization of formaldehyde to CO_2 and H_2O_2 was not accomplished since 37% of residual TOC remained in solution, even in the lowest concentration of pollutant applied. As expected, the higher the initial concentration of pollutant, the higher the amount of TOC residuals, such as at initial formaldehyde concentrations of 0.167, 0.167 and 0.999 M, the consequential residuals TOC were 40, 65 and 88%, respectively. From the graph, it can be depicted that significant TOC reduction was observed at 120 after irradiation in most of initial concentrations investigated except for the initial concentration of 0.033 M, where a high TOC reduction rate was found at 15 min after irradiation. It might due to the fact that formaldehyde rapidly decomposed in only 5 min after irradiation, while the other cases, took a much longer time to remove formaldehyde completely.

(c)

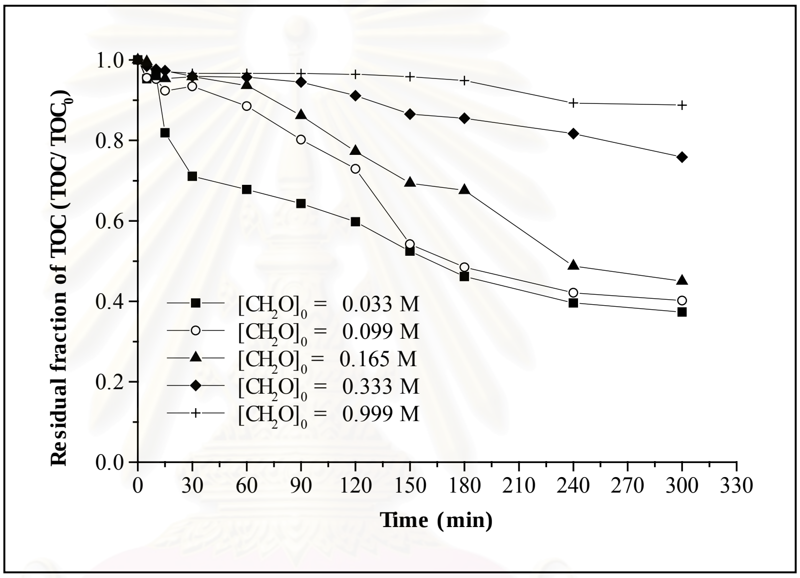


Figure 4.6 Degradation of formaldehyde by UV/H_2O_2 process with different initial concentrations of formaldehyde**.** (CH_2O:H_2O_2 = 1:2, initial pH = 7**)** (c) Residual fraction of TO**C**

The alterations of pH during UV/H_2O_2 process as function of time were measured. The similar profiles of pH were observed as presented in Figure 4.6 (d). The rapid reduction of pH values from pH 7.00 ± 0.02 to 3.00 ± 0.34 were observed in first 5 min of reaction time and after that pH values were slightly declined and remained rather unchanged since then. At the end of reaction time the measurable pH values were as follows; 2.54, 1.94, 2.18, 1.97, and 1.77 for initial formaldehyde concentrations of 0.033, 0.999, 0.167, 0.333, and 0.999 M, respectively.

(d)

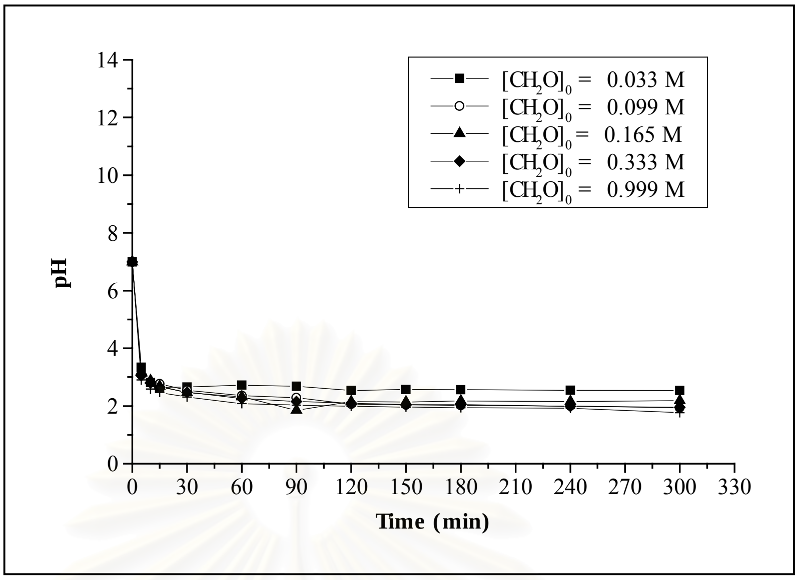


Figure 4.6 Degradation of formaldehyde by UV/H_2O_2 process with different initial concentrations of formaldehyde**.** (CH_2O:H_2O_2 = 1:2, initial pH = 7). **(d)** pH profile

4.6 Kinetic Study of Formaldehyde Degradation by UV/H_2O_2 Process.

Under the experiment conditions in section 4.2 - 4.5, the degradation rate for formaldehyde was formed to follow first order kinetics. When the first order kinetic sufficiently characterized the reaction rate, it could be explained as:

$$R = -d[C] / dt = k[c] \qquad (4.1)$$

where: k is the first order rate constant (hr^{-1})

R is reaction rate

t is the irradiation time (hr)

C is an initial concentration of the reactant or formaldehyde in this study

Integral of equation (4.1) is

$$\ln C_t/C_o = -kt \qquad (4.2)$$

where: C_o and C_t are concentrations at the beginning and at certain time (mole/l)

t is the irradiation time (hr)

A plot of -ln (C_t/C_o) versus irradiation time should give a straight line whose slope equals the first order rate constant, k for a half life of first order kinetics will correspond with the first order rate constant. It also expressed as:

$$t_{1/2} = 0.693/k \qquad (4.3)$$

where: $t_{1/2}$ is a half–life of first order kinetic (min)

For the experiments in part one which covered section 4.2 - 4.4 the initial rate constants of formaldehyde (K_{CH2O}) and hydrogen peroxide (K_{H2O2}) decomposition were calculated and the plots of their initial rate constants with different initial experimental conditions were presented.

The initial rate constants of formaldehyde (K_{CH2O}) at different initial pH were illustrated in Figure 4.7 (see more details in Table A-26 in Appendix A). When compared the K_{H2O2} values at pH 3 to pH 5 at every molar ratios of formaldehyde to hydrogen peroxide applied, the K_{CH2O} values at pH 3 was higher than those at pH 5 excepted for a molar ratio of 1:0.1 of formaldehyde to hydrogen peroxide. The K_{CH2O} values trended to be raised at pH 7, and finally dropped down at pH 9 (the molar ratios of 1:0.1, 1:1, 1:2 and 1:3 of formaldehyde to hydrogen peroxide) excluded at a molar ratio of 1:0.5 of formaldehyde to hydrogen peroxide. The highest K_{CH2O} values

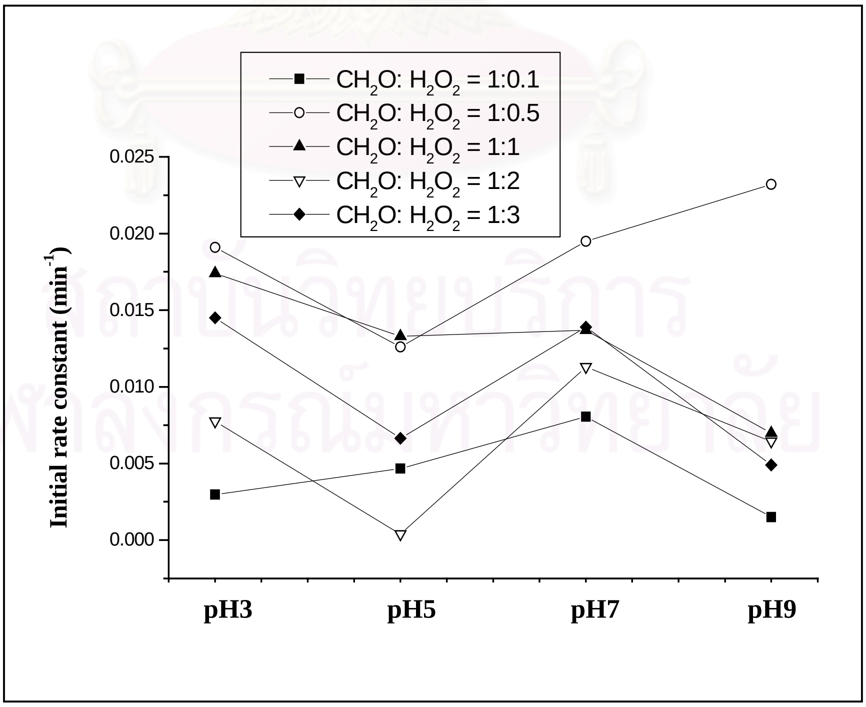


Figure 4.7 The initial rate constants of formaldehyde (K_{CH2O}) at different initial pH in the formaldehyde degradation using UV/H_2O_2 process.

were observed at a molar ratio of 1:0.5 of formaldehyde to hydrogen peroxide; 19.05 x 10^{-}3, 19.45 x 10^{-1} and 23.24 x 10^{-1} min^{-1} at pH 3, pH 7 and pH 9, respectively, with exception of pH 5 that the highest K_{CH2O} value, 13.33 x 10^{-3}, was established at a molar ratio of 1:3 of formaldehyde to hydrogen peroxide employed.

The decay of formaldehyde in UV/H_2O_2 process at different initial molar ratios of formaldehyde to hydrogen peroxide which represented as K_{CH2O} were exemplified in Figure 4.8 (see more information in Table A-26 in Appendix A). The comparisons of K_{CH2O} values at different molar ratios of formaldehyde to hydrogen peroxide explain that at a molar ratio of 1:0.1 gave the lower values than those at a molar ratio of 1:0.5, then they continued to decline at molar ratios of 1:1 and 1:2, and increase at a molar ratio of 1:3 at last for most pH conditions used. With exceptions of a molar ratio of 1:1 (where at pH 9 the K_{CH2O} value was lower than that at a molar ratio of 1:0.5) and 1:3 (where at pH 9 K_{CH2O} value was tended to decline at last).

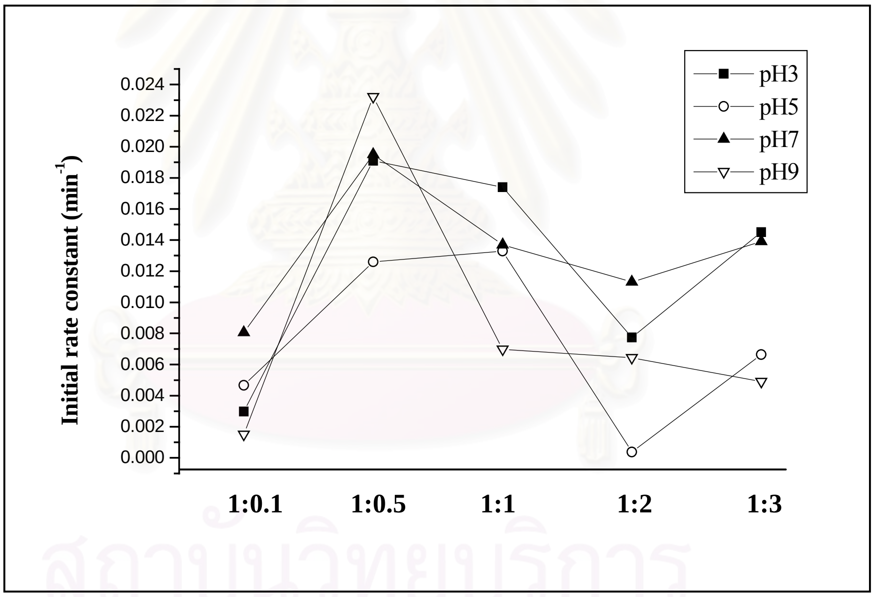


Figure 4.8 The initial rate constants of formaldehyde (K_{CH2O}) at different initial molar ratios of formaldehyde to hydrogen peroxide in the formaldehyde degradation using UV/H_2O_2 process.

The comparisons of initial rate constants of hydrogen peroxide (K_{H2O2}) at certain pH with variable molar ratios of formaldehyde to hydrogen peroxide in Figure 4.9 (see more details in Table A-27 in appendix A) indicated that the similar K_{H2O2} values (2.59x 10^{-2} – 6.07 x 10^{-2} min^{-1}) were found at pH 3. With a molar ratio of 1: 0.1 of formaldehyde to hydrogen peroxide, the lowest $K_{H2O2,}$ 1.57 x 10^{-2} min^{-1}, was observed at pH 5. While at other ratios this value was closed to each other in the range of 7.30 x 10^{-2} to 1.10 x 10^{-1} min^{-1}. The K_{H2O2} values were obviously different at pH 7. At a molar ratio of 1:0.1 of formaldehyde to hydrogen peroxide gave highest value of K_{H2O2} (5.58 x 10^{-1} min^{-1}). At a molar ratio of 1:0.5 and 1:1 of formaldehyde to hydrogen peroxide gave the lower values (2.05 x 10^{-1} and 1.76 x 10^{-1} min^{-1}) and at 1:3 gave the lowest values (5.03 x 10^{-2} min^{-1}). For the experiment conducted at pH 9, the highest to the lowest K_{H2O2} values; 5.75 x 10^{-1}, 2.98 x 10^{-1}, 1.04 x 10^{-1}, 7.33 x 10^{-2} and 6.03 x 10^{-2} min^{-1}) were found at the molar ratios of formaldehyde to hydrogen peroxide of 1:0.1, 1:0.5, 1:1, 1:2 and 1:3, respectively.

