DEGRADATION OF FORMALDEHYDE BY UV/TiO_2 PROCESS

Mr. Ratchata Titayanurak

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การย่อยสลายฟอร์มัลล์ดีไฮด์โดยใช้รังสียูวีร่วมกับไททาเนียมไดออกไซด์

นายรัชตะ ฐิตยานุรักษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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By	Ratchata Titayanurak
Field of Study	Environmental Management
Thesis Advisor	Puangrat Kajitvichyanukul, Ph.D.
Thesis Co-advisor	Professor Ming-Chun Lu, Ph.D.

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

……………………………………………… Dean of the 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 Ming-Chun Lu, Ph.D.)

……………………………………………… Member

(Associate Professor Wanpen Wirojanagud)

……………………………………………… Member

(Assistant Professor Jarurat Voranisarakul)

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ความเป็นพิษของฟอร์มัลดีไฮด์ซึ่งเป็นสารเคมีที่ถูกนำมาใช้อย่างกว้างขวางในปัจจุบัน ได้ก่อให้เกิดปัญหามลภาวะทางแหล่งน้ำ การระบายสารเคมีชนิดนี้โดยตรงหลังจากผ่านการใช้งานแล้วโดยปราศจากการกำจัดพิษอย่างเหมาะสม จะก่อให้เกิดความเสียหายต่อระบบบำบัดน้ำเสีย ดังนั้นจึงจำเป็นต้องมีการลดความเป็นพิษของฟอร์มัลดีไฮด์ก่อนที่จะทิ้งลงสู่ระบบบำบัดน้ำเสีย งานวิจัยนี้มุ่งเน้นที่จะย่อยสลายฟอร์มัลดีไฮด์โดยวิธีการที่นำมาใช้คือการใช้รังสียูวีร่วมกับไททาเนียมไดออกไซด์ ซึ่งจัดได้ว่าเป็นกระบวนการหนึ่งของกระบวนการออกซิเดชั่นขั้นสูง

การศึกษาความเป็นไปได้ของการใช้รังสียูวีร่วมกับไททาเนียมไดออกไซด์เพื่อใช้เป็นการบำบัดเบื้องต้นในการลดความเป็นพิษก่อนระบายลงสู่ระบบบำบัดน้ำเสียที่มีอยู่เดิม จำเป็นต้องศึกษาสภาวะที่เหมาะสมของระบบ ซึ่งได้แก่ ความเข้มข้นของไททาเนียมไดออกไซด์ ค่าพีเอช ตลอดจนความเข้มข้นเริ่มต้นของฟอร์มัลดีไฮด์ พบว่าเมื่อมีการย่อยสลายฟอร์มัลดีไฮด์โดยวิธีใช้แสงยูวี ร่วมกับ ไททาเนียมไดออกไซด์ รังสียูวีช่วยกระตุ้นการแตกตัวของไททาเนียมไดออกไซด์ให้เป็นไฮดรอกซิลเรดิคอล (OH•) ซึ่งมีความสามารถสูงในการทำลายโมเลกุลของฟอร์มัลดีไฮด์ โดยพบว่าความเข้มข้นที่เหมาะสมของไททาเนียมไดออกไซด์ที่ใช้คือ 0.1 กรัมต่อลิตร รวมทั้งพบว่า ค่าพีเอช และ ความเข้มข้นเริ่มต้นของฟอร์มัลดีไฮด์ มีผลต่อประสิทธิภาพในการย่อยสลายฟอร์มัลดีไฮด์ ประสิทธภาพสูงสุดจะเกิดในสารละลายผสมที่มีสภาวะเป็นกรด ที่พีเอช 3 จากการศึกษายังพบว่าการย่อยสลายฟอร์มัลดีไฮด์ด้วยกระบวนการนี้ไม่สามารถย่อยสลายฟอร์มัลดีไฮด์เป็นคาร์บอนไดออกไซด์และน้ำได้ทั้งหมด ความเข้มข้นเริ่มต้นของฟอร์มัลดีไฮด์ที่น้อยกว่า 3,000 มก./ล. น้ำที่ผ่านการบำบัดจึงจะไม่มีความเป็นพิษต่อสิ่งมีชีวิต

สาขาวิชาการจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต...
ปีการศึกษา 2546 ลายมือชื่ออาจารย์ที่ปรึกษา.......................................
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Photocatalysis by UV/TiO_2 process was evaluated for the degradation of the synthetic formaldehyde solution using a lab scale-batch reactor. The effects of titanium dioxide dosage, pH of mixture solution, and initial concentration of formaldehyde were systemically studied. The highest efficiency of formaldehyde degradation was achieved with the dosage of titanium dioxide 0.1 g/l. At the larger dosage, an excess amount would inhibit the transimission of light and furtherly caused decreasing in removal efficiency. Additionally, both pH and the initial concentration of formaldehyde in mixture solution affected the efficiecy removal. The photocatalytic of formaldehyde degradation was favored under an acidic condition at pH 3 and decreased with increasing initial formaldehyde concentration. The reduction of toxicity and Total Organic Carbon were also investigated because the total mineralization is an important criteria in assessing the feasibility of this process for formaldehyde degradation. The toxicity reduction below EC_{50} was only attained when the initial concentration was less than 3,000 mg/l.

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

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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

In general, wastewater treatment plant for hospital mostly is the biological process. Regarding to King Mongkut's University of Technology Thonburi (KMUTT)'s studies (Charuratana and Voranisarakul, 1993; Cheawchanthanakit and Sangphromma 1997), the failure of the wastewater treatment plant was caused by the batch direct discharge of toxic chemicals causing shock load to the biological treatment process. The toxic chemicals used in hospital include formalin solution as 40% formaldehyde and other chemicals such as acetone, chloroform. It was reported that, for instance, the medical wastewater from Srinakarinvirot hospital was discharged formalin solution with 500 ml once a week from laboratory room and 67.5 m^3/time twice a year from embalming room. On the other hand, other chemicals such as acetone, alcohol, organic acids, and chloroform were discharged in very small amount compared with the volume of formalin solution. For example, chloroform was discharged approximately 5,000 ml once a month and alcohol was discharged with 1,000 ml once a month, whereas the concentration of formaldehyde in formalin solution from the laboratory and embalming room were approximately 5,000 mg/l and 40,000 mg/l respectively.

Formaldehyde, is considered as the highest toxic organic contaminant in the medical wastewater causing such a failure due to its relatively high concentration with large volume discharged. Formaldehyde solution is discharged into the bioogical wastewater systems from various sources-labolaratory. As it is commonly used as the preservative in laboratory and embalming room in hospital. From the analysis, the concentration of formaldehyde in formalin solution from the laboratory and embalming room were about 5,000 mg/l and 40,000 mg/l respectively. With the large discharge volume and high concentration, the formalin solution becomes the most significant pollutant that was focused in this study. Accordingly, the purification of wastewater contaminated by formaldehyde is to become and important envrionmental protection task. However, the conventional biological treatment is not able to efficiently remove formaldehyde contamination and sometimes it may be failure by itself. Bacteria die-off and system upset in the biological system are common because of the toxic nature of formaldehyde containimation.

Aim of this research was to explore the photocatalytic technique as a means for the treatment of formaldehyde in synthetic solution, using chemical treatment methods UV/TiO_2 advance oxidation process for formaldehyde degradation. The reasons of this method selection are as follow:

1. UV/TiO_2 process is the high efficiency technology to remove organic contaminant from wastewater and it does not required the post-treatment process, for example, sludge handling.
2. Titanium dioxide was used in this study due to its stability in water, availability, low price and extensive use as catalyst support material.
3. UV/TiO_2 process is considered as the cheapest method among available 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/TiO_2 photo decomposed process.

1. To study the role of TiO_2 on degradation for treating formaldehyde in the synthetic formalin solution by UV/TiO_2 process.
2. To determine the optimum conditions for treating formaldehyde in the synthetic formalin solution by UV/TiO_2 process.
3. To investigate the factors including pH, initial concentration of formaldehyde that influence UV/TiO_2 process on the removal efficiency of formaldehyde.

1.3 Hypotheses

The photocatalytic degradation of organic compounds is a new method for elimination of contaminants from water. Photocatalytic degradation over illuminated

TiO_2 has been viewed with great interest as a promising method for the removal of trace organic and inorganic contaminants from water.

1. The removal efficiency of the UV/TiO_2 oxidation process for treating formaldehyde depends on pH, dosage of TiO_2 and the initial concentration of formaldehyde.

2. Formaldehyde degradation can be achieved by UV/TiO_2 advance oxidation process

1.4 Scopes of Work

Scopes of this work was as follows:

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

2. Investigated variables include pH, e.g., acidic, neutral and basic, molar ratio of formaldehyde to hydrogen peroxide, and initial concentration of formaldehyde.

3. Measured parameters were residual of formaldehyde and, total organic carbon (TOC), and toxicity.

This research covered two phases.

- Study of the adsorption characteristics of formaldehyde onto the TiO_2 surface.

- Evaluation of the mineralization efficiencies of toxic chemicals with illuminated the TiO_2. Various factors affecting the mineralization of formaldehyde removal were studied. The extent of mineralization was measured by the change in total organic carbon (TOC). Toxicity assessment of the original formaldehyde and its photocatalytic degradation products were also tested. The UV spectra of the photocatalytically treated and untreated samples were compared.

1.5 Advantages of this Work

Results from this research could be beneficial for treatment of medical wastewater containing formaldehyde. This UV/TiO_2 technology can be transferred to the engineering application in a large scale, pilot plant, to modify for pretreatment of formalin solution and the safety level of formaldehyde for microorganism in a biological wastewater treatment plant.

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CHAPTER 2

BACKGROUNDS AND LITERATURE REVIEW

2.1 Introduction

Photocatalytic oxidation using a semiconductor such as TiO_2 as photocatalyst is one of Advanced Oxidation Processes. As TiO_2 is illuminated by light rays with wavelength below 380 nm, the photons excite valence band electrons across the band gap into the conduction band, leaving holes behing in the valence band. The holes in TiO_2 will react with water molecules or hydroxide ions (OH^-) and then produce hydroxyl radicals ($^{\bullet}OH$) Oxygen is usualy supplied as electron acceptor to prolong the recombination of electron-hole pairs during photocatalytic oxidation (Kuo, Ho, 2001).

Photocatalytic degradation over illuminated TiO_2 has been viewed with great interest as a promising mehtod for the removal of trace organic and inorganic contaminants from water (Borgarello, E., Harris, R., Pelizzetti, E., and Minero, C 1986, Ollis, D. F., Pelizzetti, D., and Serpone, N, 1989). Additionally, this technology requires inexpensive catalysts with high turnovers which can be supported in appropriate reactors (Ollis, D. F., Pelizzetti, D., and Serpone, N., 1989). It is well established that conduction band electron(e^-) and valence band holes (h^+) are generated when aqueous TiO_2 suspension is irradiated with light energy greater than its band gap energy. The photogenerated electrons could reduce the organic substrate or react with the adsorbed molecular O_2 on the Ti(III)-surface, reducing it to superoxide radical anion O^{2-}. The photogenerated holes can also oxidize either the organic molecules directly or the OH- ions and the H_2O molecules adsorbed at the TiO_2 surface to $^{\bullet}OH$ radicals. Together with other highlhy oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates.

2.1.1 Theoretical Backgrounds of UV-TiO_2 Photocatalysis

The concept of Advanced Oxidation Processes (AOPs) was established as the chemical oxidation technologies that rely on the formation of the hydroxyl radical ($OH^{\bullet}$) to further oxidize organic and/or inorganic contaminants (Glaze *et al*., 1993). During recent decades, the photocatalytic degradation of various toxic organic compounds has been proposed as a viable process to detoxify wastewater. (Schiavello 1997; Bahnemann et al., 1994; Bahnemann, 1999; Pichat, 1997; Ollis and Al-Ekabi, 1993; Robert et al., 2000). The basic process of photocatalysis consists of ejecting an electron from the valence band (VB) to the conduction band (CB) of the TiO_2 semi-conductor creating a h^+ hole in the valence band. Electrons are produced at the conduction band and positive holes are formed in the valenced band (Frank, A. J. and Honda, k., 1983).

The irradiation of this process is provided by ultraviolet (UV) with an energy equal or superior to the band gap (>3.2 eV) of TiO_2 with the equation shown below:

$$TiO_2 + hv \longrightarrow e^-_{cb} + h^+_{vb}$$

This process is followed by the formation of extremely reactive radicals (like $OH^{\bullet}$) at the semi-conductor (TiO_2) surface and / or a direct oxidation of the polluting species (R) as shown below (2):

$$h^+_{vb} + H_2O \longrightarrow OH^{\bullet} + H^+$$
$$h^+_{vb} + OH^- \longrightarrow OH^{\bullet}_{ad}$$
$$h^+_{vb} + R_{ads} \longrightarrow R^{\bullet}$$

From these equations, organic contaminants can undergo mineralization process and transform to oxygen and water.

In recent years, the photocatalytic-UV/TiO_2 process has been received considerable attention as an alternative remediation technology since the method offers a number of advantages over conventional technologies, in particular a large number of organic compounds dissolved or dispersed in water can be completely mineralized (Jesus Beltran De Heredia, 2001). The reaction is relatively high if large surface areas of the photocatalyst are available; The TiO_2 is chosen for this process due to an inexpensive, safe and very stable catalyst showing high photocatalytic efficiency (Edmondo Pramauro, 2001).

2.1.2 Hydroxyl Radicals

Hydroxyl radicals are extremely reactive, short lived and unselective transient species. The mean lifetime of $OH^{\bullet}$ radicals 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 radical 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 (M, R-H ...) by different types of reactions (equation 2.1 to 2.3) (Legrini et aI. 1993, Hoigne, 1998):

Electron Transfer Reaction:

$$OH^{\bullet} + M^{n} \longrightarrow M^{n+1} + (OH^-)_{aq} \qquad (2.1)$$

Hydrogen Abstraction:

$$OH^{\bullet} + R\text{-}H \longrightarrow R^{\bullet} + H_2O \qquad (2.2)$$

Electrophilic addition:

$$OH^{\bullet} + R_2C{=}CR_2 \longrightarrow {}^{\bullet}CR_2\text{-}C(OH)R_2 \qquad (2.3)$$

In equation 2.2, the hydroxyl radical is capable of oxidizing organic compounds mostly by hydrogen abstraction. Electron transfer to hydroxyl radicals (equation 2.1) is interesting in the case where the hydrogen abstraction or electrophilic adition reaction may be disfavored by multiple halogen substitution or steric hindrance. Finally, electrophilic addition of hydroxyl radicals to organic system, another mechanism of oxidative degradation presents in equation 2.3.