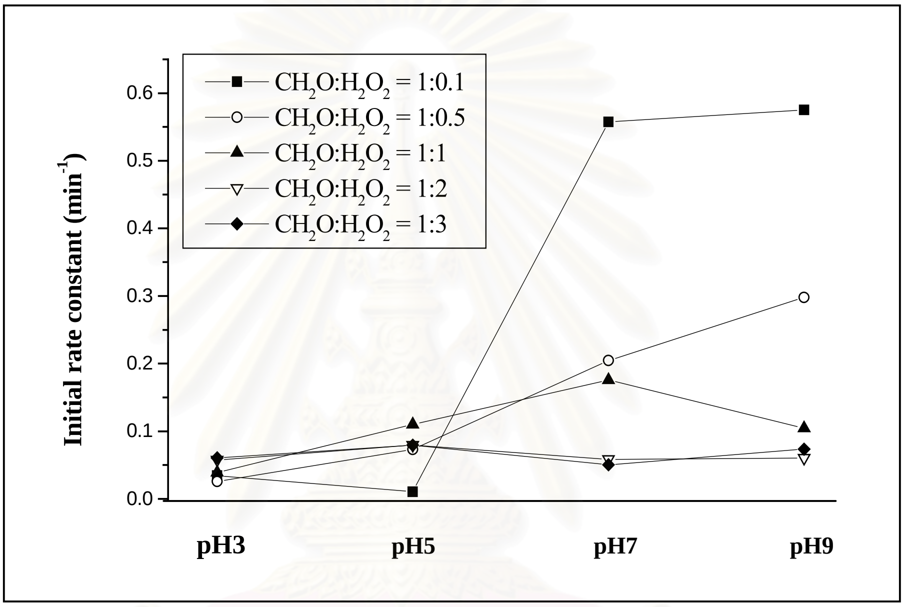


Figure 4.9 The initial rate constants of hydrogen peroxide (K_{H2O2}) at different initial pH in the formaldehyde degradation using UV/H_2O_2 process.

Figure 4.10 shows relationships of the initial rate constants of hydrogen peroxide decomposition (K_{H2O2}) with different initial molar ratios of formaldehyde to hydrogen peroxide (more details in Table A-27 in Appendix A). At an initial molar ratio of 1:0.1 of formaldehyde to hydrogen peroxide, the difference of K_{H2O2} values between the two groups of experimental conditions was clearly seen. For a group of pH 7 and pH 9 the K_{H2O2} values were 5.58 x 10^{-1} and 5.75 x 10^{-1} min^{-1} which was higher than those at a group of pH 3 and pH 5 (3.46 x 10^{-2} and 1.06 x 10^{-2} min^{-1}). The similar observed were found at an initial molar ratio of 1:0.5 of formaldehyde to hydrogen peroxide, where at pH 7 and pH 9 which gave the higher values (2.05 x 10^{-1} and 2.10 x 10^{-1} min^{-1}) than those at pH 3 and pH 5 (2.59 x 10^{-2} and 7.30 x 10^{-2} min^{-1}). With an initial molar ratio of 1:1 of formaldehyde to hydrogen peroxide, the highest

K_{H2O2} value (1.76×10^{-1} min^{-1}) was found at pH 7, the lower values were 7.92×10^{-2} and 6.03×10^{-2} min^{-1} at pH 5 and pH 9, and the lowest value was 3.90×10^{-2} at pH 3. For the latter conditions (at initial molar ratios of 1:2 and 1:3 of formaldehyde to hydrogen peroxide), the K_{H2O2} values were closed to each other at different initial pH conditions applied.

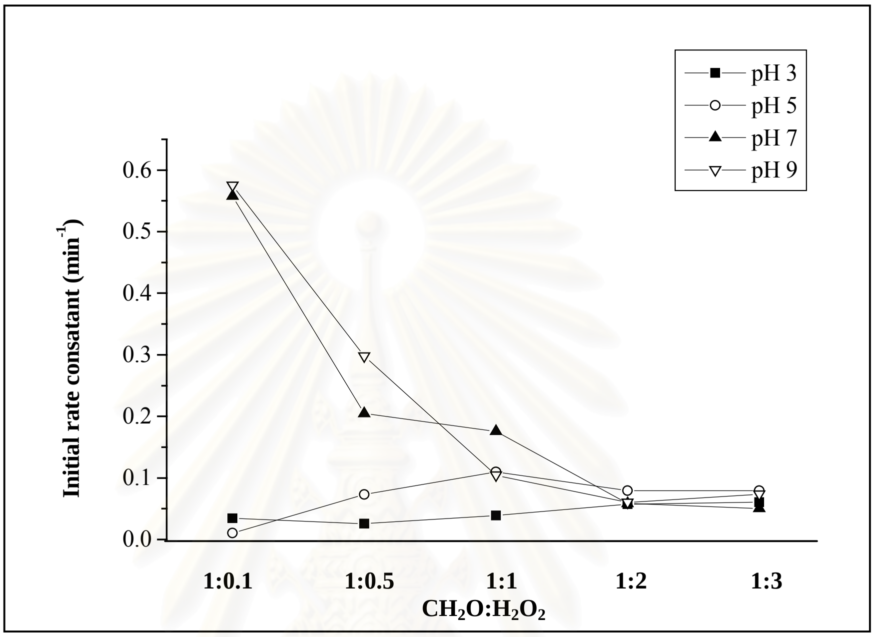


Figure 4.10 The initial rate constants of hydrogen peroxide (K_{H2O2}) at different initial molar ratios of formaldehyde to hydrogen peroxide in the formaldehyde degradation using UV/H_2O_2 process.

The k values for formaldehyde degradation at different initial concentrations are presented in Table 4.1 along with the values of $t_{1/2}$. From kinetic study, the simplified reaction pathway for formaldehyde decomposition by UV/H_2O_2 process follows a first-order reaction rate. It was observed that the high initial formaldehyde concentration had a negative effect on the pseudo-first-order reaction rate constant (R). when comparing the rate constant of an initial amount of formaldehyde of 0.033 M ($R = 3.09 \times 10^{-1}$ min^{-1}) and 0.999 M ($R = 3.12 \times 10^{-3}$ min^{-1}), it was clearly shown that 30 times of increasing initial concentration resulted in about a 100 times of reducing its rate constant. In other words, formaldehyde removal efficiency decreased when initial formaldehyde concentration was increased.

Table 4.1 The first order rate constants at different initial concentration of formaldehyde

[CH_2O]	initial rate constant* (min^{-1})	$t_{1/2}$ (min)	R^2	n
0.033 M	3.09×10^{-1}	2.24	-	2
0.099 M	3.09×10^{-2}	22.43	1.000	3
0.165 M	1.50×10^{-2}	46.20	0.996	7
0.333 M	1.27×10^{-2}	54.57	0.996	7
0.999 M	3.12×10^{-3}	222.12	0.982	7

Note: * based on pseudo first order reaction kinetic
n = number of data taken to account for initial rate constant calculations

Figure 4.11 illustrates the effect of the initial concentration of formaldehyde on the initial rate constant, the higher the initial concentration of formaldehyde the lower the initial rate constant expected to be seen. This was clearly observed at an initial formaldehyde concentration of 0.999 M was employed; about 36% of formaldehyde residual remained in the solution. However, the disappearance of formaldehyde residual might be expected if longer irradiation time was used since the reaction was proceeding in constant oxidation rate, as can be noticed from the graph.

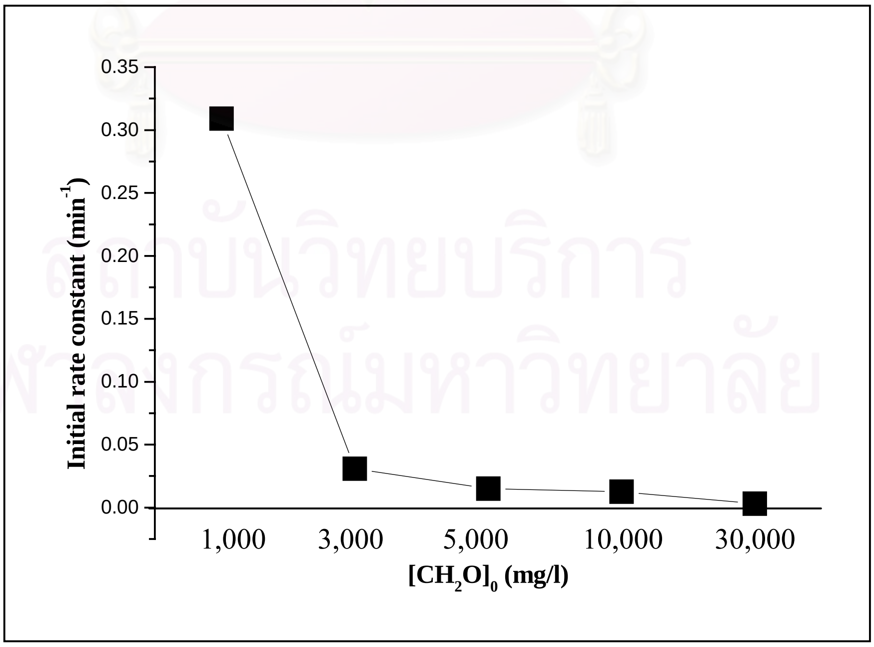


Figure 4.11 Effect of initial concentrations of formaldehyde on the initial rate constants

4.7 Factors affecting on efficiency of formaldehyde degradation by UV/H_2O_2

The efficiency of pollutant abatement by UV/H_2O_2 system can be affected by many variables such as, pH, concentration of hydrogen peroxide (a molar ratio of pollutant to hydrogen peroxide, pollutant: H_2O_2), the initial concentration of pollutant and presence of hydroxyl radical scavenger species. The factors affecting the efficiency of formaldehyde degradation by UV/H_2O_2 are as follows: molar ratio of formaldehyde to hydrogen peroxide, dissociation of hydrogen peroxide, initial pH, and initial concentration of formaldehyde

4.7.1 Influence of Molar Ratio of Formaldehyde to Hydrogen Peroxide

In the UV/H_2O_2 process, hydroxyl radicals are generated through the photolysis of hydrogen peroxide as shown in the initiation step of hydroxyl radicals formation (equation (4.4)).

$$H_2O_2 + h\nu \longrightarrow 2OH^{\bullet} \qquad (4.4)$$

The hydroxyl radicals attack organic compounds relatively non-selectively with rate constants ranging from 10^6 to 10^{10} M^{-1} s^{-1} (Buxton et al. 1988), oxidizing them by hydrogen atom abstraction or by addition to double bonds. This generated hydroxyl radical can react with hydrogen peroxide and thus leads to many reactions as follows:

$$OH^{\bullet} + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O \qquad (4.5)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad (4.6)$$

$$OH^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O + O_2 \qquad (4.7)$$

$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2 \qquad (4.8)$$

In this study the range of formaldehyde to hydrogen peroxide molar ratios from 1:0.1, 1:0.5, 1:1, 1:2 and 1:3 was investigated at an initial concentration of formaldehyde of 0.333 M. From previous results presented, it was indicated that in order to gain a high performance on formaldehyde degradation by UV/H_2O_2 process, an optimum molar ratio of formaldehyde to hydrogen peroxide of 1:2 should be applied. The reported results well agree with several previous studies that hydrogen

peroxide has two opposing effects on oxidation rate (Alnaizy and Akgerman, 2000). Firstly, the positive influence of the initial concentration of hydrogen peroxide on UV/H_2O_2 process; by increasing the initial hydrogen peroxide concentration (from the ratio of 1:0.1 to 1:2) the process performance was enhanced up to a certain point at which hydrogen peroxide start to inhibit the photolytic degradation (where the concentration of hydrogen peroxide more than 0.666 M or when the molar ratio more than 1:2 was employed). Secondly, in the negative influence, at higher initial hydrogen peroxide concentrations, equation (4.5) hydroxyl radical acted as a free-radical scavenger itself, and low potential radicals, e.g. $HO_2^{\bullet}$, were produced at large amounts of hydrogen peroxide in solution (Schultei et al., 1991; Kochany and Bolton, 1992) , thereby decreasing the hydroxyl radicals concentration. In the meantime, termination reactions (equation (4.6)-(4.8)) might be expected to occur. These can be further lead to the lower efficiency of formaldehyde photodegradation. In additional, the rate constant of hydrogen peroxide with hydroxyl radical was reported to be
$2.7 \times 10^{7}\ M^{-1}\ s^{-1}$ (Buxton et al. 1988)

As compared to others factors, the molar ratio of pollutant to hydrogen peroxide is a main factor that influences the formaldehyde degradation by UV/H_2O_2 process. As can be seen from the trend of formaldehyde residual profiles reported at each molar ratio at different initial levels of pH, the pollutant removal efficiencies can be expected in the similar outcomes. As depicted in Figures 4.2(a), 4.3(a), 4.4(a) and 4.5(a), the highest formaldehyde removal efficiency was achieved at a molar ratio of 1:2; the lower efficiencies attained at the following molar ratios 1:1, 1:3 and 1:0.5; and finally, the worst efficiency was gained at 1:0.1.

4.7.2 Influence of the Dissociation of Hydrogen Peroxide

The degradation of organic pollutant by UV/H_2O_2 photooxidation employs hydroxyl radical to attack molecule of pollutant, thus the dissociation of hydrogen peroxide is one of a factors that affects its removal efficiency. According to experimental results of hydrogen peroxide residual versus time (Figures 4.2(b), 4.3(b), 4.4(b) and 4.5(b)), as mentioned above, the dissociation rates of hydrogen peroxide to hydroxyl radicals in neutral and alkaline pH (Figures 4.4(d) and 4.5(d)) were much higher than that in acidic pH (Figures 4.2(d) and 4.3(d)). It was remarkably seen that 96%, 78% and 40% of hydrogen peroxide in pH 7 (Figure

4.4(b)) were consumed within the first 5 min after irradiation when 1:0.1, 1:0.5 and 1:1 molar ratio of formaldehyde to hydrogen peroxide were applied. It can be explained that the rate of photolysis of aqueous hydrogen peroxide bas been found to be pH dependent and to increase when more alkaline conditions are used **(**Legrini et al. 1993)

In addition, it is interesting to point out that hydroxyl radical concentration is much more sensitive to change due to pH variation than due to chloride concentration change (Liao et al. 2001). Thus as pH change from acidic to neutral and basic pH, the dissociation rate of hydrogen peroxide is increased. Another supported agreement was presented that the residual of hydrogen peroxide decreased with increasing solution pH values because the dissociated HO_2^- species overcome higher photolytic decomposition rate (Yung et al. 1995). Moreover, the reaction between $OH^{\bullet}$ and HO_2^- (Kochany and Bolton, 1992) and the base catalyzed decomposition of hydrogen peroxide (Weir et al. 1987) were also possible reasons for the lower amount of residual hydrogen peroxide in the alkaline solution.

4.7.3 Influence of the initial pH

As mentioned earlier, pH during UV/H_2O_2 process in several ranges of molar ratios of formaldehyde to hydrogen peroxide input at different initial pH, presented a similar trend of pH profiles (Figures 4.2 (d), 4.3 (d), 4.4 (d) and 4.5 (d)). It was found that the sharp reduction of pH from the initial values (3, 5, 7, 9) to values about 3 were achieved in only 5 min after irradiation, then gradually declined, and finally remained constant from the point around 60 min until the end of the reaction period, 300 min, at pH value about 2. It can be implied that during the photooxidation processes the pH of the reaction medium decreases due to the formation of acidic species (Andreozzi et al. 1999) and the fast decomposition rate as can be deduced from the residual profiles of hydrogen peroxide (Figures 4.2 (d), 4.3 (d), 4.4 (d) and 4.5(d)) where rapid hydrogen peroxide depletion occurred. In this study, formic acid is a primary identified as an acidic by-product found in GC Chromatograms. By the time of the reaction, there were more amounts of formic acid formation and more amounts of formaldehyde deterioration.

From all experiment sets, pH was also the important factor that affects the efficiency of formaldehyde degradation. The results for oxidation of formaldehyde at different pH levels by UV/H_2O_2 process were given in Figure 4.12. Obviously, the best formaldehyde removal efficiency in this study was obtained in the region of pH 3-7. When the pH solution was higher than this pH region the formaldehyde oxidation efficiency was reduced. In agreement with previous research, the efficiency of UV/H_2O_2 oxidation system was more deteriorated by increasing the reaction pH value to alkaline (Alaton et al. 2002). The highest rate of formaldehyde degradation was observed at pH 7 as shown in Figure 4.7.

It is important to consider that during the photooxidation processes, the pH of the reaction medium decreases due to the formation of acidic species. Therefore, it is necessary to adjust the pH of the treated water to the value which enables the achievement of the highest efficiency of pollutant abatement. It has been reported that the best oxidation was obtained at acidic pH for ultraviolet and hydrogen peroxide process in the presence of carbonate species (Liao and Gurol, 1995; Mokrini et al. 1997). However, the higher dissociation rate for hydrogen peroxide at the higher pH has also been reported (Ku et al. 1998). In addition, the effect of pH on the efficiency of hydroxyl radical production and its final reaction will mostly depend on the nature of the contaminant (Hernandez et al. 2002).

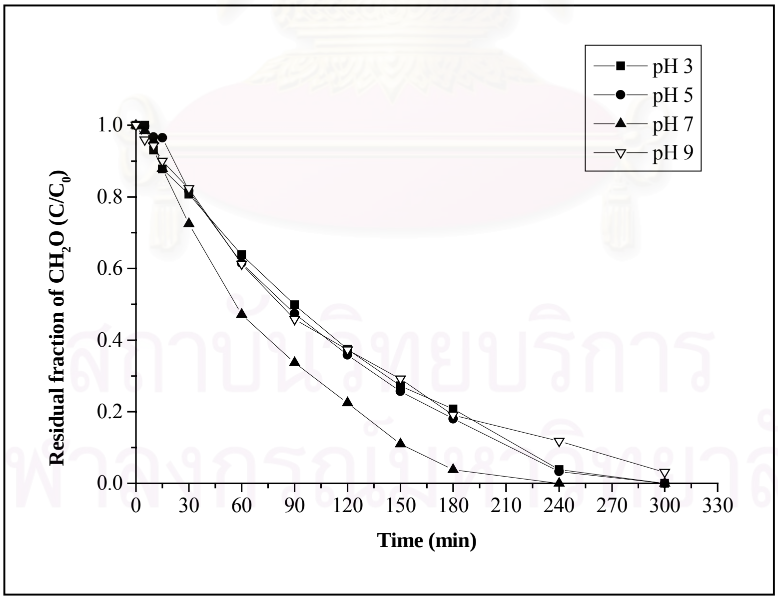


Figure 4.12 Degradation of formaldehyde by UV/H_2O_2 process at different initial pH ($[CH_2O]_0$ = 10,000 mg/l, CH_2O: H_2O_2 = 1:2

4.7.4 Influence of the initial concentration of formaldehyde

The influence of the initial concentration of formaldehyde was investigated by conducted experiment at initial conditions of a 1:2 molar ratio of formaldehyde to hydrogen peroxide, at an initial pH 7, which is the optimum condition obtained from previous work, and at various initial concentrations from 0.033 to 0.333 M. Figure 4.2(a) presents residual profile of formaldehyde at five different concentrations of pollutant. The molar ratio of formaldehyde to hydrogen peroxide was 1:2 initially. It appears that the higher initial formaldehyde concentration the lower the formaldehyde is expected to be removed. As can be seen from the residual profiles, retardation of formaldehyde destruction rate was increased as its initial concentration increased. Thus it is necessary to extend the reaction period to accomplish the desired formaldehyde abatement level.

What we learn from this set of experiment is the higher initial concentration of formaldehyde the lower formaldehyde itself expected to be removed. This finding is well conformity to Arslan et al., 1999 who reported that the efficiency of the UV/H_2O_2 process decreased drastically with increasing amount of pollutant. This phenomenon can be explained by plot percentage of formaldehyde removal efficiency at 60 min of the reaction versus the initial concentration of formaldehyde and hydrogen peroxide (Figure 4.13). The removal efficiency as a function of initial concentration of formaldehyde based on data from figure 4.6(a) was shown in chessboard-patterned column, with increasing initial concentrations of formaldehyde, the removal efficiency is decreased. The removal efficiency as a function of initial concentration of hydrogen peroxide based on data from figure 4.4(a) was shown in another column, by increasing the initial concentration of hydrogen peroxide the removal efficiency is increasing up to the critical point (where initial concentration of hydrogen peroxide of 0.033 M). Beyond this point, if hydrogen peroxide concentration was continued increasing further, the removal efficiency is reduce. By combining the two lines together; the black line and the dot line represent the removal efficiency as function of initial concentration of formaldehyde and hydrogen peroxide, respectively, we found that at the first region before the critical point influence of the initial concentration of hydrogen peroxide is dominated whereas at the latter region influence of the initial concentration of formaldehyde is dominated. In conclusion, even at the optimum condition, 1:2 molar ratio of formaldehyde to hydrogen peroxide was applied, at initial concentration of formaldehyde higher than 0.165 M or 5,000 mg/l the removal efficiency of UV/H_2O_2 process may not achieved 100 percent removal within 60 min. On the other words, for treating formaldehyde relatively high concentration, the longer retention time is required for a better performance of UV/H_2O_2 process.

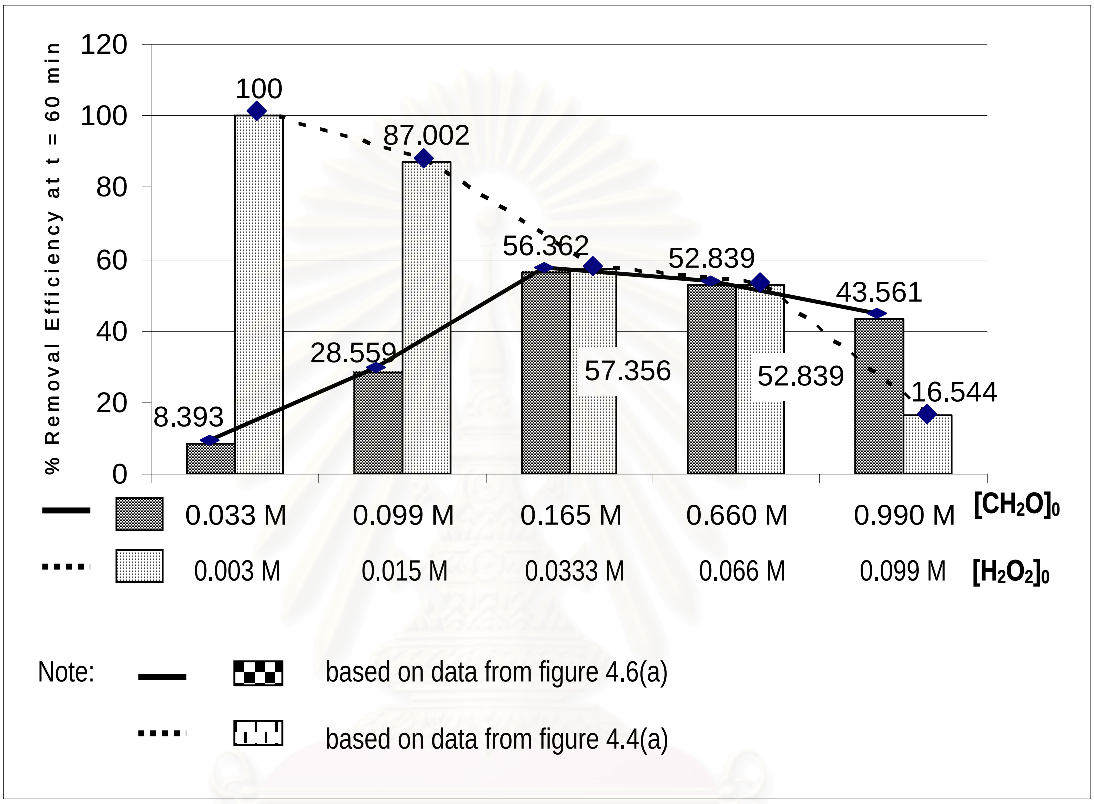


Figure 4.13 Effect of initial concentrations of formaldehyde and hydrogen peroxide on the formaldehyde removal efficiency using UV/H_2O_2 process

As we take a further look at the residual profile of hydrogen peroxide shown in Fig. 4.2(b), the residual fraction for the high initial formaldehyde concentration is higher residual hydrogen peroxide than that for the low initial concentration. Such as for 0.165 M of initial formaldehyde concentration resulting in the absence of residual hydrogen peroxide, for 0.333 M of initial formaldehyde concentration resulting in 16% of residual hydrogen peroxide (5,928 mg/l). The possible way can lead to such a result is that higher formaldehyde concentration can compete with H_2O_2 for more UV light photons adsorption as discussed earlier in section 4.1 and thus reduce light absorption by H_2O_2 to a greater degree.

4.8 Degradation Pathway of Formaldehyde by UV/H_2O_2 Process

The degree of mineralization of formaldehyde was quantified by TOC evaluation. Figure 4.2(c) shows TOC removal as a function of irradiation time at a molar ratio of formaldehyde to hydrogen peroxide of 1:2, at six different initial formaldehyde concentrations. Apparently, degradation of formaldehyde does not reach complete mineralization since TOC still remained in the solution. This phenomenon can be explained because formaldehyde was oxidized into its reaction byproduct, formic acid, which is refractory to hydroxyl radical oxidation. The mechanism of the mineralization of formaldehyde by hydroxyl radicals is presented in Figure 4.14. Refer to results reported in earlier studies (Stefan and Bolton, 1998; Heit et al., 1998; Gonzalez and Braun, 1996), formaldehyde itself reacts with hydroxyl radicals ($^{\bullet}OH$) by way of hydrogen abstraction, resulting in the formation of formyl radicals ($^{\bullet}CHO$) or their hydrated form. The latter are oxidized by dissolved molecular oxygen to yield formic acid and hydroperoxyl radicals. Again, formic acid reacts with $^{\bullet}OH$ to give formoyl radicals that react with molecular oxygen finally yielding carbon dioxide and hydroperoxyl radicals. From previous study, it point out that formic acid is one kind of formaldehyde byproduct produced during UV/H_2O_2 oxidation process in agreement to the finding in this study that there is a presence of formic acid, evidenced by its peak in GC chromatogram. As shown in Figure 4.15, chromatograms show the disappearance of formaldehyde and appearance of its acidic by-product Formaldehyde and formic acid were identified by retention time matched with the external standards at 1.85 and 2.00 min, respectively. For by-product identification, the samples with formic acid (spiked sample) and without formic acid were taken and analyzed at certain time. The formaldehyde by product peak as labeled at 2.00 min in chromatogram of spiked sample showed higher peak height than that of ordinary sample hence it can be concluded that the by-product produced during formaldehyde degradation by UV/H_2O_2 is formic acid. The major contribution of this work is to highlight the fact that significant quantities of one product are formed and persist beyond the time when formaldehyde is largely transformed.

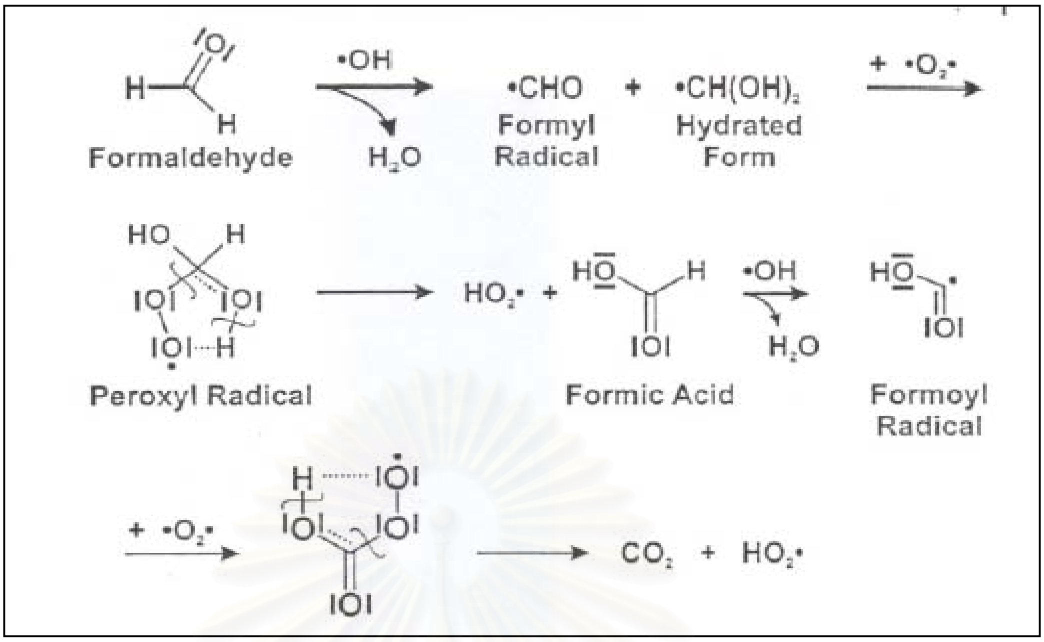


Figure 4.14 Mechanism of the mineralization of formaldehyde by hydroxyl radicals.