2.1.3 General Information and Properties of Titanium Dioxide

The photocatalyst used in this study was obtained from the Degussa Company (Frankfurt, Germany). The product is a highly dispersed solid with the properties noted in Table 2.2 (Degussa Technical Bulltin No. 56, 1982, Aluminum Oxide, Titanium Dioxide P25 Two highly Dispersed Metallic Oxide from Degussa Produced by the AEROSIL Process, 3rd Edition).

Table 2.1. Physico-chemical properties for Degussa Titanium Dioxides P25

Description	Units	Value
BET surface area	m^2/g	50±15
Averageprimary particle size	nm	30
Moisture at leavng plant site (2 hours at 105 °C)	%	<1.5
Ignition loss (2 hours at 100 °C)	%	<1.5
PH in 4% aqueous suspension	-	3-4
X-Ray structure	-	primary anatase
Isoelectric point at pH value	-	6.6
Density	g/cm^3	3.98
Titanium dioxide	%	>99.5
Aluminum oxide	%	<0.3
Silica	%	<0.01
Iron oxide	%	<0.01
HCL	%	<0.3

2.1.4 Properties of Formaldehyde

Generally, formaldehyde has been used as a formalin mixture solution in which its mixture is contained with approximately 30-50% of Formaldehyde in water and a small amount of methanol (methyl alcohol) also added to prevent polymerization. Formaldehyde is a colorless, flammable gas with a strong, pungent and irritating odor. It is organic chemical and a preservative and bonding agent which has been also known as methyl aldehyde, or methylene oxide. Basically, Formaldehyde can be soluble in water, ethanol, ether, acetone. The chemical formula for formaldehyde is CH_2O, shown in figure 2.1, Formaldehyde has itself molecular weight equal to 30.0262 g/mole (CRC Handbook of Chemistry and Physics, 1994).

Regarding to its properties and characteristics, Formaldehyde generally has been widely used in various purposes as an antiseptic, disinfectant, and preservative for biological materials. In aspects of medical purpose, for instance, Formaldehyde has been generally known as a preservative in medical laboratories including as an embalming agent in mortuaries. While to the industry manufacturing purpose, formaldehyde has been used as a sterile chemical, leather tanner, platter, preservative, and fumigant. Moreover, it has been also used for making commercial products such as resins, wrinkle-proof fabrics, rubber products, dyes, textiles, plastics, paper products, and cosmetics, etc. In addition to Formaldehyde purpose, it has been found in insulation materials, plywood, particleboard, and adhesives. Formaldehyde also presents in combustion products, such as fuel exhaust and tobacco smoke.

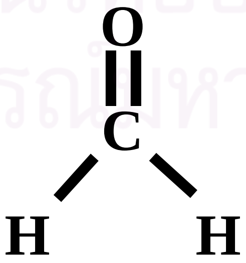


Figure 2.1 The structure of formaldehyde

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 following table:

Table 2.2 Summary of Chemical Properties of Formaldehyde

Molecular formula	CH_2O
Molecular weight	30.03 g/mol
Density	1.0800 g/L @ -20°C
Boiling point	97°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

Toxicology

Formaldehyde, because of its toxic in nature, can cause adverse effects on human health such as skin irritation and respiratory tract disease when it is dispersed into the air (IPCS, 1989). Moreover, it was found to critically cause damage to DNA and mutation in microorganisms and mammalian cells (Grafstrom et al. 1985). Generally known, Formaldehyde can cause health effects to human and mammalian cell even at low levels exposured. The severity is present at low levels of exposure of Formaldehyde airborne in concentrations above 0.1 ppm (per million parts of air). At even such a level, Formaldehyde can promptly irritate to the eyes, nose and throat. The increase of concentration, the higher severity of irritation would be presented, for instance at 100 ppm of Formaldehyde exposed into the air, is seriously dangerous to life and health immediately. Definitely, it also cause serious breathing problems and can possibly increase your risk to certain kinds of cancer. Nowadays, Occupational Health and Safety Agency (OSHA) regulates Formaldehyde to be a cancer-causing substance (www.oehha.ca.gov).

***Short term exposure**:*

There is considerable individual variation in 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 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 has brought on tearing and irritation. Small amounts of liquid in the eye can cause damage to the cornea.

Ingestion: As little as 0.35 grams has resulted in deaths to humans. Smaller amounts can damage the throat, stomach, and intestine resulting in nausea, vomiting, abdominal pain, and diarrhea. Accidental exposure may also cause loss of consciousness, lower blood pressure, kidney damage and, if the victim is pregnant, the possibility of the fetus being aborted.

***Long term exposure**:*

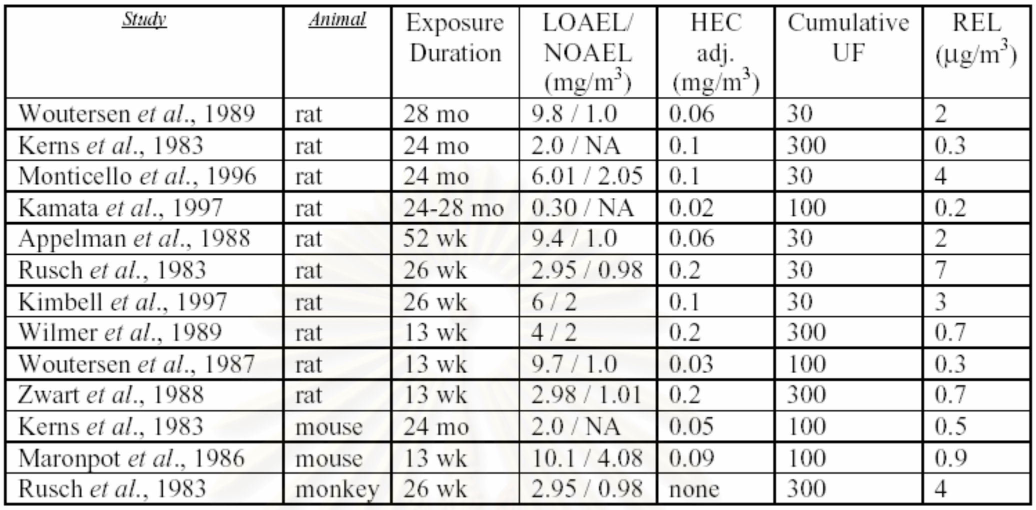
Inhalation can result in respiratory congestion with associated coughing and shortness of breath. Daily skin contact can lead to drying and scaling. Some individuals may experience allergic reactions after initial contact with the chemical. Subsequent contact may cause skin rashes and asthma and reactions 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 2.2 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 2.3 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 (µg/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
HEC = High explosive concentration
Cumulative CF = Cumulative Uncertain Factor
RELs = Reference Exposure Levels

2.2 Fundamentals of UV-TiO$_2$ Photocatalysis

2.2.1 Mechanism of Irradiated TiO$_2$ by UV illumination

Titanium dioxide, a wide range of organic compounds can be oxidized to CO$_2$ and H$_2$O at room temperature on TiO$_2$ catalysts in the presence of UV or near-UV illumination. However, slow reaction rates and poor solar efficiency have hindered the commercialization of this technology. It has been shown that the photocatalytic activity of TiO$_2$ is influenced by the crystal structure, surface area, size distribution, porosity, band gap, a surface hydroxyl group density. An electron is promoted from the valence band into the conduction band, leaving a hole. The separate electron or hole would react with electron donors and electron acceptors adsorbed on the semiconductor surface to run the light – induced redox process. The strong absorption intensity implied that more electrons could be promoted from the valence band into the conduction band and more separate electrons or holes could be produced, which were help to enhance the photocatalytic activity. Surface acidity is thought to take the form of stronger surface hydroxyl groups. These groups accept holes generated by illumination and, in turn, oxidize adsorbed molecues. Hole traps such as the hydroxyl groups prevent electron-hole recombination and, therefore, increase quantum yield. Thus, a greater number of surface hydroxyl groups may be expected to yield a higher reaction rate (Yuhong Zhang, Guoxing Xiong, Nan Yao, Weishen Yang, Xianzhi Fu, 2001).

A comparison between the kinetic rate constants for two oxidation systems reveals that the constants for the TiO_2/UV system are clearly greater (between 220-435%) than those obtained in the direct UV photooxidation (Jesus Beltran De Heredia, 2001). In order to achieve chemically productive photocatalysis, electron-hole pair recombination must be suppressed. This can be achieved by “trapping” these species with the surface adsorbates. The photo-excited electrons are trapped by molecular oxygen. The pricipal hole traps are adsorbed water molecules and OH^- ions producing OH radicals. It is well known that the titania surface possesses both acidic and basic sites. The acidic sites are asociated with coordinatively unsaturated surface metal ions while the latter are associated with surface anions or anion vacancies. Two different types of surface sites are hypothesised to be involved in the adsorption processes of the reacting species.

2.2.2 Application of Photocataltic UV-TiO_2

Recent reports indicated that the illumination of the photocatalytic-UV/TiO_2 system can significant enhance decomposition of many refractory organics. The examples of organic pollutants that have been successfully degraded by photocatalytic-UV/TiO_2 are as follow: CN^- solutions (Hisao Hidaka, 1992); Trihalomethanes (THMs) and chlorinate byproducts in chlorinated drinking water (Susan D. Richardson, 1996); alcohols and organochlorides (Jian Chen, 1998). Another research studied on the degradation of short-chain alkyl- and alkanolamines by TiO_2- and Pt/TiO_2-assisted photocatalysis. (M. Klare, J. Scheen, K. Vogelsang, H. Jacobs, J.A.C. Broekaert, 2000).

2.3 UV/TiO_2 Process and Factors that affect Efficiency

The production of hydrogen hydroxyl radicals within a UV/TiO_2 system can be affect by variables such as dosage of Titanium Dioxide, pH, initial concentration of pollutant and presence of hydroxyl radical scavenger species.

The major factors affecting the removal efficiency of the Photocatalytic-UV/TiO_2 reaction to degrade organic compounds are TiO_2 dosage, pH value, and the initial concentration of organic compounds. These factors are also investigated in this study to find the optimum condition to degrade formaldehyde from formalin solution. The effect of these factors are reported as follow:

2.3.1 Influence of Titanium Dioxide Dosage

In 1992 Hisao Hidaka studied the degradation of CN^- in industrial solution and found that it can be decomposed by photo-oxidation UV/TiO_2. Initial concentration of CN^- was 23500 ppm. With 2 mg/l of TiO_2 dosage, the degradation of CN^- is of a 69% yield of OCN^- that was further photo-oxidized to CO_2 and N_2. However, in 1999, J.A.C. Broekaert demonstrated the degradation of short-chain alkyl- and aldanolamines by TiO_2 and Pt/TiO_2 assisted photocatalysis. His experiment showed that with a TiO_2 dosage of 0.2 g l^{-1}, an optimum decrease of the concentration of $(C_2H_5)_2NH$ and $(HOC_2H_4)_2NH$ up to 55-80% of the initial nitrogen concentration, which is 5 x 10^{-4} mol l^{-1}. With higher TiO_2 dosage the dispersion of TiO_2 in water will inhibit the transiimission of light and cause the decrease in removal efficiency. For application in industrial scale, the in-depth investigation of optimum TiO_2 dosage is required.

2.3.2 Influence of pH

One of the important parameters in the photocatalytic reaction is the pH of the solution. According to the organic pollutant, an increase of the pH will have a positive or negative effect on their degradation rate and consequently the mineralization rate of the solution (Wang et al., 1998).

In the decomposition of industrial waste CN^- ions by photo-oxidation, the initial pH at 12 was applied to this study and the results was the removal of 69% yield of OCN^-. In 1998, Jian Chen studied the photacatalyzed oxidation of alcohols and organochlorides in the presence of native TiO_2 and metallized TiO_2 suspensions. It was observed that at a low pH, around 65% of the total amount of oxidized methanol was promptly converted to the final product (CO_2). At pH values >9, no or only very little mineralization (CO_2 production) of methanol and ethanol was observed. In 1999, the photocatalytic disinfection of urban wastewater was studied by J.A. Herrera Melian. It was found that, at pH 5 the presence of TiO_2 in solution enhances the total coliforms inactivation. At lower pH, total coliforms are not affected by this process.

However, J.A.C. Broekaert (2000) demonstrated the photocatalytic degradation of $C_2H_5NH_2$, $(C_2H_5)_2NH$, $HOC_2H_4NH_2$, $(HOC_2H_4)_2NH$ and $(HOC_2H_4)_3N$ (5×10^{-4} mol l^{-1}) was optimized in a wide range of pH from 3 to 11.5. The sum of nitrogen recovered after the degradation experiments were found to amount up to 55-80% of the initial nitrogen concentration. For the formaldehyde degradation, there is no report about the optimum pH to get the highest efficiency for formaldehyde removal by this process.

The change in solution pH affects not only the photocatalytic activity of TiO_2 but also the TiO_2 surface ionic speciation, because of the amphoteric behavior of this semi-conductor. According to the organic pollutant, an increase of the pH will have a positve or negative effect on their degradation rate and consequently the mineralization rate of the solution. These were the results from studing on the solar photocatalysis: a clean process for water detoxification (Didier Robert, Sixto Malato, 2001).

Several studies have shown that changes in reaction rates were rather insignificant over a wide pH range. For charged subsrates, on the other hand, a significant dependecy of the photocatalytic degradation efficiency upon the pH value has often been observed, since the overall surface charge and hence the adsorptive properties of TiO_2 particles depend strongly on solution pH. Generally spoken, alkaline pH values have been found to be favorable for the photocatalytic degradation of pollutant molecules in their cationic form while negatively chaged molecules are more readily degraded at low pH values when the photocatalyst surface is positively charged. At high pH values, adsorbed OH^- ions on the surface of the photocatalyst particles act as efficient traps for the photogenerated holes. Recent investigations have shown that photocatalyst activity not only depends on the surface properties of TiO_2, but also on the chemical characteristics of the pollutant. It has also been concluded that higher BET surface area results in better adsorption properties due to more OH- groups on the photocatalyst surface.

2.3.3 Influence of initial concentration of Formaldehyde on removal efficiency

Some literatures had been studied on the effect of initial concentration of pollutant on removal efficiency of photocatalytic. For example, in 1992 Hisao Hidaka studied the degradation of CN^- in industrial solution and found that it can be decomposed by photo-oxidation UV/TiO_2. It was found that the time required for the decomposition of cyanide increased with the initial concentration. That meant the degradation of 200, 100 and 50 ppm solutions required 10, 5, 3 hour of illumination respectively. Solutions of high concentration (about 500 ppm of CN^-) could also be photodegraded easily (within 25 h of illumination) with the large-scale reactor.

Another study was on the photocatalytic degradation of 1, 10-Dichlorodecane in Aqueous Suspensions of TiO_2 by Ken J. Friesen (2000). It revealed that the photodegradation rates increased as the initial concentrations of D_2C_{10} increased from 120 μg/l to its solubility limit of 240 μg/l. Degradation rate was optimal with 150 mg/l of TiO_2 and a D_2C_{10} concentration (240 μg/l) approaching its solubility limit.