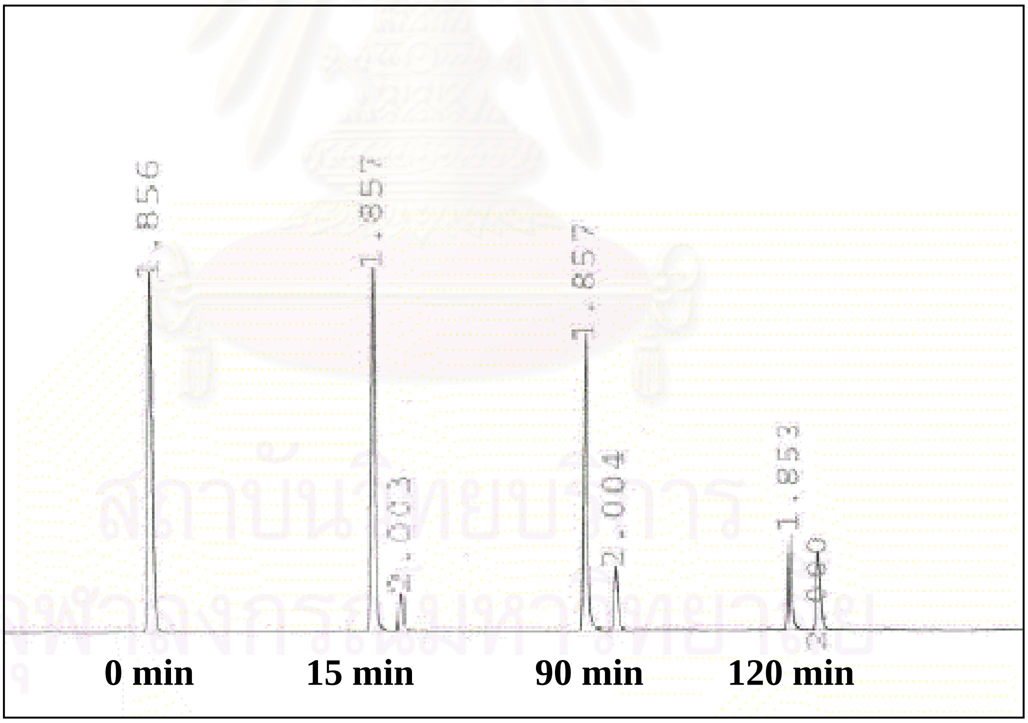


Figure 4.15 GC-Chromatograms of Formaldehyde and formic acid during UV/H_2O_2 process (where at 1.85 and 2.00 min identified as formaldehyde and formic acid)

4.9 Toxicity of Residual Formaldehyde Treated by UV/H_2O_2

Based on background of this study, direct discharged of used formaldehyde solution to biological wastewater treatment plant causes failure in the system. Hence, UV/H_2O_2 process was selected as the pretreatment unit for treating this kind of waste before being further discharged to the biological unit. In order to access the toxicity degree of the treated formaldehyde, toxicity tests were performed prior to conducting the experiment, at the middle (150 min) and at the end (300 min) of the reaction period. Note that, our experimental samples were diluted 100 folds before analysis. The results shown in Table 4.2 indicate that in the first part of experiment, at the initial formaldehyde concentration of 10,000 mg/l, only in a small degree of toxicity was reduced. However at the reaction period of 300 min, the disappearance of remained formaldehyde (pH 3, pH 5 and pH 7) and only 3% of formaldehyde residual (pH 9), and a high toxicity of treated solution was observed. This is due to the formation of an intermediate, formic acid, which also has toxicity in some degree during oxidation reaction which remained in solution.

Table 4.2 Toxicity of formaldehyde after UV/H_2O_2 treatment at different initial pH levels ($[CH_2O]_0 = 0.333$ M, $CH_2O:H_2O_2 = 1:2$)

Treatment Conditions	150 min		300 min	
	Toxicity (% inhibition)	CH_2O (mg/l)	Toxicity (% inhibition)	CH_2O (mg/l)
1:2 pH3	98.83	2,568	80.91	0.00
1:2 pH5	93.30	2,097	77.62	0.00
1:2 pH7	91.63	1,104	73.95	0.00
1:2 pH9	99.14	2,937	87.65	348

At variations of initial formaldehyde concentrations (Table 4.3) in the second part of experiment, the toxicity values were remarkable reduced in 150 min and almost non toxic of samples were observed at 300 min of the reaction (at $[CH_2O]_0 =$ 0.033 M and 0.099 M). It can be noticed that after complete formaldehyde degradation, it requires long reaction period to achieve the reduction of toxicity. For example, at initial concentration formaldehyde of 0.165 M, it requires the extension of reaction period of about 150 min after the completed formaldehyde degradation to reduce the toxicity to safety level for microorganism where the percent inhibition is below EC_{50}. At initial formaldehyde concentrations beyond 0.165 M, reductions of toxicity degree to the safety level were not reached. Nevertheless, at initial formaldehyde concentration of 0.165 M, safety level was reached in 300 min after irradiation. In other conditions where initial formaldehyde concentrations over 0.165 M, even though formaldehyde were completely oxidized during the photooxidation the effluent still had high toxicity. Due to formic acid which remained in solution poses some degree of toxicity. Therefore, it is necessary to point out that at initial formaldehyde concentrations more than 0.165 M, the application of UV/H_2O_2 should be considered.

Table 4.3 Toxicity of formaldehyde after UV/H_2O_2 Treatment at different initial formaldehyde concentrations (CH_2O:H_2O_2 = 1:2, initial pH = 7)

Treatment Conditions	**150 min**		**300 min**	
	Toxicity (% inhibition)	**CH_2O (mg/l)**	**Toxicity (% inhibition)**	**CH_2O (mg/l)**
0.033 M	10.20	0.00	0.71	0.00
0.099 M	18.89	0.00	4.90	0.00
0.165 M	80.63	0.00	21.30	0.00
0.333 M	91.63	1,104	73.95	0.00
0.999 M	100.00	6,342	98.91	3,571

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1 Conclusions

The results of formaldehyde degradation by UV/H_2O_2 process can be concluded in several aspects as following:

- In this study, the best conditions for formaldehyde degradation by UV/H_2O_2 photooxidation process is 1:2 molar ratio of formaldehyde to hydrogen peroxide at initial pH 7. At this condition, completed formaldehyde destruction was achieved within 240 min of reaction period with the degradation rate constant of $1.27 \times 10^{-2}\ M^{-1}s^{-1}$.
- In comparative study on an optimum molar ratio of formaldehyde to hydrogen peroxide, at the ratio lower than that at the best condition, results present an inadequate amount of hydrogen peroxide for further oxidize formaldehyde. On the contrary, at the higher ratio than that at the bet condition, results present the excess amount of hydrogen peroxide. In addition, at high amount of hydrogen peroxide input resulting in drop down of formaldehyde degradation due to self-scavenging of hydroxyl radicals.
- Effects of pH on formaldehyde removal efficiency were investigated. Results showed that experiments conducted in acidic solution give a favorable oxidation rate than that in basic solution. On the other words, retardation of formaldehyde degradation rate was observed when the applied pH beyond the optimum value.
- The UV/H_2O_2 photodecomposition of formaldehyde is not attained total mineralization, as indicated in GC-Chromatogram that during formaldehyde degradation, an unclassified refractory intermediate species was formed.
- Contrastly, as formic acid is formed, the formaldehyde most degraded. Even though the completely formaldehyde abatement was accomplished at the end of reaction period, this acid byproduct was remained and pose some degree of

toxicity or reaction inhibition on luminescence bacteria tested when the initial concentration of formaldehyde higher than 5,000 mg/l (or 0.165).

- It was found that the higher initial formaldehyde concentration, the lower in formaldehyde removal efficiency.

5.2 Suggestions for Future Work

1. The optimum conditions for formaldehyde degradation by UV/H_2O_2 process obtained from this work can applicable for further researches development and/or for real situation. It is also provide an alternative treatment method for wastewater containing formaldehyde.

2. In application of UV/H_2O_2 process in the real situations which has various variables of formaldehyde concentration containing, the reaction rate constant obtained form this work is beneficial for forecasting degradation behavior. An example of parameter can be predicted is the retention time required at any initial concentration of pollutant, well described that when initial concentration of formaldehyde is unknown, the time required is quantifiable using reaction rate constant.

3. From results of toxicity reduction study, it is suggested that the well consideration of UV/H_2O_2 process application should be accounted at which initial concentration of formaldehyde beyond 5,000 mg/l. Due to the high toxicity of treated effluent over EC_{50} which is considered as unsafe level for microorganism.

4. To assure that the highest formaldehyde attenuation was accomplished the results of factors that affect formaldehyde degradation would also be considered for real wastewater application. Due to the fact that, there are several hydroxyl radical scavenger species, carbonate, bicarbonate and chloride etc., in real wastewater.

REFERENCES

Alaton, I A., Balcioglu, I. A. and Bahnemann, D. W. (2002). Advanced oxidation of a resction dyebath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A process. Water Research 36: 1143-1154.

Alnaizy, R. A., and Akgerman, A. (2000). Advanced oxidation of phenolic compounds. Advances in Environmental Research 4: 233-244.

Andreozzi, R., Caprio, V., Insola, A., and Marotta, R. (2000). The oxidation of metol (N-methyl-*P*-aminophenol) in aqueous solution by UV/H_2O_2 photolysis. Water Research 34: 463-472.

Andreozzi, R., Caprio, V., Insola, A., and Marotta, R. (1999). Advanced oxidation process (AOP) for water purification and recovery. Analysis Today 53: 51-59.

Appelman, L. M., Wouterson, R. A., Zwart, A., Falke, H. E., and Feron, V. J. (1988). One-year inhalation toxicity study of formaldehyde in male rats with a damaged or undamaged nasal mucosa. Journal Apply Toxicology 8: 85-90.

Arslan, I., Balcioglu I. A., and Tuhkanen, T., (1999). Advance oxidation of synthetic dyehouse effluent by O_3, H_2O_2/O_3, and H_2O_2/UV processes. Enviromental Technology 20: 91-99.

Aurand, K. et al. (1991). Die Trinkwasserverordnung, 3rd ed., Erich SchmidtVerlag, Berlin, cited in: Offermanns et al., 2000.

Baxendale, J. H., and Wilson, J. A. (1957). Photolysis of hydrogen peroxide at high intensities. Trans. Faraday Soc. 53: 344-356.

Beltrán, F. J., Gonzá1ez M., Acedo, B. and Jaramillo J. (1996). Contribution of free radical oxidation to eliminate volatile oganochlorine compounds in water by ultraviolet radiation and hydrogen peroxide. Chemosphere 32: 2873-2885.

Beltrán, F. J., Ovejero, G. and Acedo, B. (1993). Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide. Water Research 27: 1013-1021.

Beltrán, F. J., Ovejero, G., and Rivas, J. (1996). Oxidation of polynuclear aromatic hydrocarbon in water 3. UV radiation combined with hydrogen peroxide. Industrial Engineering Chemical Research 35: 883-889.

Benitez, F. J., Acero, L. J., Real, J. F., Rubio, J. F., and Leal, I. A. (2001). The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions. Water Research 35: 1338-1343.

Bolton, J. R., and Cater, S. R. (1994). Homogeneous photodegradation of pollutants in contaminated water: an introduction. In: Helz, G. R., Zepp, R. G., Crosby, D. G. (Eds.), Aquatic and surface photochemistry. EEUU, Lewis, Boca Raton, FL: 467-490.

Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B. (1988). Critical review of rate constants for reaction of hydrated electrons hydrogen atoms and hydroxyl radicals ($OH^\bullet/O^{-\bullet}$) in aqueous solution. Journal of Physical Chemistry Ref. Data 17: 513-886.

Carlson, R. W., Anderson, M. S., Johnson, R. E., Smythe, W. D., Hendrix, A.R., Barth, C. A., Soderblom, L. A., Hansen, G, B., McCord, T. B., Dalton, J, B., Clark, R. N., Shirley, J. H., Acampo, A. C., and Matson, D. L. (1999). Hydrogen peroxide on the surface of Europa, Science 283: 2062-2064.

Charuratana U., and Voranisarakul J. (1993) Wastewater Treatment Plant Research and Development for 25 Hospitals Nationwide. Report submitted to Health Department, Ministry of Health, Thailand.

Cheawchanthanakit S., and Sangphromma A. (1997). Effect of Lysol on activated sludge for hospital wastewater treatment, Environmental Study Project, Environmental Engineering Department, King Mongkut's University of Technology Thonburi, Thailand.

Christensen, H., Sehested, K., and Corftizen, H. (1982). Reactions of hydroxyl radicals with hydrogen peroxide. Journal of Physical Chemistry 86: 1588-1590.

Chronic toxicity summary of formaldehyde. Available form: http://www.oehha.ca.gov/air/chronic_rels/pdf/50000.pdf

Chu, W. (2001). Modeling the quantum yields of herbicide 2,4-D decay in UV/H_2O_2 process. Chemosphere 44: 935-941.

Chun, H., and Yizhong, W. (1999). Decolorization and biodegradability of photocatalytic treated azo dyes and wool textile wastwater. Chemosphere 39: 2107-2115.

Cooper, W. J., Zika, R. G., Petasne, R. G., and Fisher, A. M. (1989). Sunlight-induced photochemistry of humic substances in natural waters: major reactive species. In: Suffet, I. H., MacCarthy, P.(Eds.), aquatic humic substances: influence on fate and treatment of pollutants. American chemical Society, Washington, DC (Chapter 22).

CRC. (1994). CRC Handbook of Chemistry and Physics, 75th edition. Lide DR, ed. Boca Raton, FL: CRC Press Inc.

Crittenden, J. C., Hu, S., Hand, D. W., and Green, S. A. (1999). A kinetic model for UV/H_2O_2 process in a completely mixed batch reactor. Water Research 33 (10): 2315-2328.

De Laat, J., Tace, E., and Dore, M. (1994). Degradation of chloroethanes in dilute aqueous solution by H_2O_2/UV. Water Research 28: 2507-2519.

Duguet, J. P., Anse, C., and Mallevialle, J., (1989). New advances in oxidation processes: Some examples of application of ozone/hydrogen peroxide combination for removal of micropullutants for drinking water. Water Nagoya, ASPAC IWSA.

Environmental Application overview. Available from: http://www.h2o2.com/applications/industral wastewater/hcho.html

Fung, P. C., Huang, Q., Tsui, S. M., and Poon, C. S. (1999). Treatability study of organic and color removal in desizing/dyeing wastewater by UV/us system combined with hydrogen peroxide. Water Science and Technology 40: 153-160.

Glaze, W. (1993). An Overview of Advanced Oxidation Processes: Current Status and Kinetic Models. Eckenfelder, W., Bowers A.R., Roth, J.A., Editors. Proceedings of the Third International Symposium Chemical Oxidation: Technology for the Nineties. Technomic. Lancanster.

Glaze, W. H. (1987). Drinkingwater treatment with ozone. Environmental Science and Technology 21: 224-230.

Glaze, W. H., Kang, J. W., and Chapin, D.H. (1987). The chemistry of water treatment processes involving ozone, hydrogen peroxide, and ultraviolet radiation. Ozone Science and engineering 9: 335-352.

Glaze, W. H., Lay, Y. and Kang, J. W. (1995). Advanced oxidation processes. A Kinetic model for the oxidation of 1,2-dibromo-3-chlopropane in water by the combination of hydrogen peroxide and UV radiation. Industrial Engineering Chemical Research 34: 2314-2323.

Gonzalez M. C., and Braun, A. M. (1996). Vacuum UV photolysis of aqueous solution of nitrate effect of organic matter. II. Methanol. Journal of Photochemical Photobiology Analysis 95: 67-72.

Grasfstrom, R. C., Yang, L. L. and Harris, C. C., (1985). Genotoxicity of formaldehyde in cultural human cronchial fibroblasts. Science 228: 89-91

Haag W. R. and Yao D. C. C. (1992). Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. Environmental Science Technology 26: 1005-1013.

Hanzon, B. and Vigilia, R. (1999). UV Disinfection. Wastewater Technology 2: 24-28.

Heit, G., Neuner, A., Saugy, P. Y., and Braun, A. M. (1998). Actinometry: The quantum yield of the photolysis of water. Journal Physical Chemical Analysis 102: 5551-5561

Himebaugh, W.S., (1994). Advance oxidation of munitions in water, Fer III and WM II Conference and Exhibition.

Hoigné J. (1998). Chemistry of Aqueous Ozone and Advanced Oxidation Processes, in: Hutzinger O (ed.). The Handbook of Environmental Chemistry, Springer-Verlag, Berlin 5, Part C: 83-141.

Hoigne, J., Faust, B. C., Haag, W. R., Scully Jr., Zepp, R. G. (1989). Aquatic humic substances as sources and sinks of photochemically produced transient reactants. In: Suffet, I. H., MacCarthy, P. (Eds.), Aquatic Humic Sucstances: Influence on Fate and Treatment of Pollutants. American Chemical Society, Washington, DC (Chapter 23).

Hong, A. Zappi, E. M., Kuo H. C., and Hill, O.D. (1996). Modeling the kinetics of illuminated and dark advanced oxidation processes, ACSC. Journal of environmental engineering 122: 58-62.

Höppke, K. E., and Hagel, V. G. (1991). Überlegungen Zur oxidativen Abwassserbehandlung mit Wasserstoffperoxid, gwf-Wasser/Abwasser 132, No. 6: 313-317.

HSDB. (1994). Hazardous Substances Data Bank. National Library of Medicine, Bethesda, MD (TOMES® CD-ROM version). Denver, CO: Micromedex, Inc. (edition expires 11/31/94).

Huang, C. P., Dong, C. H., and Tang, Z. (1993). Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. Waste Management 13: 361-377.

Ince, N. H., Stefen, M. I., and Bolton, J. R. (1997). UV/H_2O_2 degradation and toxicity reduction of textile azo dyes: Removal Black-B, a case study. Journal of Advanced Oxidation and Technology 2: 442-448.

International program on Chemical safety (IPCS) (1989). Formaldehyde Environmental Health Criteria 89: 219 World Health Organization, Geneva.

Juang, L. C., Tseng D. H., and Yang, S. C. (1997). Treatment of petrochemical wastewater by UV/H_2O_2 photodecomposed system. Water Science and Technology 36: 357-365.

Kamata, E., Nakadate, M., Uchida, O., Ogawa, Y., Suzuki, S., Kaneko, T., Saito, M., and Kurokawa, Y. (1997). Results of a 28-month chronic inhalation toxicity study of formaldehyde in male Fisher- 344 rats. Journal Toxicology Science 22: 239-254.

Kerfoot, E. J., and Mooney, T. E. (1975). Formaldehyde and paraformaldehyde study in funeral homes. Am. Ind. Hyg. Assoc. J. 36: 533-537.

Kerns, W. D., Pavkov, K. L., Donofrio, D. J., Gralla, E. J, and Swenberg, J. A. (1983). Carcinogenicity of formaldehyde in rats and mice after long-term inhalation exposure. Cancer Research 43: 382-4392.

Kimbell, J. S., Gross, E. A., Richardson, R. B., Conolly, R. B., and Morgan, K. T. (1997). Correlation of regional formaldehyde flux predictions with the distribution of formaldehyde-induced squamous metaplasia in F344 rat nasal passages. Mutation Research 380: 43-154.

Kochany, J. and Bolton, J.R. (1992). Mechanism of photodegradation of aqueous organics pollutant 2. Measurement of the primary rate constants for reaction of OH radicals with benzene and some halobenzene Using an EPR spin-trapping method following the photolysis of H_2O_2. Environmental Science and Technology 26(2): 262-265.

Ku, Y., Wang, L. S. and Shen, Y. S. (1998). Decomposition of EDTA in aqueous solution by UV/H_2O_2 process. Journal of Hazardous materials 60: 41-45.

Legrini,O., Oliveros, E., and Braun, A.M., (1993). Photochemical processes for water treatment. Chemical Revision 93: 671.

Levine, R. J., Andjelkovich, D. A., and Shaw, L. K. (1984). The mortality of Ontario undertakers and a review of formaldehyde-related mortality studies. Journal of Occupational Medicine 26: 740-746.

Liao, C. H., (1993). The investigation of hydrogen peroxide photolysis as a water treatment process. Ph.D. dissertation in environmental engineering, Drexel University, PA.

Liao, C. H., and Gural, M. D. (1995) Chemical Oxidation by Photolytic Decomposition of Hydrogen peroxide. Environmental Science and Technology 29(12): 3007-3014.

Liao, C. H., Kang S. F. and Wu F. A. (2001). Hydroxyl radical scavenging role of chloride and bicarbonate ions in the H_2O_2/UV process. Chemosphere 44: 1193-1200.

Liao, C. H., Lu, M. C., Yang, H. Y. and Lu, I. C., (2000). UV-Catalyzed Hydrogen Peroxide Treatment of Textile Wastewater. Environmental Engineering Science. 17: 9-18.

Lin, S. S., and Gurol, M. D. (1996). Heterogeneous catalytic oxidation of organic compounds by hydrogen peroxide, Water Science Technology 34(9): 57-64.

Lipczynska-Kochany, E. (1993). Hydrogen peroxide mediated photodegradation of phenol as studied by a flash photolysis/HPLC technique. Environmental Pollution 61: 147-152.

Maronpot, R. R., Miller, R. A., Clarke, W. J., Westerberg, R. B., Decker, J. R., and Moss, O. R. (1986). Toxicity of formaldehyde vapor in B6C3F1 mice exposed for 13 weeks. Toxicology 41: 253-266.

Masten S., Davies S., (1994). The use of ozonation to degrade organic contaminants in wastewater. Environmental Science Technology 28: 180A-185A

Monticello, T. M., Swenberg, J. A., Gross, E. A., Leininger, J. R., Kimbell, J. S., Seilkop, S., Starr, T. B., Gibson, J. E., and Morgan, K. T. (1996). Cancer Research 56: 1012-1022.

Namboodri, C. G. and Walsh, W. K. (1996). Ultraviolet Light/Hydrogen Peroxide System for Decolorizing Spent Reactive Dyebath Waste Water. American Dyestuff Reporter.

Offermanns, H., Dittrich, G., and Striner, N. (2000). Wasserstoffperoxide in Umweltschutz and Synthese, Chem Unserer Ziet 34, No.3: 150-159.

Oppenländer, T. (2002). Photochemical Purification of Water and Air.WILEY-VCH Verlag GmbH & Co. KGaA,Weinhiem,Germany.

Paulette B. L. C., and Thomas M. Y. (2000). Kinetics of methyl *tert*-butyl ether degradation and by-product formation during UV/hydrogen peroxide water treatment. Water Research 34: 2233-2240.

Prengle, H. W., Symons, M. J., Belhateche, D. (1978). H_2O_2/visUV process for photo-oxidation of waterborne hazardous substances C_1-C_6 Chlorinated hydrocarbons. Waste management 16: 327-333.

Product Information - Hazard Classes of Different Concentrations. Available from: http://www.h2o2.com/intro/hazard.html

Rafael, H., Mark Z., Jose, C., and Robert, J. (2002). Comparing the performance of various advanced oxidation processes for treatment of acetone contaminated water. Journal of hazardous madterials 2789: 1-18.

Rosario, L. C., Espinoza, G. A., and Litter, I. M. (2002). Photodegradation of an azo dye of the textile industry. Chemosphere 48: 393-399.

Rott, U., and Minke, R. (1999). Overview of wastewater treatment and recycling in the textile processing industry. Water Science and Technology 40: 137-144.

Rusch, G. M., Clary, J. J., Rinehart, W. E., and Bolte, H. F. (1983). A 26-week inhalation study with formaldehyde in the monkey, rat, and hamster. Toxicology Apple Pharmacol 68: 329-343.

Schltei, P., Volkmer, M. and Kuhn, F., (1991). Activated hydrogen peroxide to eliminated pollutant in water (UV/H_2O_2). Degussa Industrial and Fine Chemicals Division, Frankfurt, Germany.

Shu, H., Huang, C., and Chang, M. (1994). Decolorization of Mono-Azo Dyes in Wastewater by Advanced Oxidation Processes: A Case Study of Acid Red 1 and Acid Yellow 23. Chemosphere 29: 2597-2607.

Stefan, M. I., and Bolton, J. R. (1998). Mechanism of the degradation of 1,4-Dioxan in dilute aqueous solution using the UV/H_2O_2 process. Environmental Science Technology 32: 870-873.

Stefan, M. I., Hoy, A. R., and Bolton J. R. (1996). Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide. Environmental Science and Technology 30: 2382-2390.

Stock, N. L., Peller, J., Vinodgopal, K., and Kamat, P.V. (2000). Combinative sonolysis and photocatalysis for textile dye degradation. Environmental Science and Technology 34: 1747-1750.

Trapido, M. and Kallas, J. (2000). Advanced oxidation processes for the degradation and detoxification of 4-nitrophenol. Environmental Technology 21: 799-808.

Venkatadri, R. and Peters, R. W. (1993). Chemical oxidation technologies: UV light/hydrogen peroxide, Fenton’s reagent, and titanium dioxide assisted photocatalysis. Hazardous Waste & Hazardous materials 10: 107-149.

Walling C. (1975). Fenton reagent revisited. ACC Chemical research 29: 125-134.

Wang, G. S., Hsieh, S. T., and Hong, C. S. (2000). Destruction of humic acid in water by UV light-catalyzed oxidation with hydrogen peroxide. Water Research 34: 3882-3887.

Wang, G. S., Liao C. H., and Wu, F. J. (2001). Photodegradation of humic acids in the presence of hydrogen peroxide. Chemosphere 42: 379-387.

Weir, B.A., and Sundstrom, D. W. (1993). Destruction of trichloroethylene by UV light-catalyzed oxidation with hydrogen peroxide. Chemosphere 27: 1279-1291.

Weir, B.A., Sundstrom, D.W., (1987). Destruction of benzene by ultraviolet light-catalyzed oxidation with hydrogen peroxide. Hazardous Wastewater and Hazardous Material 4(2): 165-176.

Wilmer, J. W., Wouterson, R. A., Appelman, L. M., Leeman, W. R., and Feron, V. J. (1989). Subchronic (13-week) inhalation toxicity study of formaldehyde in male rats: 8-hour intermittent versus 8-hour continuous exposures. Toxicolo. Lett. 47: 287-293.

Woutersen, R. A., Van, G. A, Bruijntjes, J. P., Zwart, A., and Feron, V. J. (1989). Nasal tumours in rats after severe injury to the nasal mucosa and prolonged exposure to 10 ppm formaldehyde. Journal Apply Toxicology 9: 39-46.

Wouterson, R. A., Appelman, L. M., Wilmer, J. W., Falke, H. E., and Feron, V. J. (1987). Subchronic (13-week) inhalation toxicity study of formaldehyde in rats. Journal Apply Toxicology 7: 43-49.

Yang, Y., Wyatt, D. T. II., and Bahorshky, M. (1998). Decolorization of Dyes Using UV/H_2O_2 Photochemical Oxidation. Textile Chemist and Colorist. 30: 27-35.