Additionally, S. Hager, R. Bauer and G. Kudielka studied the photocatalytic oxidation of gaseous chlorinated organics over titanium dioxide in the year of 2000. The study also investigated the effect of inlet contaminant concentration. It was found that the degradation was enhanced at the lower inlet concentration. Conversion of degradation efficiency was decreased from 60.1% to 19.9% for TCE when the initial contaminant concentration was raised from 10 to 78 g/m^3. In the recent year

(2001), study of Jesus Beltran De Heredia, showed the result that the initial ρ-hydroxybenzoic acid concentration has a pronounced effect on the degradation rate, at the same illumination time the percentage of ρ-hydroxybenzoic acid decomposed is smaller if the initial ρ-hydroxybenzoic acid concentration is higher.

2.4 Ultraviolet Radiation

2.4.1 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.

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.

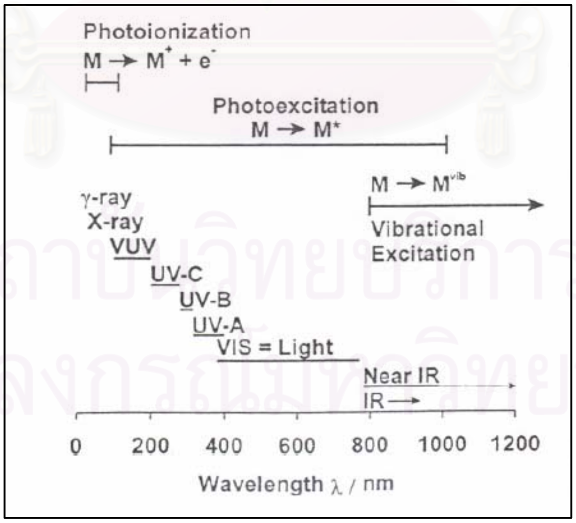


Figure 2.3 Classification of electromagnetic radiation in the wavelength range below A of 1200 nm as bands with specific names, and the interaction with molecules M (VUV: vacuumUV) (Oppenländer, 2002)

2.4.2 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 refer 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 and 300 watts for a medium pressure lamps (Glaze 1993; Yang et al. 1998).

2.4.3 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 2.4. 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.

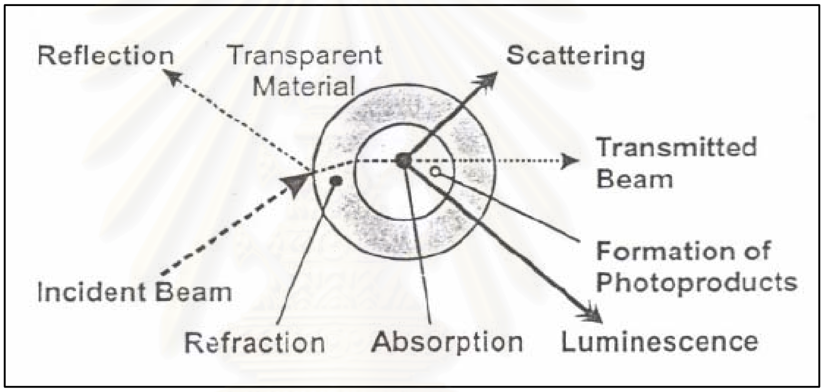


Figure 2.4 Schematic representation of physical, photo physical and photochemical phenomena and processes observed during interaction of UV/VIS radiation with matter. (Oppenländer, 2002.)

The light absorbance and photolytic properties of chlorophenols and hydrogen peroxide were found to be high 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).

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Chemicals

The major reagents used in this study include, formaldehyde solution 40%(CH_2O) purchased form Carlo erba chemical., titanium dioxide P25, predominantly anatase with specific surface areas of $50m^2/g$ and mean particle size of 30 nm. The photocatalyst Titanium Dioxide was obtained from the Degussa Company (Frankfurt, Germany). The product is a highly dispersed solid with the properties noted in Appendix I [69]. All solutions and suspensions were prepared from RO (reverse osmosis) water. The following reagents were purchased from Merck Company, and used as received: Sodium sulfite (Na_2SO_3), sulfuric acid (H_2SO_4, 96%), Sodium hydroxide (NaOH). Additionally, the reagents used in the experiment were analytical grade except the commercial grade of formaldehyde 40%.

3.1.2 Batch Adsorption Experiment

Adsorption experimets were conducted in the flasks 125 ml with screw covers using the set TiO_2 dosage (0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 g/l loaded with 10,000 mg/l in the neutral pH = 7 synthetic formaldehyde 40% CH_2O. The synthetic solution containing TiO_2 was magnetically stirred for 180 min in dark. Cautions were exercised to prevent any light impingement on the flasks as to minimize any photocatalytic degradation reactions. Because the photocatalytic mechanism would not be definitely allowed to occur in this experiment. Thus, the sample had to be kept without irradation during the entire of time by covering the flask with the aluminum foil.

For the adsorption kinetics, the experimental procedures were essentially the same as described except that samples were taken periodically. To obtain the adsorption isotherm, samples were allowed to equilibrate by shaking for approximately 180 minutes on a shaker. The amount of formaldehyde adsorbed was determined by the concentration difference between the final and the blank.

3.1.3 Experiments with Suspension TiO_2 in Photochemical Reactor

The experiments were performed in a photochemistry batch reactor. A 1-litre photochemical batch reactor used in all experimental performed includes of two compartments consisting of outer and inner compartments. The outer compartment is the glass to contain the treating wastewater and the chemical with 2 sampling ports. The inner part is an angular vessel for low pressure mercury lamp with 10 watts. This inner well is jacketed to permit a water flow for cooling purpose. The cooling water is provided for the inner part to keep the constant room temperature. The sampling solution was well mixed with a magnetic stirrer. For all the exerimental runs performed in this system, the pH of the reacting mixture was adjusted initially. During experiments, oxygen was bubbled into the solution at a constant flow-rate of 40 ml/min in the system. Suspension of TiO_2 powder in water was well agitated thoroughly by the magnetic stirrer. The picture of photochemical reactor is provided in Figure 3.1

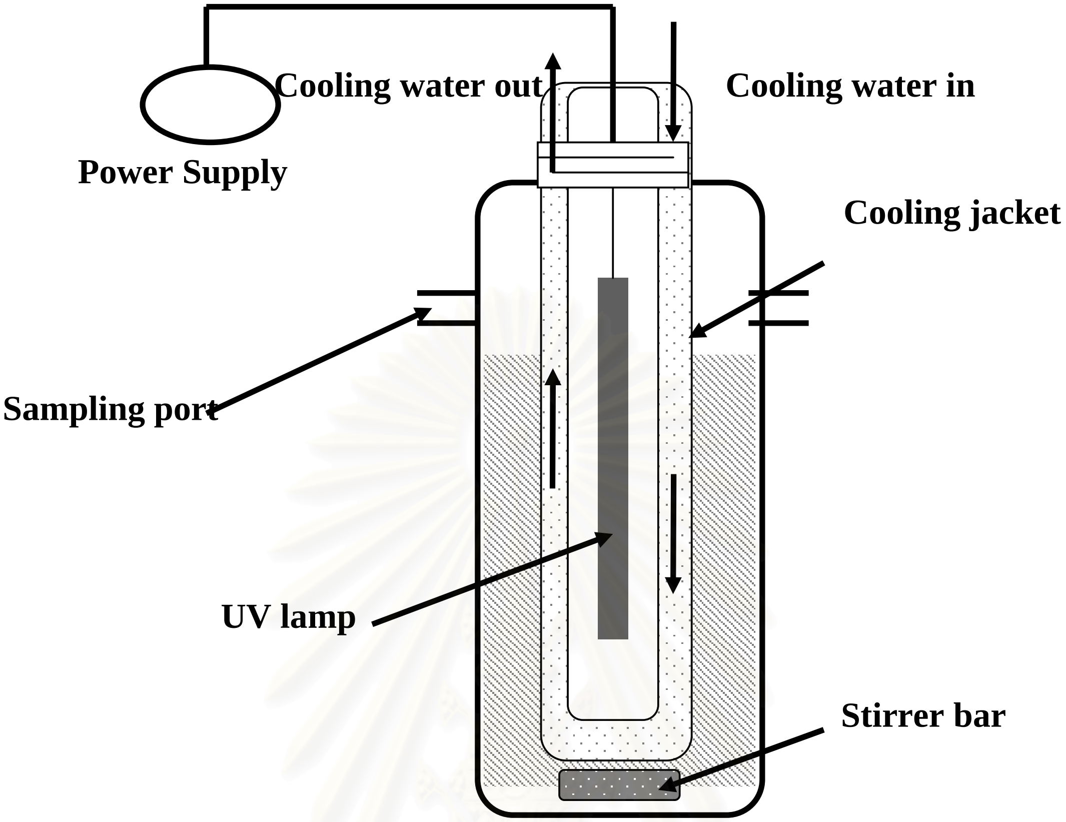


Figure 3.1 Photochemical reactor used in this study

3.2 Experimental Procedure and Equipment Specification

To investigate the formaldehyde degradation in the synthetic formalin solution by UV/TiO_2, it had to investigate the following factors, optimum dosage of TiO_2, optimum pH value and the effect of initial concentration. Therefore, the optimum condition for treating formaldehyde in the synthetic formalin solution would be obtained. The experiment was divided into 2 parts as follows:

Part 1. Role of TiO_2 in formaldehyde degradation
    (Volatilization, Photolysis, and Adsorption onto TiO_2 surface)
Part 2. Investigation of optimum conditions for formaldehyde degradation:
    (Optimum dosage of TiO_2, and pH value)

Part 3. Investigation of the effect of initial concentrations of formaldehyde on removal efficiency

Part 1: Role of TiO_2 in formaldehyde degradation

1.1 Volatilization

To understand clearly the role of UV/TiO_2 in formaldehyde degradation, the anticipation to the possible losses of formaldehyde via volatilization should be firstly launched. The dark reaction experiment was conducted in absence of UV radiation and TiO_2. This set of experiment was conducted in the same initial conditions with 10,000 mg/l of formaldehyde concentration at neutral pH = 7. Aim of this set of experiment was to investigate the role of volatilization mechanism to the degradation of formaldehyde solution.

1.2 Photolysis

The set of this reaction experiment was conducted in absence of TiO_2 in order to show the efficiency of formaldehyde removal by photolysis and volatilization. The set of experiment was conducted in the same initial conditions with 10,000 mg/l of formaldehyde concentration at neutral pH = 7. In order to carry out all the experiments always under dark conditions, the sample were covered by aluminium foils. The sample no.1 and no.2 were conducted without and with oxygen respectively to investigate the effect of oxygen in photolysis system. Whereas, the sample no.3 was controlled temperature in the range 34 ± 2 °C with oxygen bubling at the flow rate of 40 l/h continuously in order to keep the well mixing and oxygen saturated condition.

1.3 Adsorption onto TiO_2 surface

In general, after preparation of TiO_2 loaded with formaldehyde (CH_2O), the CH_2O will be absorbed on the TiO_2 surface at the first of time. The suspension should be left for a period of time in the dark in order to make sure that it could achieve the maximum adsorption of formaldehyde onto TiO_2 surface. Accordingly, the study of the behavior of formaldehyde absorbed by TiO_2 is necessary to promote good understanding on UV/TiO_2 efficiency.

The aim of this part is to state the variation of TiO_2 dosage on the degradation formaldehyde in formalin solution as a function of absorbance in dark. Eventually, the results would be expected to reveal the saturation stage of TiO_2 to absorb formaldehyde solution.

Part 2: Investigation on the optimum conditions for formaldehyde degradation

To study the degradation of formaldehyde in the synthetic formalin solution, the optimum dosage of Titanium Dioxide employed at each studied pH has to be investigated. The solutions of TiO_2 and formaldehyde were prepared by stirring an excess amount of these chemicals in water at room temperature and control temperature at 34 ± 2 °C. Amount of TiO_2 was varied at the dosages of 0.05, 0.1, 0.5, and 1.0 g/l, respectively, in order to investigate the effect of TiO_2 concentration on the removal efficiency. At each pH studied, the effect of TiO_2 dosage was accordingly investigated. The studied pH included pH of 3, 7, and 10. From these studies, the optimum conditions for treating formaldehyde in the synthetic formalin solution of each pH solution were obtained. The experimental procedure were detailed as follows:

2.1 Investigation on the optimum of TiO_2 dosage

The dosage of TiO_2 were varied from 0.1 g/l to 5 g/l. The TiO_2 dosage would reflect the surface area of TiO_2 for the oxidation reaction. This process would be conducted at the neutral pH with the fixed concentration of formaldehyde. From this experimental set, the optimum dosage of ratio of TiO_2 would be obtained. The profile of formaldehyde removal efficiencies with time was reported.

(1) Filling a 1 liter-reactor with the synthetic formalin solution containing 10,000 mg/l of formaldehyde.
(2) Adjusting pH value of solution to neutral pH value at 7.
(3) Adding the Titanium dioxide P25, varied from 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 g/l corresponding to 10,000 mg/l of formaldehyde solution.
(4) Keep the solution without any irradation for approximately 180 minutes on a shaker by covering the flask with the aluminum foil.

(5) Taking the sample to analyze at 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 hour of adsorption period.
(6) Turning on the UV lamp to irradiate the solution.
(7) Taking the sample to analyze at 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 hour of reaction period.
(8) After taken the sample the pH value was measured immediately.
(9) Then, the sample was analyzed for formaldehyde residual, TOC, toxicity and the residual TiO_2 dosage.

From this experiment set, the optimum dosage of ratio of TiO_2 was obtained. The profile of formaldehyde removal efficiencies with time was reported. To be noted that the experiments were conducted by varying the dosage of TiO_2, firstly in neutral pH solution at 7, then performing the experiment in acidic region at 3 and eventually in basic pH solution at 10, respectively after receiving the optimum dosage of TiO_2. In this research the wide range of conducted pH from 3-10 was correspondent the pH of real wastewater that might occur. The analysis parameters of this study include pH, Formaledehyde residual, total organic carbon, and toxicity, which were conducted as explained in the sample analysis section. The optimum condition that provided the best performance of formaldehyde degradation, which were the optimum dosage of TiO_2, initial optimum pH, the profile of formaldehyde residual with time and the profile of Total Organic Carbon with time, were reported from these studies.

2.2 Investigation on the optimum of pH value

The pH value was varied from acidic region to neutral and finally to basic region. The optimum TiO_2 dosage from the first experiment was used in this step. The experiment steps are shown below:

(1) Filling a 1 liter-reactor with the synthetic formalin solution containing 10,000 mg/l of formaldehyde.
(2) pH value of solution was varied from acidic pH at 3 to the basic pH at 10.
(3) The optimum dosage of TiO_2 from 1.1 was added.

(4) Keep the solution without any irradation for approximately 180 minutes on a shaker by covering the flask with the aluminum foil.
(5) Taking the sample to analyze at 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 hour of adsorption period.
(6) Turning on the UV lamp to irradiate the solution.
(7) Taking the sample to analyze at 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 hour of reaction period.
(8) After taken the sample the pH value was measured immediately.
(9) Then, the sample was analyzed for formaldehyde residual, TOC, Toxicity and the residual TiO_2 dosage.

The parameter analysis was conducted as explained earlier in 1.1. From this experiment set, the optimum pH value was obtained. The profile of formaldehyde removal efficiencies with time was reported

Part 3: Investigation on the effect of initial concentration of formaldehyde on removal efficiencies

The initial concentrations of formaldehyde was varied correspondence to the concentrations that might found from the real wastewater, which are 1,000, 3,000, 5,000, 8,000, 10,000 and 30,000 mg/l, respectively. The optimum condition that provides the best performance in formaldehyde degradation such as the TiO_2 dosage, and the optimum pH from the earlier experiment set was applied for this set of experiments. The experimental set are shown as below.

(1) Filling the 1 liter-reactor with synthetic formalin solution containing the interested amount of formaldehyde; 1,000, 3,000, 5,000, 8,000, 10,000, and 30,000 mg/l, respectively.
(2) Adjusting pH value of solution to the optimum value obtained form the earlier experiment.
(3) Adding the optimum dosage of TiO_2 received from the previous study.
(4) Keep the solution without any irradation for approximately 180 minutes on a shaker by covering the flask with the aluminum foil.

(5) Taking the sample to analyze at 0, 0.5, 1.0, 1.5, and 2.0 hour of adsorption period

(6) Turning on the UV lamp to irradiate the solution.

(7) Taking the sample to analyze at 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 hours of reaction period.

The parameter analysis was conducted as state earlier in part 1. From this experiment set, the effect of initial concentration of formaldehyde will be obtained. The profile of formaldehyde removal efficiencies with time will be reported and the rate of formaldehyde removal correspondence with initial concentration of formaldehyde was calculated. From this experiment set, the efficiencies of UV/TiO_2 process for treating formaldehyde in synthetic formalin solution was reported.

3.3 Analytical Measurement

At appropriate time intervals, samples were taken from the reactor into the glass vials. The samples were immediately analyzed to avoid further reaction.

The concentrations of residual formaldehyde 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 is used as carrier gas. The injection sample volume was 2 µl with 20% split mode. The concentrations of formaldehyde were calculated from the corresponding peak area.

The initial and the 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).

3.4 Experimental Chart

The experimental activity chart is demonstrated as below:

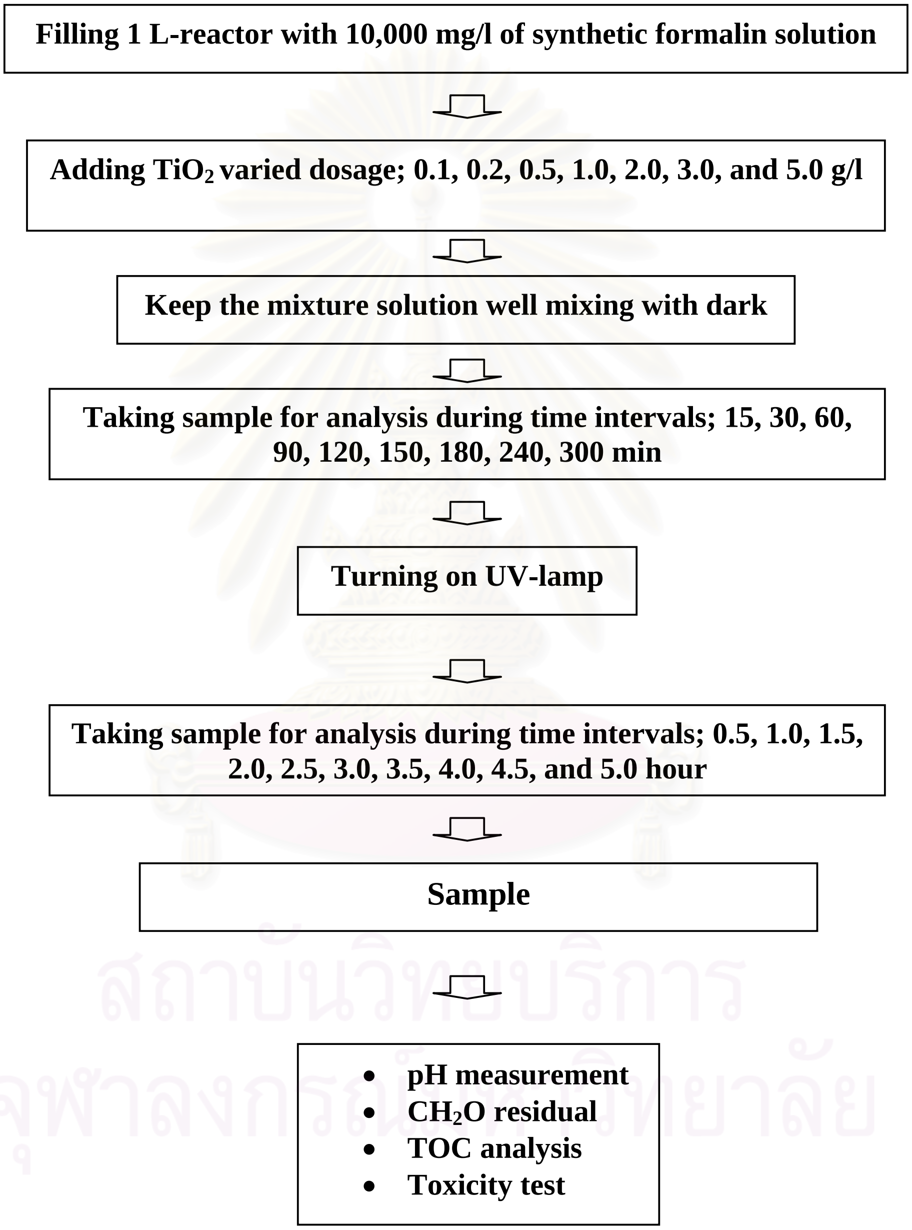


Figure 3.2 Experiment Flow Chart

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Role of TiO_2 in formaldehyde degradation

4.1.1 Volatilization

To understand clearly the role of UV/TiO_2 in formaldehyde degradation, the anticipation to the possible losses of formaldehyde via volatilization should be firstly launched. The dark reaction experiment was conducted in absence of UV radiation and TiO_2. The samples was prepared to four sets. The blank sample no.1 was conducted in room temperature, the sample no.2 was controlled temperature at 34 ± 2 °C by the hot plate stirrer. Whereas, the sample no.3 was supplied oxygen bubling at the flow rate of 40 l/h in room temperature and the sample no.4 was controlled at 34 ± 2 °C with oxygen bubling supply). This set of experiment was conducted in the same initial conditions with 10,000 mg/l of formaldehyde concentration at neutral pH = 7.

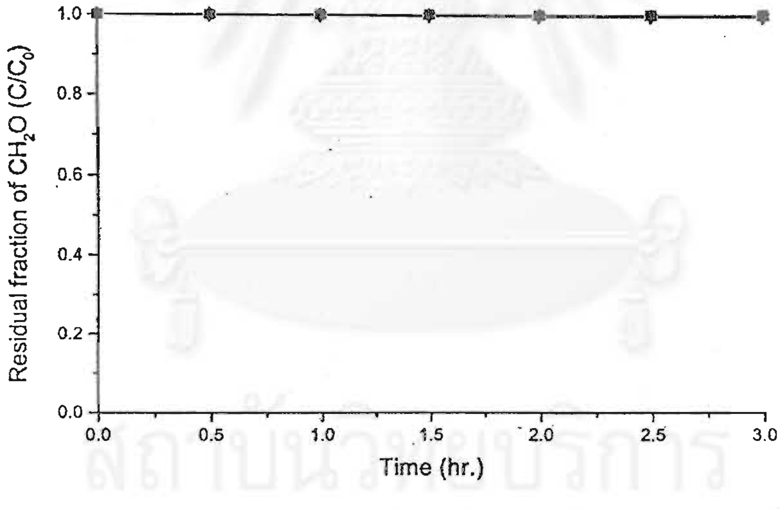


Figure 4.1 Volatilization of formaldehyde ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 7)

From figure 4.1, only about 0.8% and 1.1% of formaldehyde removal were observed after 3 hour of reaction period by volatilization and volatilization with oxygen mixing, respectively. Regarding to a series of control experiment as above, the results of the present study have clearly delineated that the adding of oxygen enhance the well mixing that further affect to volatilization. However, results concluded that over 1.1% efficiency from the volatilization with oxygen at controlled 34 ± 2 °C. The procedure of oxygen addition is necessary to promote mixture well mixing and consequently enhance the volatilization of formaldehyde, even a small fraction.

4.1.2 Photolysis

The set of this reaction experiment was conducted in absence of TiO_2 in order to show the efficiency of formaldehyde removal by photolysis and volatilization. The set of experiment was conducted in the same initial conditions with 10,000 mg/l of formaldehyde concentration at neutral pH = 7. In order to carry out all the experiments always under dark conditions, the sample were covered by aluminium foils. The sample no.1 and no.2 were conducted without and with oxygen respectively to investigate the effect of oxygen in photolysis system. Whereas, the sample no.3 was controlled temperature in the range 34 ± 2 °C with oxygen bubling at the flow rate of 40 l/h continuously in order to keep the well mixing and oxygen saturated condition.

Experimentally, the temperature of the sample in the reactor recommendedly need to be controlled in the range 34 ± 2 °C. The cooling system was done by circulating water from a bath through the reactor jacket to ensure a constant temperature of 34 ± 2 °C inside the reactor.

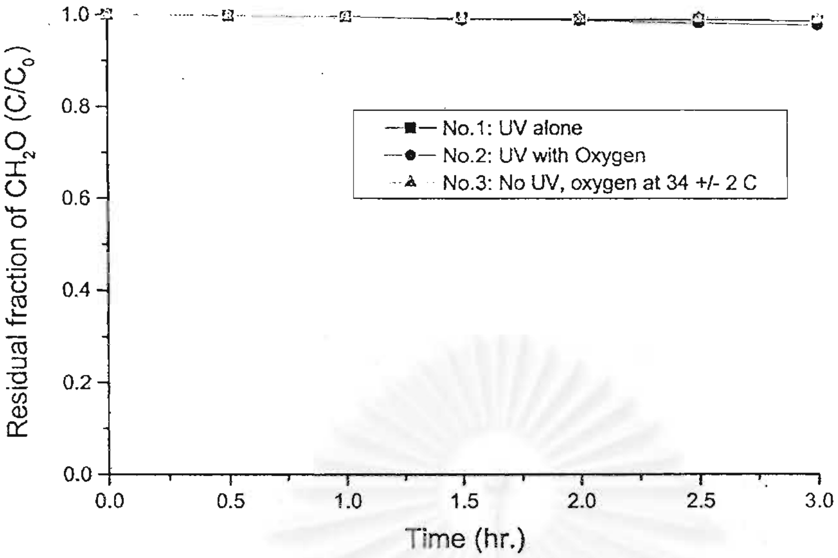


Figure 4.2 Photolysis of formaldehyde ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 7)

A series of control experiment reveals the fact that formaldehyde could be slightly degraded by both of photolysis and volatilization. Noticeably, adding an oxygen exert very small effect to formaldehyde degradation via volatilization. It could be said that approximately 2% of formaldehyde removal were observed after 3 hr. by reaction of both photolysis and volatilization, whereas only 1.2% was observed by volatilization. Consequently, be deeply considering on degradation of formaldehyde in mixture solution, valatilization and photolysis could be ignored.

4.1.3 Adsorption onto TiO_2 surface

In order to explore the possibility of using UV-TiO_2 towards elimination of formaldehyde contained in mixture solution, the understandings on the adsorption of formaldehyde onto TiO_2 is recommendedly undertaken. Hypothetically, the efficiency of photocatalytic-UV/TiO_2 depends on TiO_2 dosage, the pH value and the initial concentrations of formaldehyde in formalin solution. The study of the effect of TiO_2 adsorption on the efficiency would be started at the beginning of the experiment. In general, after preparation of TiO_2 loaded with formaldehyde (CH_2O), the CH_2O will be absorbed on the TiO_2 surface at the first of time. The suspension should be left for a period of time in the dark in order to make sure that it could achieve the maximum adsorption of formaldehyde onto TiO_2 surface. Accordingly, the study of the behavior of formaldehyde absorbed by TiO_2 is necessary to promote good understanding on UV/TiO_2 efficiency.

From above, the aim of this part is to state the variation of TiO_2 dosage on the degradation formaldehyde in formalin solution as a function of absorbance in dark. Eventually, the results would be expected to reveal the saturation stage of TiO_2 to absorb formaldehyde solution.

Initially, preparation of the two set of TiO_2 0.1 and 0.2 g/l dosage loaded with 1000 mg/l of formaldehyde was performed. Unfortunately, both of them revealed the results that the residual formaldehyde at each TiO_2 dosage was too few to notify formaldehyde residual by GC (Gas chromatography equipped with FID). The GC was used to determine the formaldehyde residual could not give the obvious residual formaldehyde after the entire of 90 min. passed.

Accordingly, the experiment will be re-conducted at various TiO_2 dosage loaded with formaldehyde 10,000 mg/l in the neutral pH. A synthetic solution containing TiO_2 was magnetically stirred for 180 min in dark.

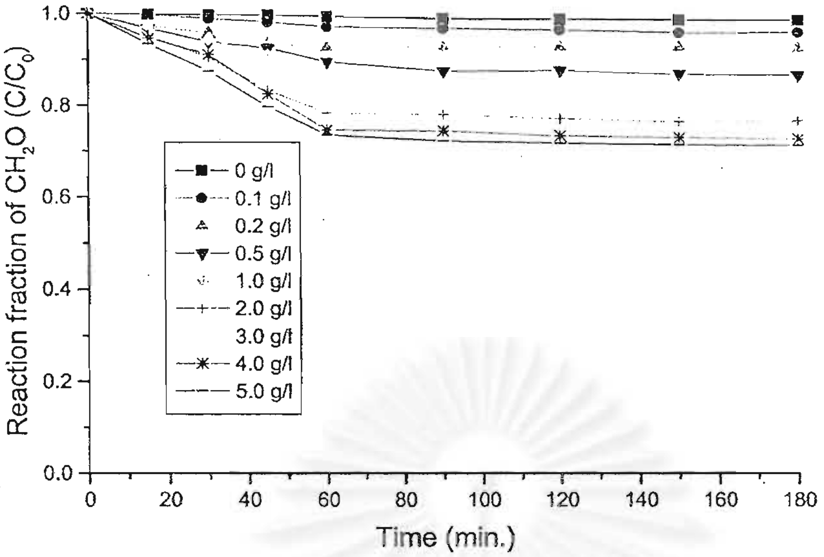


Figure 4.3 Adsorption of formaldehyde onto TiO_2 surface in dark without UV at different presence of TiO_2 employed as a function of time for 180 min. ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 7).