Yung S. S., Young K., and Kuen C. L. (1995). The effect of light absorbance on the decomposition of chlorophenols by ultraviolet radiation and UV/H_2O_2 process. Water Research 29: 907-914.

Zappi, M.E. (1995). Peroxone oxidation treatment of 2,4,6-trinitrotoluene contaminated waters with and without sonolytic catalyzation, dissertation, submitted to the faculty of Mississippi State University in partial fulfillment of the requirements for the degree of doctoral philosophy in chemical engineering in the department of chemical engineering.

Zepp, R. G., Braun, A. M., Hoigne, J., and Leenheer, J. A. (1987). Photoproduction of hydrated electrons from natural organic solutes in aquatic environments. Environmental Science and Technology 21: 485-490.

Zwart, A., Woutersen, R. A., Wilmer, JWGM, Spit, B. J., and Feron, V. J. (1988). Cytotoxic and adaptive effects in rat nasal epithelium after 3-day and 13-week exposure to low concentrations of formaldehyde vapour. Toxicology 51: 87-99.

APPENDICES

APPENDIX A

Table A-1 Degradation of formaldehyde by volatilization, UV, H_2O_2 and UV/H_2O_2 ($[CH_2O]_0$ = 10,000 mg/l, CH_2O:H_2O_2 = 1:2, initial pH = 5)

Time	**Residual Fraction of formaldehyde (C/Co)**			
	Volatilization	**Photolysis**	**H_2O_2**	**UV/H_2O_2**
0 min	1.000	1.000	1.000	1.000
5 min	1.000	0.922	0.982	0.998
10 min	1.000	0.912	0.975	0.967
15 min	1.000	0.911	0.945	0.965
30 min	0.999	0.912	0.940	0.817
60 min	0.997	0.903	0.925	0.615
90 min	1.000	0.867	0.920	0.475
120 min	0.996	0.868	0.899	0.359
150 min	1.000	0.733	0.836	0.257
180 min	0.995	0.673	0.678	0.180
240 min	0.996	0.659	0.635	0.033
300 min	0.968	0.572	0.617	0.000

Table A-2 Degradation of Formaldehyde by UV/H_2O_2 Process ($[CH_2O]_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:0.1, pH 3)

Time	**pH**	**Residual Fraction (C/Co)**		
		CH_2O	**H_2O_2**	**TOC**
0 min	3.000	1.000	1.000	1.000
5 min	2.870	0.995	0.867	0.990
10 min	2.760	0.994	0.690	0.990
15 min	2.580	0.961	0.578	0.984
30 min	2.640	0.920	0.359	0.978
60 min	2.540	0.899	0.127	0.968
90 min	2.540	0.870	0.070	0.961
120 min	2.520	0.832	0.042	0.957
150 min	2.500	0.802	0.035	0.954
180 min	2.510	0.798	0.028	0.953
240 min	2.470	0.788	0.021	0.934
300 min	2.520	0.735	0.007	0.921

Table A-3 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:0.5, pH 3)

Time	**pH**	**Residual Fraction (C/Co)**		
		CH_2O	**H_2O_2**	**TOC**
0 min	3.000	1.000	1.000	1.000
5 min	2.890	0.938	0.874	0.997
10 min	2.760	0.834	0.775	0.996
15 min	2.700	0.757	0.676	0.987
30 min	2.510	0.692	0.310	0.972
60 min	2.360	0.595	0.113	0.969
90 min	2.250	0.526	0.035	0.966
120 min	2.220	0.467	0.018	0.963
150 min	2.180	0.457	0.011	0.957
180 min	2.240	0.452	0.007	0.950
240 min	2.210	0.415	0.003	0.932
300 min	2.200	0.392	0.003	0.915

Table A-4 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:1, pH 3)

Time	**pH**	**Residual Fraction (C/Co)**		
		CH_2O	**H_2O_2**	**TOC**
0 min	3.000	1.000	1.000	1.000
5 min	2.750	0.994	0.688	0.993
10 min	2.600	0.901	0.615	0.983
15 min	2.470	0.766	0.490	0.966
30 min	2.230	0.618	0.293	0.959
60 min	2.100	0.391	0.059	0.949
90 min	2.060	0.363	0.022	0.944
120 min	2.040	0.328	0.007	0.931
150 min	2.030	0.295	0.002	0.926
180 min	2.030	0.266	0.001	0.925
240 min	2.030	0.000	0.000	0.893
300 min	2.020	0.000	0.000	0.870

Table A-5 Degradation of Formaldehyde by UV/H_2O_2 Process
([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:2, pH 3)

Time	**pH**	**Residual Fraction (C/Co)**		
		CH_2O	**H_2O_2**	**TOC**
0 min	3.000	1.000	1.000	1.000
5 min	2.770	1.000	0.750	0.994
10 min	2.640	0.931	0.655	0.989
15 min	2.580	0.878	0.603	0.981
30 min	2.390	0.807	0.519	0.979
60 min	2.230	0.638	0.383	0.968
90 min	2.140	0.499	0.360	0.957
120 min	2.080	0.375	0.291	0.963
150 min	2.060	0.272	0.254	0.937
180 min	2.060	0.207	0.195	0.891
240 min	2.040	0.038	0.000	0.859
300 min	2.030	0.000	0.000	0.845

Table A-6 Degradation of Formaldehyde by UV/H_2O_2 Process
([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:3, pH 3)

Time	**pH**	**Residual Fraction (C/Co)**		
		CH_2O	**H_2O_2**	**TOC**
0 min	3.000	1.000	1.000	1.000
5 min	2.730	0.909	0.738	0.997
10 min	2.520	0.865	0.673	0.996
15 min	2.490	0.847	0.619	0.992
30 min	2.380	0.794	0.600	0.972
60 min	2.250	0.636	0.571	0.964
90 min	2.230	0.493	0.537	0.946
120 min	2.150	0.349	0.539	0.922
150 min	2.050	0.235	0.542	0.919
180 min	2.030	0.230	0.520	0.916
240 min	2.070	0.110	0.486	0.911
300 min	2.070	0.100	0.478	0.905

Table A-7 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:0.1, pH 5)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	5.000	1.000	1.000	1.000
5 min	3.320	0.974	0.655	0.994
10 min	3.040	0.954	0.535	0.991
15 min	2.930	0.953	0.444	0.990
30 min	2.850	0.937	0.275	0.990
60 min	2.710	0.917	0.120	0.986
90 min	2.660	0.876	0.063	0.986
120 min	2.660	0.835	0.049	0.977
150 min	2.540	0.809	0.042	0.977
180 min	2.560	0.800	0.028	0.975
240 min	2.570	0.770	0.021	0.968
300 min	2.570	0.757	0.014	0.938

Table A-8 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:0.5, pH 5)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	5.000	1.000	1.000	1.000
5 min	3.070	0.929	0.747	0.971
10 min	2.740	0.855	0.606	0.957
15 min	2.610	0.833	0.507	0.957
30 min	2.420	0.806	0.240	0.955
60 min	2.300	0.676	0.081	0.947
90 min	2.260	0.661	0.037	0.943
120 min	2.250	0.661	0.015	0.937
150 min	2.210	0.630	0.012	0.936
180 min	2.220	0.624	0.012	0.922
240 min	2.200	0.601	0.003	0.891
300 min	2.220	0.593	0.001	0.885

Table A-9 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:1, pH 5)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	5.000	1.000	1.000	1.000
5 min	3.120	0.994	0.644	0.999
10 min	3.050	0.928	0.571	0.995
15 min	2.900	0.869	0.490	0.972
30 min	2.590	0.684	0.344	0.962
60 min	2.230	0.504	0.110	0.961
90 min	2.170	0.400	0.029	0.958
120 min	2.180	0.370	0.007	0.936
150 min	2.190	0.367	0.004	0.936
180 min	2.190	0.365	0.004	0.926
240 min	ND	0.000	0.000	0.905
300 min	ND	0.000	0.000	0.873

Table A-10 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:2, pH 5)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	5.000	1.000	1.000	1.000
5 min	2.960	0.998	0.728	0.971
10 min	2.750	0.967	0.677	0.955
15 min	2.630	0.965	0.604	0.953
30 min	2.490	0.817	0.567	0.940
60 min	2.310	0.615	0.483	0.933
90 min	2.220	0.475	0.443	0.922
120 min	2.160	0.359	0.439	0.917
150 min	2.120	0.257	0.410	0.884
180 min	2.100	0.180	0.384	0.878
240 min	2.050	0.033	0.315	0.842
300 min	2.060	0.000	0.249	0.778

Table A-11 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:3, pH 5)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	5.000	1.000	1.000	1.000
5 min	3.060	0.967	0.729	0.996
10 min	2.840	0.936	0.697	0.991
15 min	2.730	0.805	0.656	0.991
30 min	2.560	0.781	0.602	0.990
60 min	2.400	0.724	0.561	0.988
90 min	2.320	0.607	0.549	0.986
120 min	2.250	0.521	0.529	0.982
150 min	2.220	0.402	0.515	0.974
180 min	2.190	0.319	0.495	0.964
240 min	2.160	0.166	0.474	0.958
300 min	2.150	0.106	0.447	0.928

Table A-12 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:0.1, pH 7)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	7.000	1.000	1.000	1.000
5 min	3.650	0.961	0.063	0.996
10 min	3.430	0.958	0.056	0.993
15 min	3.250	0.955	0.053	0.993
30 min	3.050	0.946	0.046	0.993
60 min	2.840	0.916	0.042	0.980
90 min	2.790	0.882	0.032	0.978
120 min	2.960	0.788	0.039	0.975
150 min	2.680	0.773	0.032	0.992
180 min	2.690	0.753	0.028	0.967
240 min	2.670	0.718	0.028	0.966
300 min	2.620	0.701	0.028	0.941

Table A-13 Degradation of Formaldehyde by UV/H_2O_2 Process
([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:0.5, pH 7)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	7.000	1.000	1.000	1.000
5 min	3.970	0.956	0.359	0.968
10 min	2.550	0.808	0.275	0.956
15 min	2.450	0.765	0.225	0.951
30 min	2.320	0.722	0.134	0.948
60 min	2.210	0.714	0.035	0.939
90 min	2.170	0.649	0.021	0.928
120 min	2.190	0.648	0.009	0.915
150 min	2.150	0.636	0.007	0.909
180 min	2.160	0.629	0.005	0.908
240 min	2.150	0.597	0.004	0.890
300 min	2.200	0.577	0.003	0.871

Table A-14 Degradation of Formaldehyde by UV/H_2O_2 Process
([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:1, pH 7)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	7.000	1.000	1.000	1.000
5 min	2.820	0.932	0.415	0.989
10 min	2.520	0.872	0.393	0.975
15 min	2.420	0.814	0.372	0.965
30 min	2.250	0.769	0.284	0.945
60 min	2.090	0.436	0.102	0.925
90 min	2.020	0.264	0.025	0.888
120 min	2.070	0.193	0.008	0.886
150 min	2.020	0.192	0.003	0.876
180 min	2.070	0.182	0.002	0.874
240 min	2.080	0.172	0.001	0.862
300 min	2.110	0.142	0.000	0.832

Table A-15 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:2, pH 7)

Time	**pH**	**Residual Fraction (C/Co)**		
		CH_2O	**H_2O_2**	**TOC**
0 min	7.000	1.000	1.000	1.000
5 min	3.050	0.985	0.747	0.985
10 min	2.810	0.957	0.681	0.976
15 min	2.660	0.879	0.654	0.973
30 min	2.480	0.725	0.600	0.959
60 min	2.260	0.472	0.508	0.957
90 min	2.160	0.337	0.469	0.945
120 min	2.100	0.225	0.450	0.911
150 min	2.050	0.109	0.408	0.866
180 min	2.050	0.038	0.377	0.855
240 min	1.990	0.000	0.319	0.817
300 min	1.950	0.000	0.262	0.758

Table A-16 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:3, pH 7)

Time	**pH**	**Residual Fraction (C/Co)**		
		CH_2O	**H_2O_2**	**TOC**
0 min	7.000	1.000	1.000	1.000
5 min	3.080	0.941	0.778	0.995
10 min	2.940	0.889	0.758	0.989
15 min	2.810	0.816	0.745	0.982
30 min	2.600	0.663	0.708	0.977
60 min	2.390	0.564	0.688	0.919
90 min	2.340	0.515	0.669	0.919
120 min	2.280	0.426	0.679	0.899
150 min	2.300	0.280	0.664	0.893
180 min	2.270	0.253	0.649	0.854
240 min	2.240	0.245	0.634	0.837
300 min	2.220	0.234	0.594	0.831

Table A-17 Degradation of Formaldehyde by UV/H_2O_2 Process

($[CH2O]_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:0.1, pH 9)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	9.000	1.000	1.000	1.000
5 min	4.300	0.992	0.056	0.995
10 min	3.420	0.984	0.049	0.980
15 min	3.280	0.978	0.049	0.976
30 min	3.050	0.975	0.046	0.973
60 min	2.920	0.946	0.035	0.972
90 min	2.820	0.917	0.032	0.972
120 min	2.750	0.902	0.028	0.971
150 min	2.710	0.898	0.025	0.960
180 min	2.680	0.859	0.025	0.957
240 min	2.650	0.780	0.021	0.949
300 min	2.640	0.718	0.021	0.947

Table A-18 Degradation of Formaldehyde by UV/H_2O_2 Process

($[CH2O]_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:0.5, pH 9)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	9.000	1.000	1.000	1.000
5 min	2.870	0.890	0.225	0.996
10 min	2.650	0.880	0.190	0.982
15 min	2.530	0.791	0.148	0.963
30 min	2.490	0.748	0.099	0.948
60 min	2.340	0.733	0.063	0.947
90 min	2.280	0.729	0.021	0.945
120 min	2.250	0.721	0.014	0.942
150 min	2.250	0.713	0.010	0.940
180 min	2.230	0.705	0.010	0.937
240 min	2.230	0.670	0.004	0.936
300 min	2.200	0.628	0.003	0.931