From figure 4.3, formaldehyde onto the TiO_2 without illumination showed that the adsorption was degraded during the first 60 min. and reached the equilibrium after that. Thus the influence of adsorption on the observed kinetics after 120 min. is considered not to be significant. It could be strongly said that the more TiO_2 dosage, the more adsorption degradation of formaldehyde. So it could be concluded that the 5.0 g/l of TiO_2 in the mixture solution gave the best results in adsorption mechanism in accordance with this experiment. Results of the present study was clearly delineated that after 120 min. of magnetic stirring in dark, the behavior was constantly suspended and over 20-25% reduction of formaldehyde from aqueous suspension was achieved.

Eventually, in order to achieve a maximum adsorption of the formaldehyde onto the TiO_2 surface, it was found useful to leave the suspension for 120 min in a dark room before starting the experiments.

4.2 Investigation the optimum dosage of TiO_2 for formaldehyde degradation by UV/TiO_2 in neutral aqueous solution

In the oxidation experiments with TiO_2, photoexcitation with light of an energy greater than the TiO_2 band gap promotes an electron from the valence band to the conduction band, and leaves an electronic vacancy of hole in the valence band. Accordingly, this set of experiment would be studied on the effect of TiO_2 dosage towards to the degradation percentage of formaldehyde, particularly using photocatalytic-UV/TiO_2. Initially, the prior control experiment had been demonstrated the efficiency of photolysis and volatilization, respectively in removal of formaldehyde in the neutral solution.

Theoretically, the addition of electron acceptors like O_2 in the solution contained TiO_2 can significantly increase the degradation rate of pollutant in aqueous solution. The same initial concentration of CH_2O 40% at 10,000 mg/l with TiO_2 employed were kept for all of the experiments. The illumination in the reactor was provided by UV lamp, which produced a strong peak centered at the 365 nm. Inevitably, irradiation of solutions was equipped with a cooling system to control the temperature of samples in the range of 34 ± 2 °C. Accordingly, in order to avoid unexpectable volatilization via formaldehyde evaporation, the temperature of the reactor was kept under illumination in the range of 34 ± 2 °C.

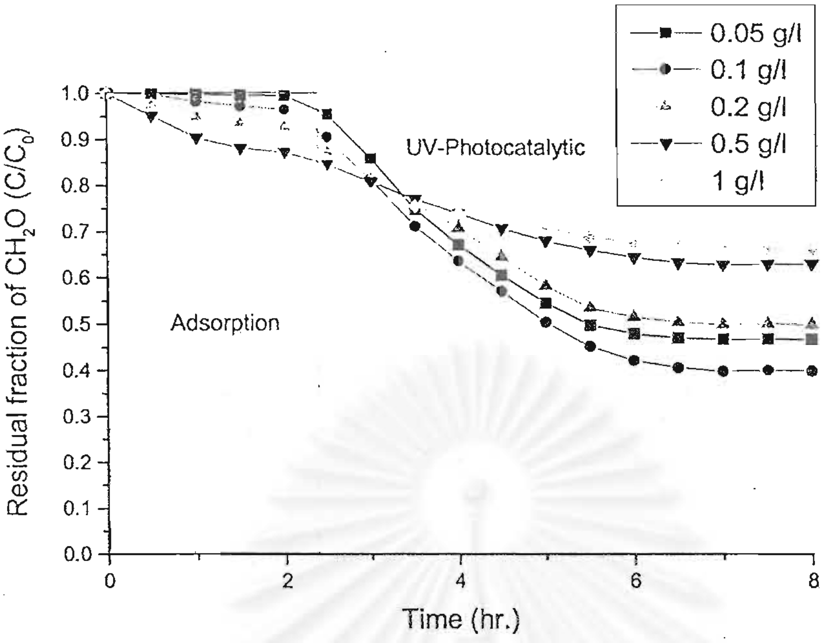


Figure 4.4 Degradation of formaldehyde by UV/TiO_2 with oxygen providing at different dosages of TiO_2 as a function of time ($[CH_2O]_0$ = 10,000 mg/l, initial pH =7)

From figure 4.4, the results of this work clearly demonstrated the ability of both adsorption onto TiO_2 surface and UV-Photolysis. Recalling from the earlier experiment set, the adsorption of formaldehyde onto TiO_2 surface had been occurred gradually at the beginning of the experiment until it had getting constantly in the later 90 min. and eventually get definitely constant within 2 hours. In this experiment set, the same adsorption behavior was seen. Thus, it could be concluded that the 1.0 g/l of TiO_2 in the mixture solution gave the best results in adsorption mechanism in accordance with this experiment.

Under illumination, the removal fraction of formaldehyde had been getting decreased very sharply compared to the adsorption reaction since the beginning of the experiment. Noticeably from the experiment, with higher TiO_2 dosage the dispersion of TiO_2 in water will inhibit the transmission of light and cause the decrease in removal efficiency. Obviously, in the case of 0.2 g/l, it could be found that the dispersionof TiO_2 was pronounced in inhibiting the transmission of light as seen from the decreasing of formaldehyde removal efficiency. In conclusion, the results of the present work clearly demonstrated that a TiO_2 dosage of 0.1 g/l was the optimum dosage which had decreased of the concentration of formaldehyde up to approximately 60% of the initial formaldehyde concentration and provide the good result of removal efficiency without the inhibition effect from the dispersion of TiO_2.

4.3 Investigation the optimum conditions for formaldehyde degradation by UV/TiO_2 in neutral aqueous solution

One of the important parameters in the UV-photolysis reaction is the pH of the mixture solution. An increase of the pH would give either a positive or negative effect on the degradation rate and consequently the mineralization rate of the solution. So far, to the formaldehyde degradation, there is no report about the optimum pH to get the highest efficiency for formaldehyde removal by this process. Thus, this experiment would be conducted at 0.1 g/l which gave the best results from the previous work in order to find the optimum pH to achieve the maximum removal efficiency of formaldehyde.

The pH value was at neutral and furtherly varied from acidic region (pH 3) finally to basic region (pH 10) respectively in the next experiment.

a)

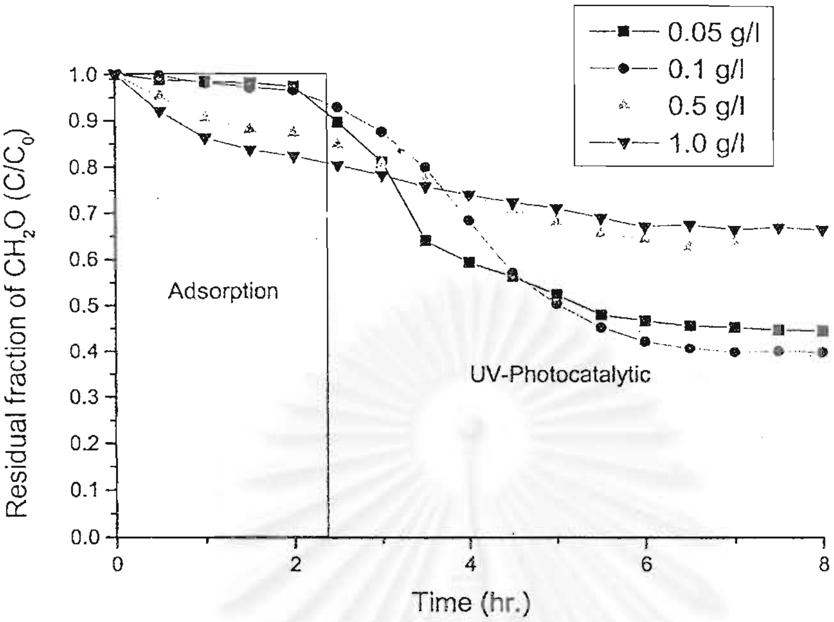


Figure 4.5 Degradation of formaldehyde by UV-TiO_2 at neutral pH with different dosages of TiO_2 as a function of time. ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 7)

Figure 4.5 (a) depicted the results obtained in this group of experiment on formaldehyde degradation by UV/TiO_2 at initial pH 7. Absorbed onto TiO_2 surface, the percentage of formaldehyde residual was approximately about 98, 97, 87 and 80 were obtained for 0.1, 0.5, 1.0 and 5.0 g/l of TiO_2 dosage, respectively. From figure 4.3.1 (a), it could be observed that the highest oxidation level was reached in 4 hours of the irradiation time at 0.1 g/l of TiO_2. The higher formaldehyde residual could be observed when 0.05, 0.5, 1.0 g/l were applied, respectively. In the last two cases, the 0.5, and 1.0 g/l TiO_2, presented significantly the excess amounts of TiO_2 input in UV/TiO_2 system causing the inhibition effect and the decreasing of efficiency as seen from graph.

b)

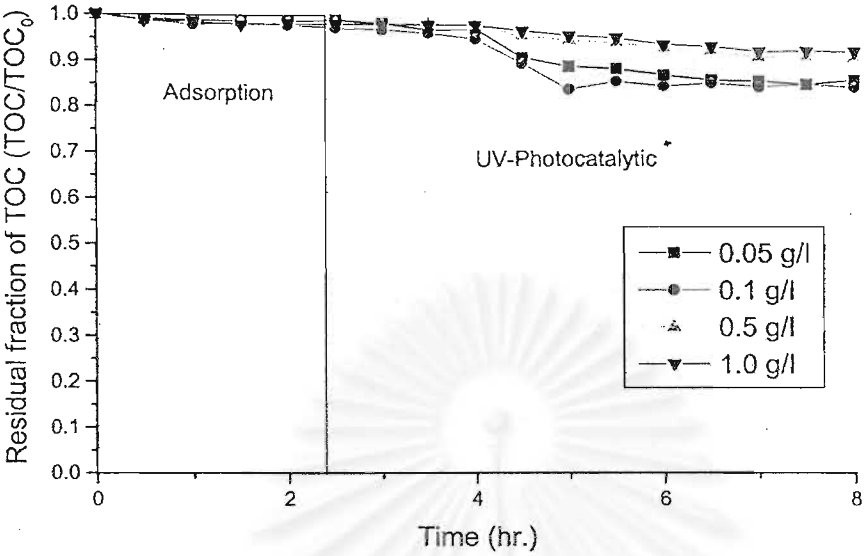
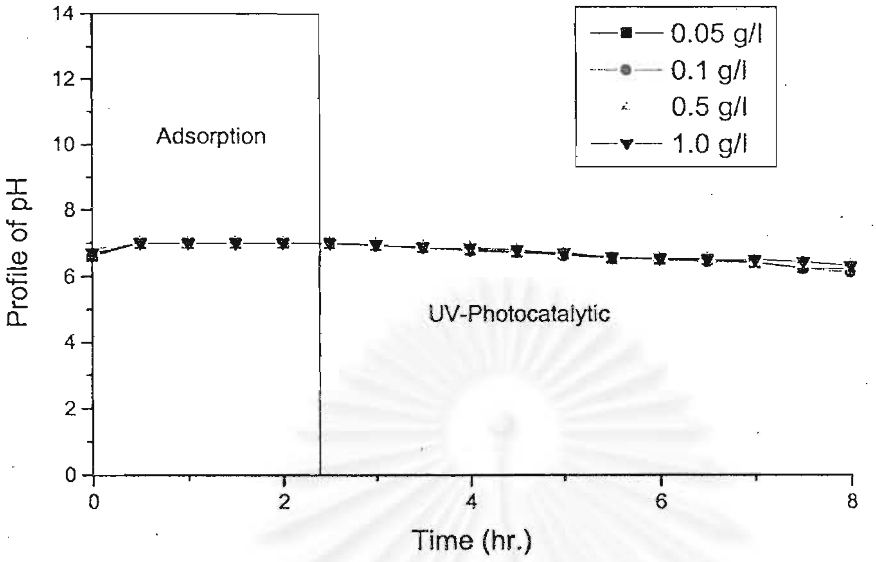


Figure 4.5 Degradation of formaldehyde by UV-TiO_2 at neutral pH with different dosage of TiO_2 as a function of time ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 7); **b)** Reaction fraction of TOC.

Theoritically, only occurs when the products of oxidation process yields H_2O and CO_2. The process efficiency could be explained in terms of grams of residual TOC. The higher residual TOC, the lower efficiency to transform pollutant to the end product. Figure 4.5 **(b)** shows the reported results of TOC removal as a function of reaction time. However, the results could not show any of the great significance that the conversion of formaldehyde was up to the large amount of mineralization, even with the applied optimum condition. It is indicated that the total mineralization was not accomplished since there are rather high amounts of TOC residuals remained in the treated solution. Even in the highest rate of TOC removal, the 0.1 g/l of TiO_2 was employed, 86% of TOC residual was left.

c)



d)

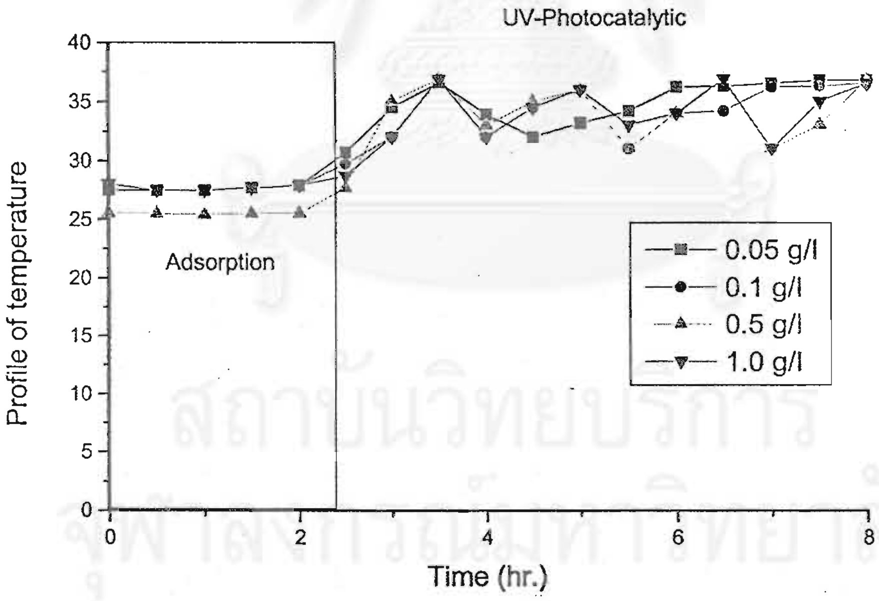


Figure 4.5 Degradation of formaldehyde by UV-TiO_2 at neutral pH with different presence of TiO_2 as a function of time. ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 7); **c)** Profile of pH, **d)** Profile of temperature.