Table A-19 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:1, pH 9)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	9.000	1.000	1.000	1.000
5 min	3.000	0.962	0.593	1.000
10 min	2.740	0.933	0.529	0.996
15 min	2.590	0.931	0.472	0.985
30 min	2.380	0.758	0.343	0.981
60 min	2.140	0.519	0.164	0.971
90 min	2.080	0.431	0.064	0.965
120 min	2.070	0.298	0.023	0.956
150 min	2.050	0.247	0.007	0.945
180 min	2.080	0.246	0.006	0.921
240 min	2.100	0.244	0.006	0.920
300 min	2.110	0.181	0.006	0.915

Table A-20 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:2, pH 9)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	9.000	1.000	1.000	1.000
5 min	3.280	0.960	0.740	0.997
10 min	2.950	0.943	0.700	0.997
15 min	2.820	0.900	0.650	0.982
30 min	2.600	0.823	0.604	0.966
60 min	2.390	0.612	0.557	0.965
90 min	2.340	0.458	0.525	0.957
120 min	2.210	0.373	0.493	0.951
150 min	2.170	0.292	0.468	0.950
180 min	2.120	0.191	0.425	0.943
240 min	2.070	0.118	0.364	0.931
300 min	2.040	0.031	0.304	0.898

Table A-21 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]$_0$ = 10,000 mg/l, molar ratio of CH_2O:H_2O_2 = 1:3, pH 9)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	9.000	1.000	1.000	1.000
5 min	3.240	0.971	0.693	0.991
10 min	2.960	0.954	0.674	0.982
15 min	2.820	0.933	0.660	0.978
30 min	2.600	0.861	0.638	0.972
60 min	2.420	0.651	0.629	0.964
90 min	2.350	0.567	0.622	0.960
120 min	2.520	0.442	0.607	0.955
150 min	2.540	0.368	0.600	0.943
180 min	2.620	0.246	0.596	0.944
240 min	2.300	0.143	0.548	0.932
300 min	2.310	0.124	0.548	0.909

Table A-22 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]o = 1,000 mg/l, molar ratio of CH2O:H2O2 = 1:2, pH7)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	7.000	1.000	1.000	1.000
5 min	3.340	0.214	0.587	0.953
10 min	2.820	0.000	0.518	0.963
15 min	2.650	0.000	0.442	0.819
30 min	2.660	0.000	0.190	0.711
60 min	2.720	0.000	0.065	0.678
90 min	2.680	0.000	0.023	0.643
120 min	2.540	0.000	0.008	0.598
150 min	2.570	0.000	0.008	0.525
180 min	2.560	0.000	0.004	0.461
240 min	2.550	0.000	0.000	0.396
300 min	2.540	0.000	0.000	0.374

Table A-23 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]o = 3,000 mg/l, molar ratio of CH2O:H2O2 = 1:2, pH7)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	7.000	1.000	1.000	1.000
5 min	3.080	0.947	0.724	0.955
10 min	2.800	0.878	0.705	0.952
15 min	2.770	0.630	0.673	0.924
30 min	2.550	0.567	0.584	0.934
60 min	2.360	0.130	0.463	0.885
90 min	2.280	0.000	0.375	0.802
120 min	2.060	0.000	0.184	0.729
150 min	2.040	0.000	0.044	0.542
180 min	2.020	0.000	0.019	0.485
240 min	2.000	0.000	0.004	0.421
300 min	1.940	0.000	0.000	0.402

Table A-24 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]o = 5,000 mg/l, molar ratio of CH2O:H2O2 = 1:2, pH7)

Time	pH	Residual Fraction (C/Co)		
		CH_2O	H_2O_2	TOC
0 min	7.000	1.000	1.000	1.000
5 min	3.180	0.946	0.743	0.996
10 min	2.880	0.922	0.705	0.958
15 min	2.680	0.846	0.678	0.953
30 min	2.460	0.643	0.606	0.958
60 min	2.320	0.426	0.507	0.936
90 min	1.850	0.266	0.408	0.862
120 min	2.150	0.069	0.331	0.773
150 min	2.140	0.000	0.259	0.694
180 min	2.170	0.000	0.171	0.676
240 min	2.160	0.000	0.038	0.488
300 min	2.180	0.000	0.000	0.450

Table A-25 Degradation of Formaldehyde by UV/H_2O_2 Process

([CH2O]o = 30,000 mg/l, molar ratio of CH2O:H2O2 = 1:2, pH7)

Time	**pH**	**Residual Fraction (C/Co)**		
		CH_2O	**H_2O_2**	**TOC**
0 min	7.000	1.000	1.000	1.000
5 min	2.900	0.991	0.648	0.987
10 min	2.590	0.970	0.542	0.977
15 min	2.470	0.951	0.525	0.971
30 min	2.310	0.880	0.521	0.967
60 min	2.080	0.835	0.516	0.966
90 min	2.030	0.755	0.499	0.966
120 min	1.990	0.660	0.470	0.965
150 min	1.960	0.623	0.453	0.958
180 min	1.940	0.527	0.436	0.948
240 min	1.920	0.426	0.432	0.893
300 min	1.770	0.364	0.360	0.888

Table A-26 Initial Rate Constants of Formaldehyde (k_{CH2O}) of Degradation of Formaldehyde using UV/H_2O_2 Process at Different Experimental Conditions.

Experimental Conditions	Initial Rate Constant * (min^{-1})	$t_{1/2}$ (min)	R^2	n
$[CH_2O]:[H_2O_2]$ = 1:0.1, pH 3	2.98×10^{-3}	232.55	0.994	5
pH 5	4.67×10^{-3}	148.39	0.996	3
pH 7	8.06×10^{-3}	85.98	-	2
pH 9	1.50×10^{-3}	462.00	0.997	4
$[CH_2O]:[H_2O_2]$ = 1:0.5, pH 3	19.05×10^{-3}	36.38	0.988	4
pH 5	12.60×10^{-3}	55.00	0.961	4
pH 7	19.45×10^{-3}	35.63	0.943	4
pH 9	23.24×10^{-3}	29.82	-	2
$[CH_2O]:[H_2O_2]$ = 1:1, pH 3	17.40×10^{-3}	39.83	0.962	5
pH 5	13.33×10^{-3}	52.11	0.968	5
pH 7	13.65×10^{-3}	50.77	1.000	4
pH 9	6.98×10^{-3}	99.28	0.995	3
$[CH_2O]:[H_2O_2]$ = 1:2, pH 3	7.74×10^{-3}	89.53	0.953	5
pH 5	0.38×10^{-3}	1823.68	-	2
pH 7	11.29×10^{-3}	61.38	0.960	5
pH 9	6.43×10^{-3}	107.78	0.994	5
$[CH_2O]:[H_2O_2]$ = 1:3, pH 3	14.5×10^{-3}	47.79	0.968	3
pH 5	6.64×10^{-3}	104.37	1.000	3
pH 7	13.89×10^{-3}	49.89	0.998	5
pH 9	4.9×10^{-3}	141.43	0.996	5

Note: * based on pseudo first order reactive kinetics

n = number of data taken to account for initial rate constant calculations

Table A-27 Initial Rate Constants of hydrogen peroxide (k_{H2O2}) in Degradation of Formaldehyde using UV/H_2O_2 Process at Different Experimental Conditions.

Experimental Conditions	**Initial Rate Constant * (min^{-1})**	**$t_{1/2}$ (min)**	**R^2**	**n**
$[CH_2O]:[H_2O_2]$ = 1:0.1, pH 3	3.46 x10^{-2}	20.04	0.996	5
pH 5	1.06 x 10^{-2}	65.57	-	2
pH 7	5.58 x 10^{-1}	1.24	-	2
pH 9	5.75 x 10^{-1}	1.20	-	2
$[CH_2O]:[H_2O_2]$ = 1:0.5, pH 3	2.59 x 10^{-2}	26.80	0.999	4
pH 5	7.30 x 10^{-2}	9.49	-	2
pH 7	2.05 x 10^{-1}	3.39	-	2
pH 9	2.98 x 10^{-1}	2.33	-	2
$[CH_2O]:[H_2O_2]$ = 1:1, pH 3	3.90 x10^{-2}	17.78	0.978	5
pH 5	1.10 x 10^{-1}	6.30	-	2
pH 7	1.76 x10^{-1}	3.94	-	2
pH 9	1.05 x 10^{-1}	6.63	-	2
$[CH_2O]:[H_2O_2]$ = 1:2, pH 3	5.74 x 10^{-2}	12.07	0.959	3
pH 5	7.92 x 10^{-2}	8.75	-	2
pH 7	5.85 x 10^{-2}	11.85	-	2
pH 9	6.03 x 10^{-2}	11.49	-	2
$[CH_2O]:[H_2O_2]$ = 1:3, pH 3	6.07 x 10^{-2}	11.42	-	2
pH 5	7.92 x 10^{-2}	8.75	-	2
pH 7	5.03 x 10^{-2}	13.77	-	2
pH 9	7.33 x 10^{-2}	9.46	-	2

Note: * based on pseudo first order reactive kinetics

n = number of data taken to account for initial rate constant calculations

APPENDIX B

Preliminary Study on biodegradability of formaldehyde using SBR biological treatment process

Procedure

Before start up the SBR biological treatment unit, the microorganism sludge from wastewater treatment plant (7,000 mg/l of SS) was raised to steady state(3,000 mg/l of SS) with glucose (1,500 mg/l COD). Then the sludge was divided to 9-liter reactor to investigate formaldehyde biodegradability at different initial concentrations using 7 reactors and a control reactor that use only glucose as energy source. The details of each SBR reactor are as shown in a table below.

Reactor	Formaldehyde concentration		COD (mg/l)
	mg/l	molar	
1	10,000	0.333	14,000
2	5,000	0.165	7,000
3	1,000	3.33×10^{-2}	1,400
4	500	1.65×10^{-3}	700
5	100	3.33×10^{-3}	140
6	50	1.65×10^{-4}	70
7	10	3.3×10^{-4}	14
8	0	0	1,500

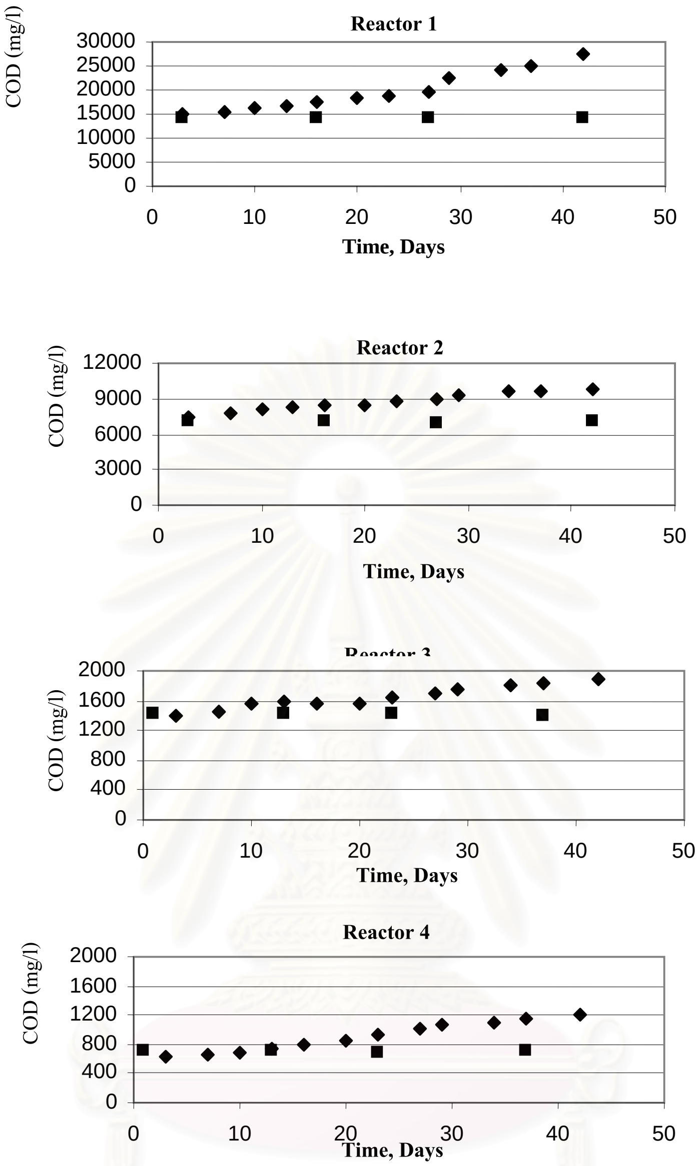


Figure B-1 Comparison of COD in influent and Effluent at different initial concentration of formaldehyde

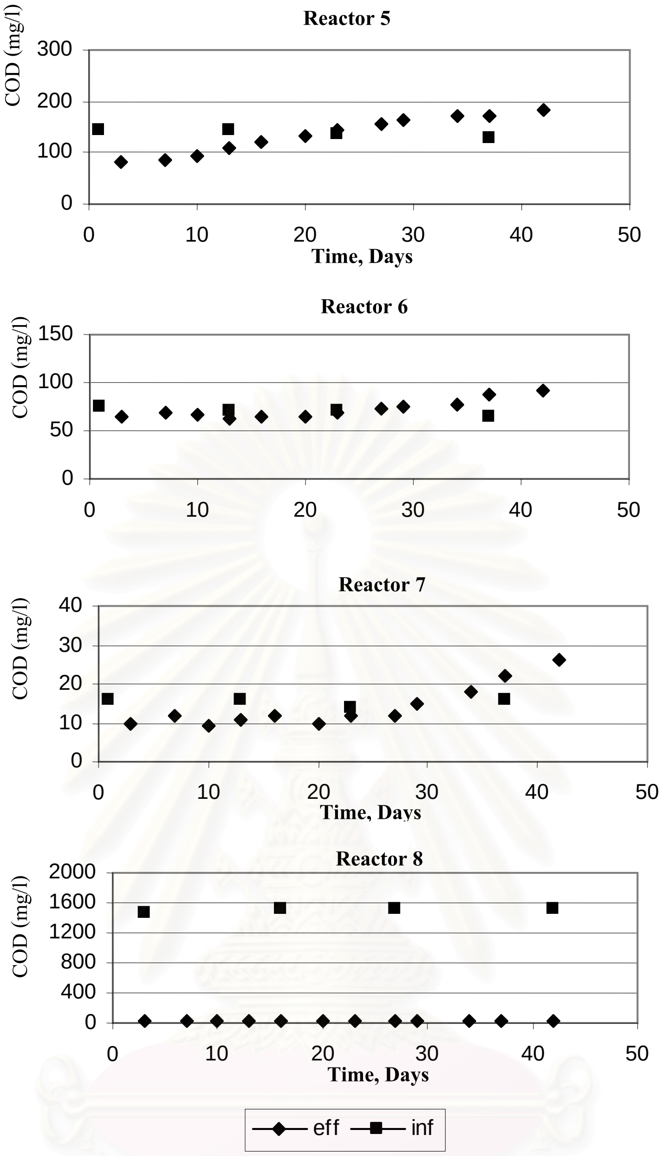


Figure B-1 (cont.) Comparison of COD in influent and Effluent at different initial concentration of formaldehyde

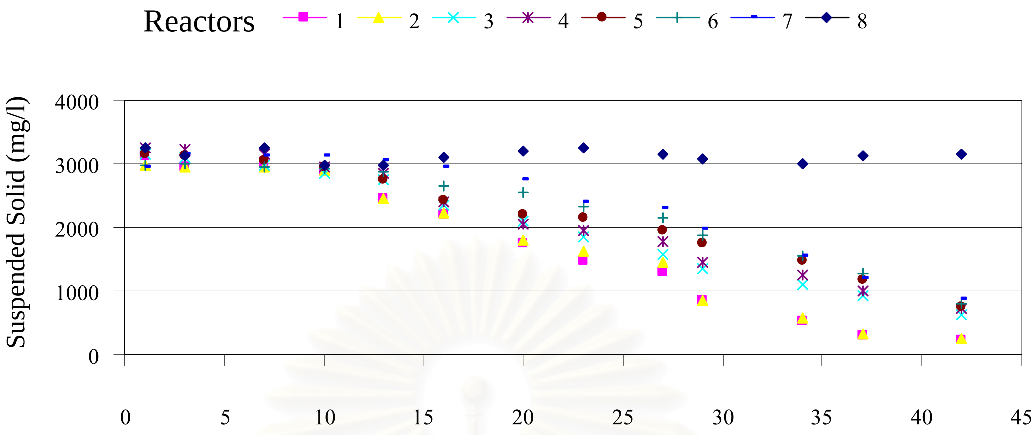


Figure B-2 Comparison of SS at different initial concentration of formaldehyde

Standard Iodometric method (Kingzett, C.T., 1880)

This method is used for measuring mg/l level of H_2O_2

Reagents

1. Potassium iodide solution (1%w/v KI). Dissolve 1.0 grams KI into 100 ml of RO water.
2. Ammonium molybdate solution. Dissolve 9 grams ammonium molybdate in 10 ml 6 N NH_4OH, add 24 grams NH_4NO_3 and dilute to 100 ml with RO water.
3. Sulfuric acid solution (1:4 H_2SO_4). Carefully add one part H_2SO_4 98 % to four parts RO water.
4. Starch indicator
5. Sodium thiosulfate (0.025 N Na_2SO_3. 5 H_2O) solution

Procedure

1. Sample was transfer to 250 ml Erlemeyer flask.
2. Adding RO water to the Erlenmeyer flask until 50 ml. Next, 10ml of 1:4 Sulfuric acid solution and 15 ml of 1% w/v of potassium iodide were added. Then 2 drops of ammonium molybdate was added.
3. Titrate with 0.025 N of sodium thiosulfate to faint yellow or straw color. Swirl or stir gentry during titration to minimize iodine loss.
4. Add about 2 ml starch indicator, and continue titration until the blue color just disappear.
5. Repeat steps 2-4 on a blank sample of water.
6. Note ml of 0.025 N of $Na_2SO_3.5H_2O$ for samples and blanks analysis.

Standardize

1. Weight out 2 grams of KI and transfer to 250 ml Erlenmeyer flask. Add RO water to 100 ml.
2. Then, 10 ml of 0.025 N of $K_2Cr_2O_7$ and 10 ml of 1+ 9 H_2SO_4 were added. After that, keep the Erlenmeyer flask in dark place for 5 minutes.
3. Add RO water to the Erlenmeyer flask until 200 ml.
4. Titrate with 0.025 N of sodium thiosulfate. And follow the procedure steps 3-4 as describe earlier.
5. Note ml of 0.025 N of $Na_2SO_3.5H_2O$ for standardize analysis.

Calculation

$$H_2O_2\ (\text{mg/l}) = \frac{(\text{A-B}) \times (\text{Normality of } Na_2SO_3) \times 17 \times 1{,}000}{\text{ml of sample}}$$

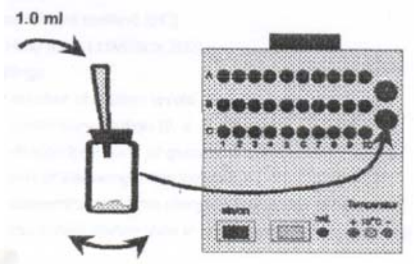
A = ml of Na_2SO_3 for sample

B = ml of Na_2SO_3 for blank

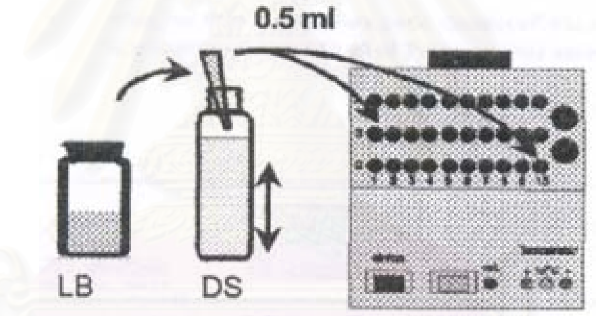
$$\text{N = Normality of } Na_2SO_3 = \frac{10 \times 0.025}{\text{ml of } Na_2SO_3 \text{ for standardize}}$$

Toxicity Test

1. Reactivate luminescent bacteria

 → Thaw reconstitution solution. Keep in refrigerator.	 → Remove luminescent bacteria from freezer just before reactivation	 → Quickly suspend the freeze-dried luminescent bacteria in 1.0 ml reconstitution solution at refrigerator temperature. → Thermostat for 15 minutes in refrigerator.

2. Dilute luminescent bacteria in line with test instructions and transfer to glass cuvettes



→ Mix 1 part luminescent bacteria suspension (LB) with 50 parts dilution solution (DS):
→ e.g.: 0.01 ml LB + 0.50 ml DS
0.25 ml LB + 12.50 ml DS
0.50 ml LB + 25.00 ml DS
1.00 ml LB + 50.00 ml DS
→ Transfer 0.5 ml of the mixture to glass cuvettes in positions B1 to C10, depending on requirements, of the LUMIStherm.
→ Thermostat for 15 minutes at 15'C.

3. In the meantime: Prepare the sample and the dilution series

Prepare Sample:

* Filter turbid sample, using filter from LUMISterra (accessories). Do not use a cellulose nitrate or a cellulose acetate filter.

* Check pH and, if necessary, adjust to pH 6 to 8 with HCI or NaOH.

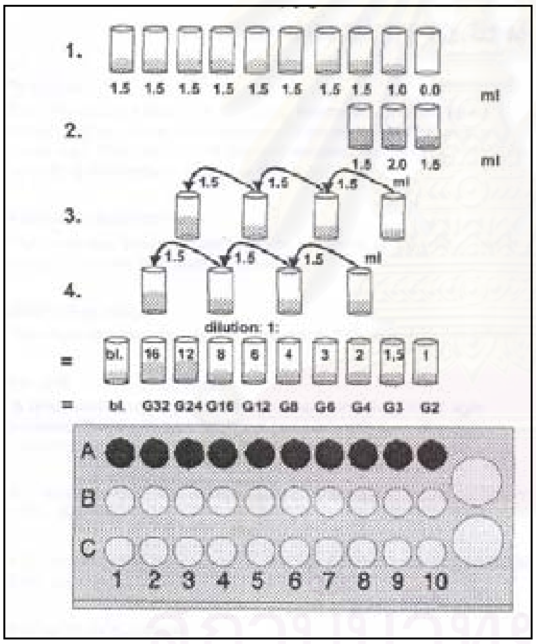
* Add solid NaCI until the concentration in the sample is 2% (wlv) (e.g.: weigh out 0.3 g NaCl and dissolve it in 15 ml sample).

* If the salt concentration of the sample exceeds 20 g/l (guide value: conductivity of 35 mS/cm) do not add any NaCl.

* The salt content of the sample should not exceed 50 g/l (corresponds to a conductivity of about 70 mS/cm without taking other conductive compounds into account).

* If necessary (high toxicity), carry out a preliminary dilution of the sample with 2% NaCI solution. Select a preliminary dilution from the levels 1:2, 1:4, 1:8, 1:16 etc.

Prepare Dilution series from the sample (If necessary):



1. Introduce 2% NaCI solution (A1 –A9).

2. Add prepared sample (A8 -A10) and mix.

3. Transfer 1.5 ml from position A9 to position A7, mix; transfer 1.5 ml from A7 to A5, mix; Transfer 1.5 ml from A5 to A3, mix.

4. Transfer 1,5 ml from position A8 to position A6, mix; transfer 1.5 ml from A6 to A4, mix; Transfer 1.5 ml from A4 to A2, mix.

This produces the dilution series referred to in DIN 38412 L34, L341 with solutions ranging from undiluted to a dilution ratio of 1:16. This corresponds to G values of 2 to 32 in the test as 0.5 ml of bacteria suspension are added to 0.5 ml of sample dilution in the test, thus increasing the dilution by a factor of two.

If this pipetting sequence is carried out after preliminary dilution of the sample by the factor 1:2, 1:4, 1:8, 1:16, etc., the DIN dilution series shifts accordingly: e.g. preliminary dilution 1:4: G values in the test 8, 12, 16,24,32,48,64, etc.

Test procedure

1. I_o Measurement

* Insert cuvette from B1 into measuring instrument and Initiate measurement. Remove cuvette, replace it in B1and add 0.5 ml sample from A1.

* Insert cuvette from C1 into measuring instrument and initiate measurement. Remove cuvette, replace it in C1and add 0.5 ml sample from A1.

* Repeat with all of the cuvettes in rows B and C, always adding the associated sample from row A.

2. Wait for the incubation period to end.

3. I_t measurement

* Insert cuvette from B1 into measuring instrument. Initiate measurement. Remove cuvette and replace it in B1.

* Repeat with the other cluvettes.

* After the final cuvette has been measured the result is displayed and is printed together with all of the measured values.

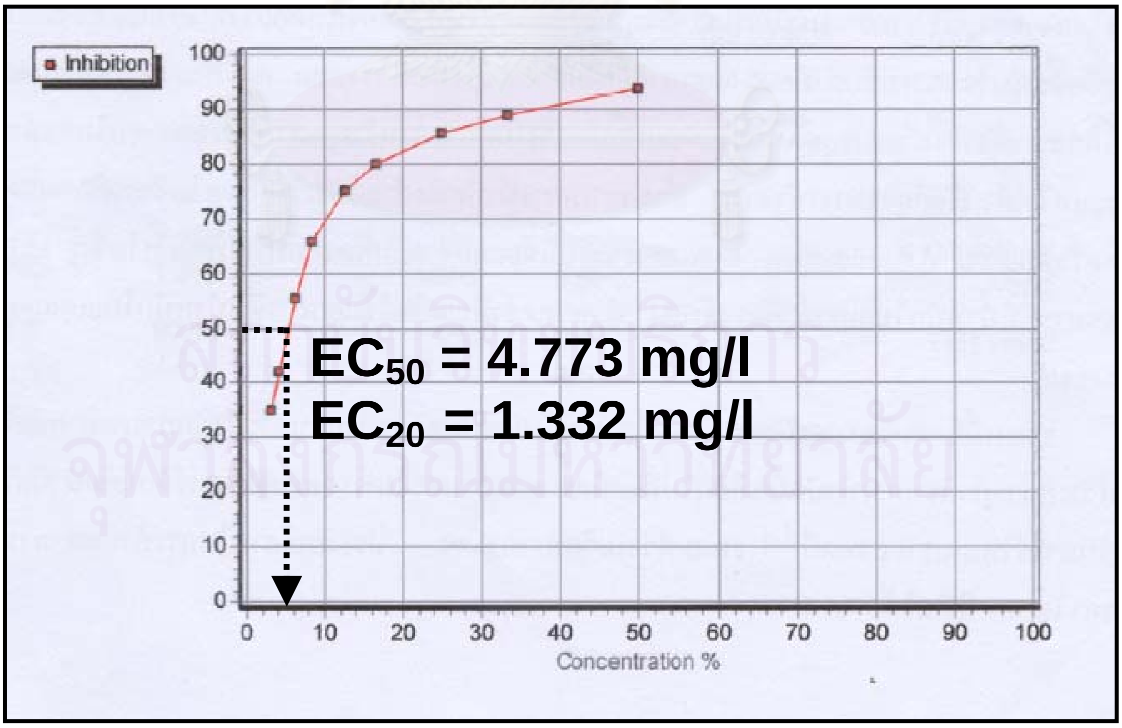


Figure B-3 Toxicity profile of Formaldehyde (10,000 mg/l of CH_2O with 10 fold predilution)

BIOGHAPHY

Miss Arissara Tariya was born on October 28, 1979 in Nan, Thailand. She attended Strisrina School and graduated in 1994. She received her Bachelor’s degree in Agricultural Science and Technology from faculty of Science and Technology, Thammasart University in 2001. She pursued her Master Degree studies in the International Postgraduate Program in Environmental Management (Hazardous Waste Management), Inter-Department of Environmental Management Chulalongkorn University, Bangkok, Thailand on February, 2003