No obviously measurable difference pH profile in the reaction was observed among these four TiO_2 dosage employed in first 2 hour of adsorption reaction. Apparently, there are very slightly pH decreased about 0.3 – 0.4 °C. In regarding to the profile of temperature from figure 4.5 **(d)** the temperature of the mixture sample in the reactor obviously had been increased to very high. Thus, in order to avoid the unexpectable formaldehyde volatilization, the cooling system was initially done. The cooling system was done to ensure a constant temperature of 34 ± 2 °C inside the reactor.

4.4 Degradation of formaldehyde in acidic pH

The experiment were conducted by preparating of the mixture solution using various TiO_2 dosage loaded with 10,000 mg/l of CH_2O as similar as in 4.3. The initial pH of the mixture solution was in acidic region at pH 3 by adding H_2SO_4.

a)

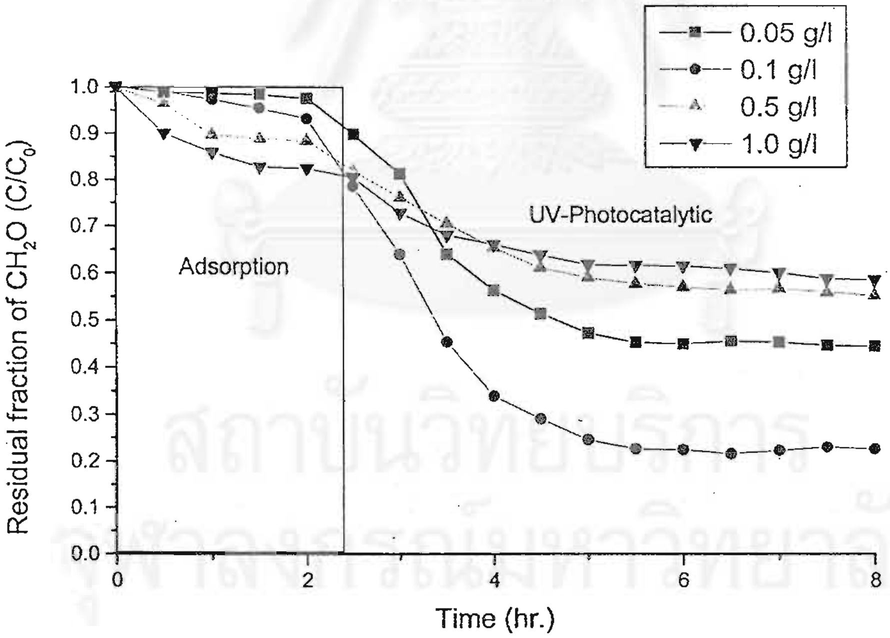


Figure 4.6 Degradation of formaldehyde by UV-TiO_2 with different dosages of TiO_2 as a function of time. ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 3); **a)** Reaction fraction of formaldehyde residual.

During the UV-photocatalysis experiment, it is observed that at 0.1 g/l of TiO_2 it took only 2 hour to drop the residual fraction of formaldehyde down from the initial value of 9,500 mg/l to 2,500 mg/l approximately. This residual value remained rather unchanged to the end of reaction time. It might conclude that after 5 hour of irradiation with 0.1 g/l of TiO_2 and UV-irradiation, over 75% degradation of formaldehyde was achieved.

b)

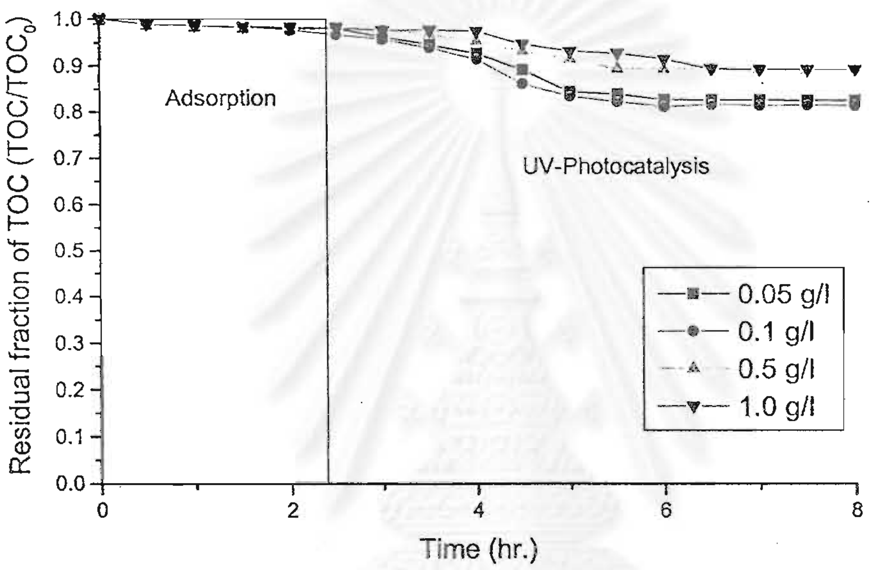


Figure 4.6 Degradation of formaldehyde by UV-TiO_2 with different dosages of TiO_2 as a function of time. ($[CH_2O]_0 = 10,000$ mg/l, initial pH = 3); **b)** Reaction fraction of TOC.

Figure 4.6 **(b)** has shown the results of TOC removal as a function of reaction time. It was indicated that the total mineralization was not accomplished since there were rather high amounts of TOC residuals remained in the treated solution. Total Organic Carbon degradation rate with time at different TiO_2 dosages presented only small reduction of TOC reduction. The high TOC reduction rate, 0.8%, could be expected at which high reduction rate on formaldehyde removal. It could be seen that even at 0.1 g/l of TiO_2 dosage in acidic aqueous solution which provided the highest formaldehyde removal efficiency, the slightly reduction of TOC were observed approximately 20%. As it was indicated in figure 4.6 (b), about 80% of TOC still remained in solution.

c)

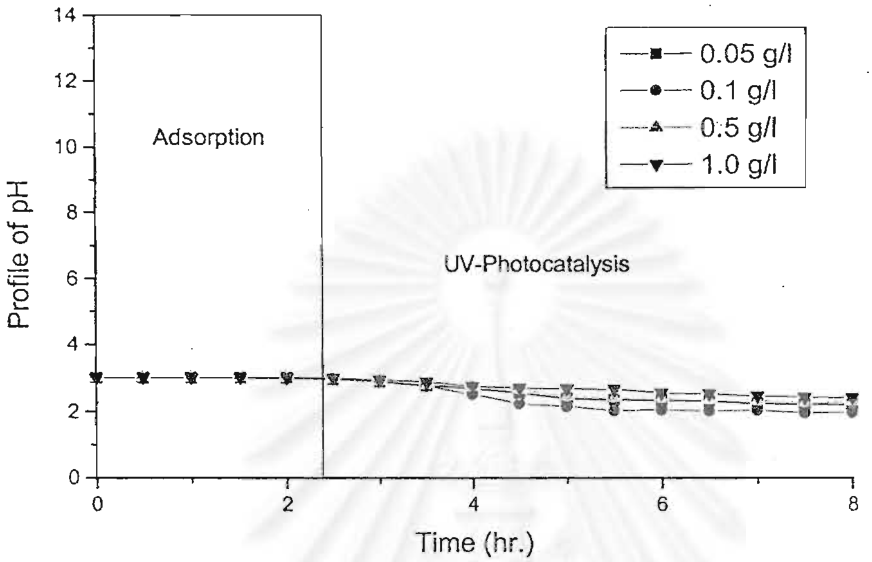


Figure 4.6 Degradation of formaldehyde by UV-TiO_2 with different dosages of TiO_2 as a function of time. ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 3); **c)** Profile of pH.

Finally, in figure 4.6 (c) a profile of pH monitored during formaldehyde degradation by UV/TiO_2 at initial pH 3 was presented. During first 2 hour of adsorption reaction, the pH remained constant at 3.00 until the beginning of photoreaction reaction. It was found that the pH values of UV/TiO_2 process on formaldehyde decomposition was rapidly reduced from 3.00 to 2.80 in the first 2 hour of irradiation. During the experiment, it was observed that the pH values were continuously declined and then remained constant. The final pH value were 2.69, 2.52 and 2.20 according to 0.05, 0.5, and 1.0 g/l respectively.

d)

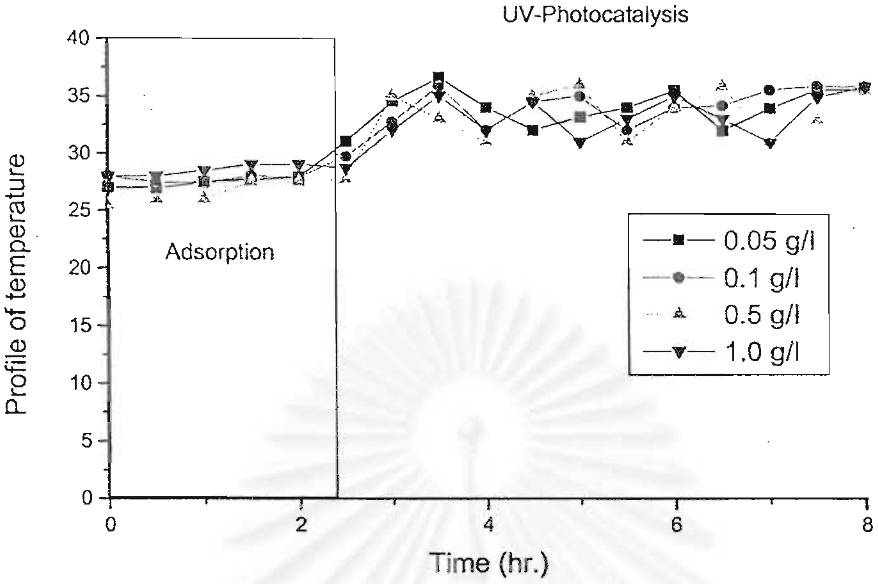


Figure 4.6 Degradation of formaldehyde by UV-TiO_2 with different dosages of TiO_2 as a function of time. ($[CH_2O]_0$ = 10,000 mg/l, initial pH 3); d) Profile of temperature.

The photocatalytic oxidation of CH_2O in mixture solution mixed with an oxygen stream was carried out after 2 hour of adsorption under the illumination in ambient temperature for 5 hour of illumination. After the first hour of irradiation with UV-lamp, the temperature of the mixture solution was getting sharply higher. The procedure of cooling system then was recommendedly necessary to avoid the high temperature in mixture solution. The temperature was effectively controlled in the range of 34 ± 2 °C. In accordance with the profile of temperature from figure 4.6 (d) the profile of temperature had been clearly shown no significantly different from the prior experiment in regarding to avoid the formaldehyde volatilized unexpectable with the cooling system at controlled temperature in the range of 34 ± 2 °C.

4.5 Investigation the optimum conditions for formaldehyde degradation by UV/TiO_2 in alkaline aqueous solution

The experiment would be conducted as similar as in 4.3 and 4.4 excepted changed the initial pH of the mixture solution prior the reaction to basic region pH 10 by adding NaOH. Preparation of TiO_2 loaded with CH_2O at the initial concentration of 10,000 mg/l kept for all of experiments. Firstly, absorbance behavior of CH_2O onto TiO_2 surface was done for 2 hour prior to impregnation under magnetic stirring. Then, UV-Photocatalysis would be launched.

a)

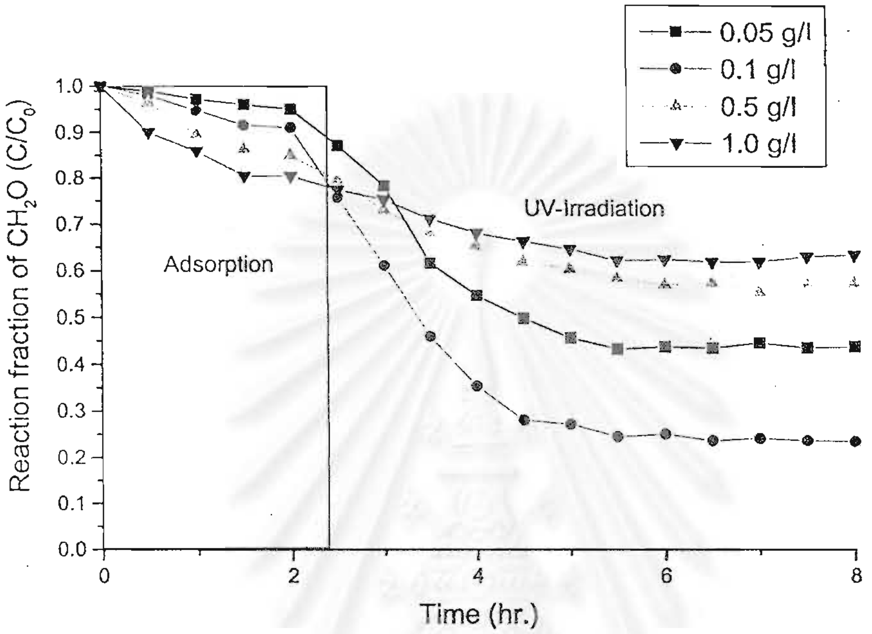


Figure 4.7 Degradation of formaldehyde by UV-TiO_2 at basic pH with different dosages of TiO_2 as a function of time. ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 10); **a)** Reaction fraction of formaldehyde residual.

The experimental results after the UV/TiO_2 performed at initial pH 10 on formaldehyde degradation in alkaline aqueous solution was presented in figure 4.7 As depicted in figure 4.7 (**a**), there is no completed formaldehyde removal in all cases. The results of formaldehyde adsorption onto TiO_2 surface in alkaline was as similar as those in acidic and neutral pH from earlier experiments. The rate of formaldehyde removal during the irradiation of basic mixture solution was faster than those in neutral pH, but slower than those in acidic. The higher formaldehyde adsorption in the first 2 hour of the reaction period was obviously seen in this pH region. Especially when 0.5 g/l, and 1.0 g/l of TiO_2 employed, the 96%, 78% and 40% of hydrogen peroxide were consumed.

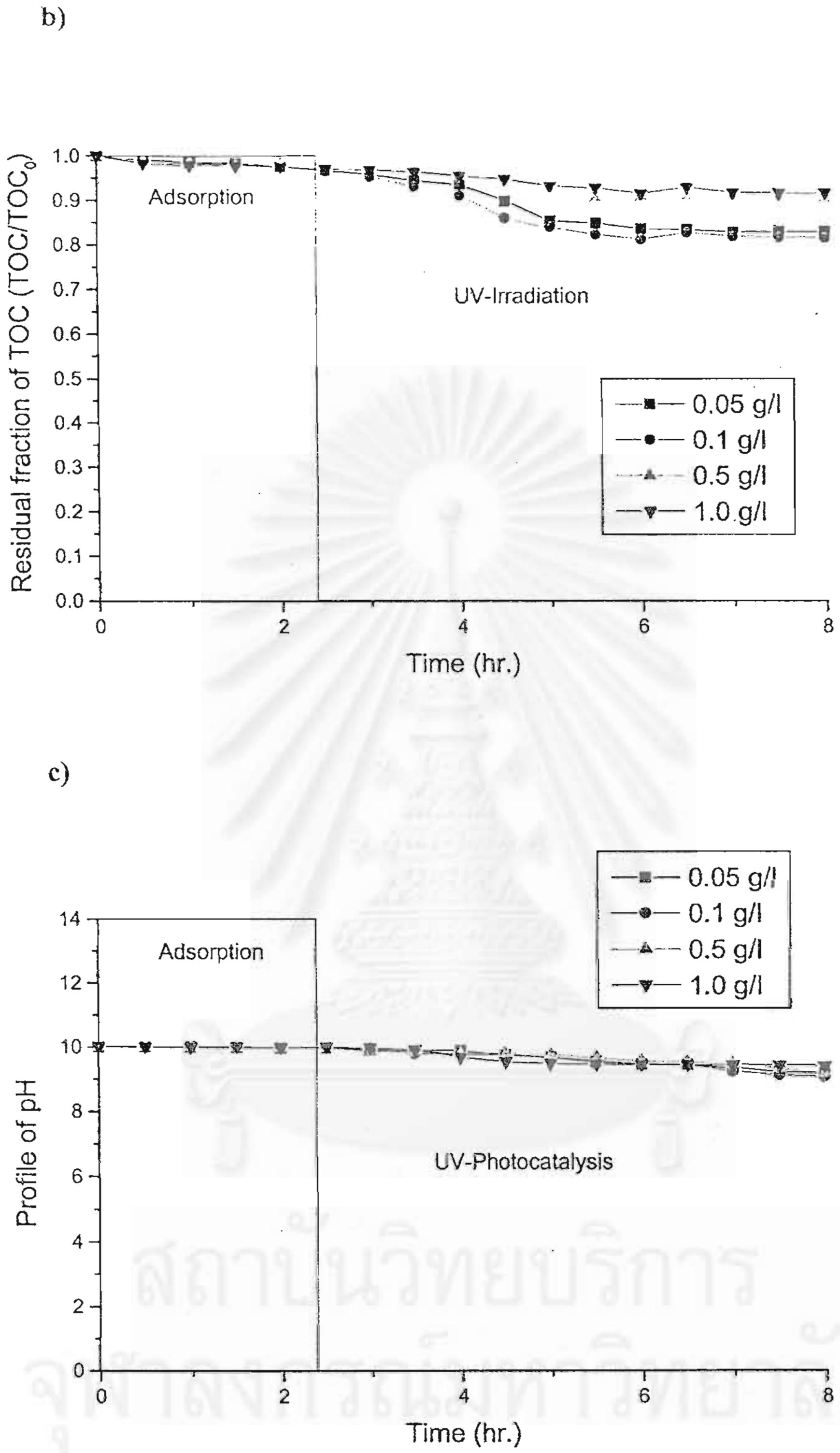


Figure 4.7 Degradation of formaldehyde by UV-TiO_2 at basic pH with different dosages of TiO_2 as a function of time. ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 10); **b)** Reaction fraction of TOC, **c)** Profile of pH.

The profile of pH as a function of reaction period was demonstrated in figure 4.7 **(c)**. From this finding pH was unchanged for the 2 hour in adsorption region and decreased gradually from the beginning until the end of reaction time with the final pH 9.70.

d)

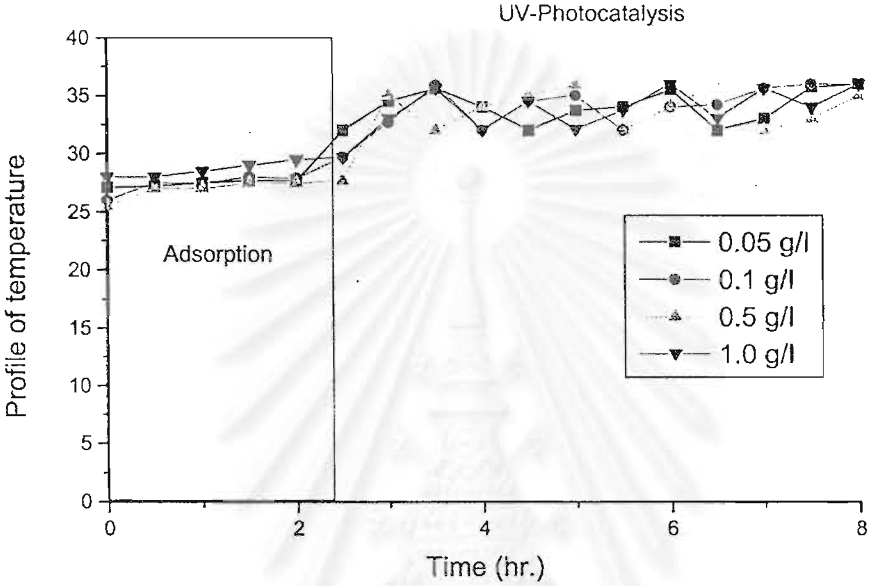


Figure 4.7 Degradation of formaldehyde by UV-TiO_2 at basic pH with different dosages of TiO_2 as a function of time. ($[CH_2O]_0$ = 10,000 mg/l, initial pH = 10); **d)** Profile of temperature.

In accordance with the profile of temperature from figure 4.7 **(d)** the profile of temperature had been clearly shown no significantly different from the prior experiments in regarding to avoid the formaldehyde volatilized unexpectable with the cooling system at controlled temperature in the range of 34 ± 2 °C.

4.6 The efficiency of UV/TiO_2 process on formaldehyde removal at different initial concentration of pollutant

The objective of the present work is to study the effect of initial concentration of pollutant on photocatalytic removal efficiency. To obtain the effect of initial concentration of formaldehyde, this experiment will be conducted in acid synthetic formalin solution with 0.1 g/l at pH 3 in which the initial concentration of formaldehyde will be varied from 1,000 mg/l to be 2,500, 5,000, 10,000 and 40,000 mg/l to cover all the concentration ranges that might occur in the real wastewater.

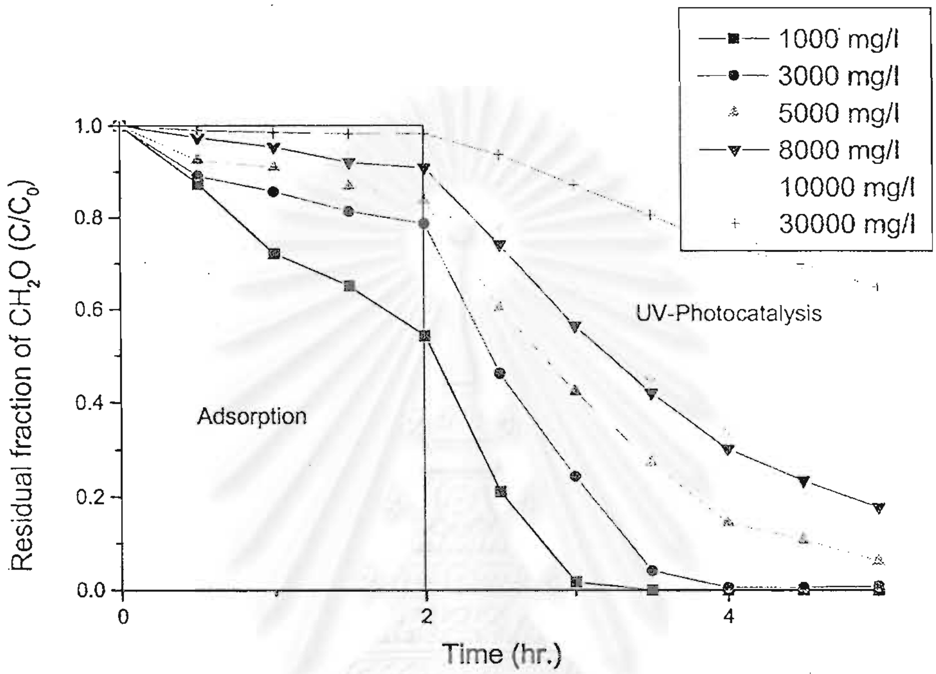


Figure 4.8 Effect of the initial syethetic formaldhyde concentration on the degradation of UV-TiO_2 at acid pH (TiO_2 = 0.1 g/l, initial pH = 3); **a)** Reaction fraction of formaldehyde residual.

Figure 4.8 (**a**) Showed different photocatalytic activities due to the influence of initial concentration of formaldehyde in mixture solution. It showed the results of the experiment which the optimum condition had been obtained from prior work, the following runs would be conducted at the 0.1 g/l of TiO_2, at acidic pH 3. At an initial concentration of 1,000 mg/l, approximately 60% of formaldehyde fraction had been taken in the 2 hr. of adsorption reaction period. Furthermore, not only 60% achieved during the adsorption reaction, but also completely formaldehyde removal have been oabtained during UV-photolysis reaction. Noticeably, the higher the initial formaldehyde concentrations, the longer time required to attain the completely formaldehyde removal. For instance, at initial formaldehyde concentration of 1,000, 3,000, and 5,000 mg/l, the required time were 2, 4, and 6 hour of reaction period to remove overall pollutant. It could be implied that the oxidation rate by UV/TiO_2 was decreased significantly when the initial concentration formaldehyde concentration increased. This was clearly observed that at an initial formaldehyde concentration of 30,000 mg/l employed, about 60% of formaldehyde residual remained in the mixture solution. Moreover, there was still no obviouly feasibility that the disappearance of formaldehyde residual would achieved if the longer irradiation time was used for such a concentration.

Apparently seen in figure 4.8 (a), none of formaldehyde residual presented at the end of 8 hour reaction with the initial concentration 1,000 , 3,000, and 5,000 mg/l of formaldehyde following respectively. Besides, it could be depicted that the significant formaldehyde removal were observed at the 2 hour after UV-irradiation in initial concentration of 1,000 and 3,000 mg/l investigated excepted for the initial concentration of 5,000 mg/l, highly formaldehyde removal can be found at 4 hour after UV-irradiation. While in the others, they had been taken more time to remove formaldehyde. It could be implied that nearly completed disappearance of 1,000, 3,000 and 5,000 mg/l of CH_2O were found at the end of 4 hour after high dissociation rate in the first 2 hour of reaction time. Meanwhile, the other mixture samples still have formaldehyde residual left after the reaction.

b)

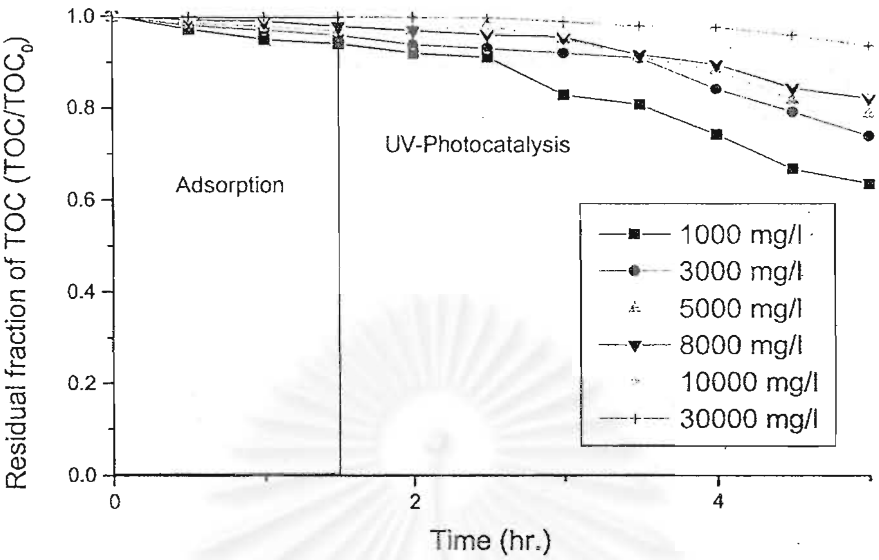


Figure 4.8 Effect of the initial syethetic formaldhyde concentration on the degradation of UV-TiO_2 at acid pH (TiO_2 = 0.1 g/l, initial pH 3); b) Reaction fraction of TOC residual.

Figure 4.8 (b) shows total organic carbon as a function of irradiation time. At this set of experiment, during the first 2 hours of adsorption reaction without UV-irradiation, there was slightly removal of TOC. After that, the fraction of TOC removal had been gradually decreased during the latter UV-irradiation period. It has been indicated that the mixture sample employed 0.1 g/l of TiO_2, approximately 40% and 30% of TOC removal efficiency have been achieved for the sample with the initial formaldehyde 1,000, and 3,000 mg/l, respectively. On the other hand, the mixture samples with initial formaldehyde of 5,000 and 8,000 mg/l, there were 75% and 80% residual fraction remained in solution after 8 hour of reaction time. Eventually, regarding to the highest initial concentration 10,000 mg/l of CH_2O, it was found that less than 5% only of TOC removal fraction was done by UV-TiO_2 process.

Considerably, the results of TOC removal as a function of reaction time have been implied that the complete mineralization of formaldehyde to CO_2 and H_2O_2 was not accomplished since 60% of residual TOC remained in solution, even in the lowest concentration of pollutant applied. Expectably, the higher initial concentration applied, the higher TOC residual obtained. For instance, at the initial formaldehyde concentration of 3,000, 8,000 and 30,000 mg/l, the consequence residual TOC were 68, 80 and 95%, respectively. From the graph, it cam be depicted that the significant TOC reduction were observed at the 3 hour after UV-irradiation in most initial concentration investigated excepted for the initial concentration of 1,000 mg/l, high TOC reduction rate can be found at 2 hour after UV-irradiation.

c)

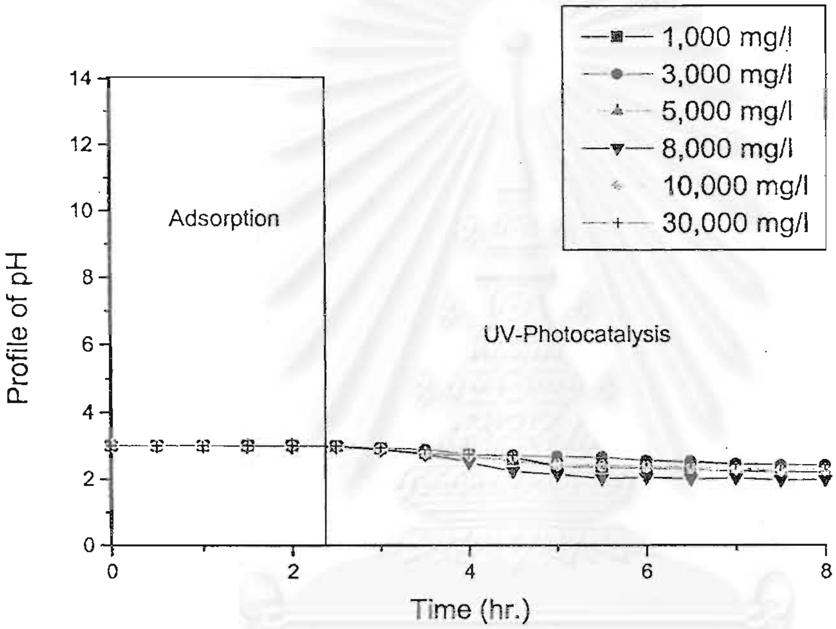


Figure 4.8 Effect of the initial syethetic formaldhyde concentration on the degradation of UV-TiO_2 at acid pH using 0.1 g/l of TiO_2 as a function of time for 8 hours. (TiO_2 = 0.1 g/l, initial pH = 3); **c)** Profile of pH.

d)

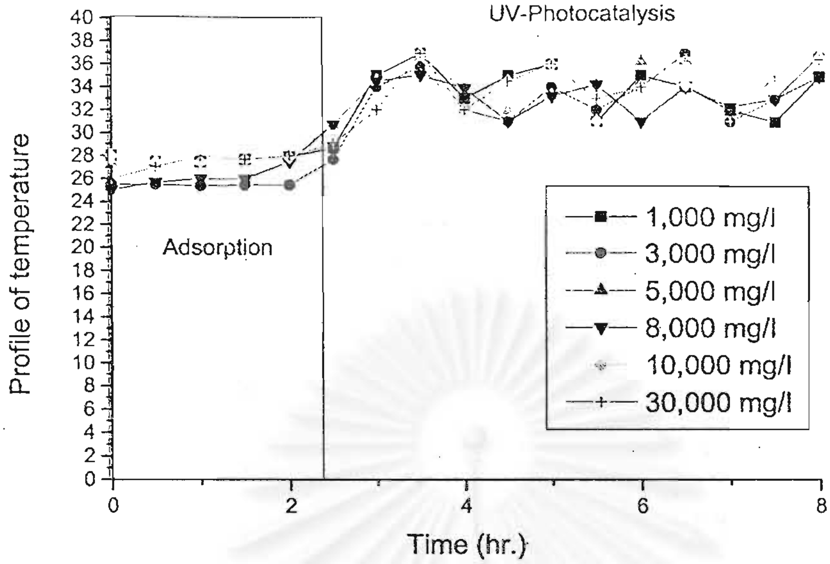


Figure 4.8 Effect of the initial syethetic formaldhyde concentration on the degradation of UV-TiO_2 at acid pH using 0.1 g/l of TiO_2 as a function of time for 8 hours. (TiO_2 = 0.1 g/l, initial pH 3); d) Profile of temperature.

The similar profiles of pH were observed as presented from earlier experiment. The reduction of pH values from pH 3.00 to 2.50 were observed since the beginning of UV-photolysis reaction time and there were quite slightly declined. While, the profile of temperature from figure 4.8 (d) was ensured that the temperature had been controlled in the range of 34 ± 2 °C all of the experiments.

4.7 Kinetics study of Formaldehyde degradation by UV/TiO_2 process

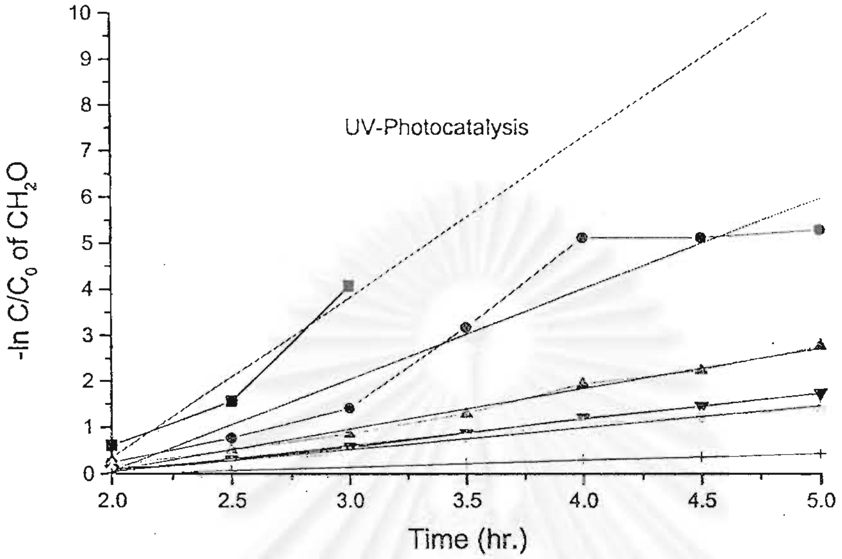


Figure 4.9 Kinetics study of Formaldehyde degradation by UV/TiO_2 process.

Regarding to the results from earlier expriments, particularly on UV/TiO_2 reaction, the degradation rate of Formaldehyde was followed the first order kinetics.

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

Where:

K = first order rate constant (hr^{-1})
R = reaction rate
t = irradiation time (hr)
C = initial concentration of formaldehyde

Integral of equation (4.1) to $\ln C_t/C_0 = -kt$ (4.2)

Where:

C_0 and C_t stand for concentrations at beginning and certain time (mg/l).

t is the irradiation time (hr.)

A plot of $-\ln (C_t/C_0)$ versus irradiation time should give a straight line whose slope equals the first order rate constant, k for half life of first order kinetics will be corresponding with the first order rate constant. Both of k values and $t_{1/2}$ were expressed in the follow table 4.1

Table 4.1 The first order rate constants at different initial concentration of CH_2O

$[CH_2O]_0$	**First order rate constant (min^{-1})**	**$t_{1/2}$ (min)**
1,000 mg/l	3.4633	0.20098
3,000 mg/l	1.96857	1.96857
5,000 mg/l	0.87729	0.87729
8,000 mg/l	0.55979	0.55979
10,000 mg/l	0.47279	0.47279
30,000 mg/l	0.14264	0.14264

4.8 Factors Influences the Formaldehyde Degradation by UV/TiO_2 process

4.8.1 Adsorption

Adsorption experiments (absence of illumination and presence of catalyst) demonstrated that the influence of adsorption on the observed kinetics is considered to be significant.

From figure 4.3, the adsorption experiment which had an absence of illumination and in the presence of catalyst demonstrated that after the equilibrated period, the adsorption of the formaldehyde onto the TiO_2 reached the equilibrium within 90 min. It could be said that the adsorption of formaldehyde onto TiO_2 surface had been occurred gradually at the beginning of the experiment until it had getting constantly in the later 90 min. and eventually get definitely constant until the end of this experiment 180 min. It could be strongly said that the more TiO_2 dosage, the more adsorption degradation of formaldehyde. However, it has not been meant that with the highest TiO_2 dosage the dispersion of TiO_2 in water would give the best results in formaldehyde degradation as the prior results of light transmission which will inhibit the transmission of light and cause the decrease in removal efficiency. Accordingly, in order to achieve a maximum adsorption of the formaldehyde onto the TiO_2 surface, it was found useful to leave the suspension for 120 min in a dark room before starting the experiments.

4.8.2 TiO_2 dosage

Photocatalytic reactors must be both transmissive and resistant to UV light. In TiO_2 heterogeneous photocatalysis, suspended catalyst systems give efficiencies higher than supported catalysts.

The adsorption of formaldehyde onto TiO_2 surface had been occurred gradually at the beginning of the experiment until it had getting constantly and eventually get definitely constant in the end of the experiment. From the figure, it could be implied that the more TiO_2 dosage, the more adsorption degradation of formaldehyde. So it could be concluded that the 1.0 g/l of TiO_2 in the mixture solution gave the best results in adsorption mechanism in accordance with this experiment.

Regarding to UV-Photocatalysis, the removal fraction of formaldehyde had been getting decreased very sharply compared to the adsorption reaction since the beginning of the experiment. Obviously, with higher TiO_2 dosage the dispersion of TiO_2 in water will inhibit the transmission of light and cause the decrease in removal efficiency. From the experiment, the TiO_2 dosage 0.1 g/l employed had been provided the best results of formaldehyde removal, particularly without inhibition of transmission of light and was furthrerly decreasing of removal efficiency.

4.8.3 Influence of the initial pH

Surface acidity is thought to take the form of stronger surface hydroxyl groups. These groups accept holes generated by illumination and, in turn, oxidize adsorbed molecues. The change in solution pH affects not only the photocatalytic activity of TiO_2 but also the TiO_2 surface ionic speciation, because of the amphoteric behavior of this semi-conductor. An increase of the pH will have a positive or negative effect on organic pollutant degradation rate and consequently the mineralization rate of the solution. Generally spoken, alkaline pH values have been found to be favorable for the photocatalytic degradation of pollutant molecules in their cationic form while negatively charged molecules are more readily degraded at low pH values when the photocatalyst surface is positively charged. At high pH values, adsorbed OH^- ions on the surface of the photocatalyst particles act as efficient traps for the photogenerated holes.

It is important to consider the pH value not only effects on the formaldehyde removal efficiency by UV-TiO_2, but also it is necessary to adjust the pH of the treated water in the industry scale. The results for oxidation of formaldehyde at different pH by UV/TiO_2 process were given, the best formaldehyde removal was obtained in the region of pH 3.

4.8.4 Influence of Oxygen

The addition of electron acceptors like O_2, H_2O_2 and O_3 in the water solution of TiO_2 can increase the degradation rate of pollutants. Hydrogen peroxide is a better electron acceptor than molecular oxygen. It limits the electron-hole recombination rate and increases the hydroxyl radical concentration at the TiO_2 surface Oxygen is usually supplied as electron acceptor to prolong the recombination of electron-hole pairs during photocatalytic oxidation.

Theoretically, the addition of electron acceptors like O_2 in the solution contained TiO_2 can significantly increase the degradation rate of pollutant in aqueous solution. Regards to the experiment showing the mechanism of O_2 acting as the electron acceptor, during irradiation the mixture solution was bubbled with oxygen at the flow rate of 40 l/h continuously to the mixture sample all of the irradiation period of this experiment to give the exceed O_2 saturation condition. In order to carry out all the experiments always under aerobic conditions, the dispersion was saturated by bubling oxygen at atmospheric pressure, before starting the irradiation, during the runs also an oxygen flow rate of 40l/h was continuously bubbled into the dispersion. Water from a thermostatic bath was circulated through the reactor jacket to ensure a constant temperature of 34 ± 2 °C inside the reactor. The adding of oxygen enhance the well mixing that further affect to volatilization.

In conclusion, it could be concluded to oxygen behavior from previous works that not only oxygen act as electron acceptor to prolong the recombination of electron-hole pairs during photocatalytic oxidation, but also it could enhance formaldehyde degradation via volatilization. Noticeably, adding an oxygen could contribute to formaldehyde degradation via volatilization. It could be said that approximately 2% of formaldehyde removal were observed after 3 hr. by reaction of both photolysis and volatilization, whereas only 1.2% was observed by volatilization from the first part of control experiment.

4.9 Toxicity of Residual Formaldehyde Treated by UV-TiO_2

In regard to the failure of biological wastewater treatment plant due to the medical wastewater directly discharged to the system, the investigation of its toxicity degree after treated by UV-TiO_2 was recommendedly done in order to consider whether or not such an AOP_s system have been selective to the pretreatment of the biological treatment plant. Note that, the sample had been diluted for 100 folds before getting into the analysis procedure. The results was obviously shown as below in table 4.2 that variations in the initial concentration of formaldehyde solution, the toxicity were remarkedly reduced to be almost non toxic solution at the end of the experiment.

Table 4.2 Toxicity of formaldehyde after UV-TiO_2 treatment for 6 hours at different initial formaldehyde concentration (TiO_2 = 0.1 g/l, initial pH 3)

Treatment Conditions	Toxicity (% inhibition)	CH_2O (mg/l)
1,000 mg/l	2.89	0
3,000 mg/l	15.68	0
5,000 mg/l	34.90	15
8,000 mg/l	91.36	984
10,000 mg/l	100.00	2,240
30,000 mg/l	100.00	18,600

It could be seen that at the initial concentration of 1,000 and 3,000 mg/l, the toxicity could be decreased down to the safety level equal to 2.89% and 15.68% inhibition at which the percentage of those considered below EC_{50}. Meanwhile, at the sample contained the initial concentration over beyond 5,000 mg/l of formaldehyde, the reduction of toxicity degree to the safety level could not successfully be reached. Even though the residual formaldehyde had been decreased obviously, the reduction of toxicity still remained significantly as seen at the sample with initial concentration of 8,000 and 10,000 mg/l. This may due to the by product of formaldehyde after UV-TiO_2 process done still has some severe toxicity. Accordingly, it was strongly recommended that in the case of handling with the mixture solution at which the initial concentration over beyond than 5,000 mg/l, the application of UV/TiO_2 should be considered.

4.10 Summary

It could be seen that the photocatalytic mineralization occurs more rapidly in the acidic solution than in the alkaline and neutral solution, respectively. Both pH and the initial concentration of foramaldehyde in the mixture solution affected the removal efficiency. The photocatalytic of formaldehyde degradation is favored under an acidic condition at pH 3 and decreased with increasing initial formaldehyde concentration. It would be concluded that pH plays an important role in the photocatalytic mineralization.

The question has been raised whether or not, incomplete oxidation produces more toxic intermediates than the parent compound. Results indicated that the complete mineraliztion is definitely necessary for the detoxification the formaldehyde solution. Moreover, the reduction of toxicity was not paralled to the loss of total organic carbon. In other words, a total mineralization is an important criteria in assessing the feasibility of the photocatalytic oxidation process.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Total mineralization is of great importantce because partial oxidation may lead to products that are more toxic than the parent compound. The question has been raised whether or not, incomplete oxidation produces more toxic intermediates than the parent compound. Therefore, total mineralization is highly desirable and complete mineraliztion is definitely necessary for the detoxification the formaldehyde solution. In other words, total mineralization is an important criteria in assessing the feasibility of the photocatalytic oxidation process. Results showed that the photocatalytic system is effective in mineralizing formaldehyde. It could be seen that the photocatalytic mineralization occurred more rapidly in acidic than in alkaline and neutral solution, respectively. Both pH and the initial concentration of formaldehyde in the mixture solution affected the efficiency removal. The photocatalytic of formaldehyde degradation was favored under an acidic condition at pH 3 and decreased with increasing initial formaldehyde concentration. In conclusion, it should be realized that pH played an important role in the photocatalytic mineralization and thereby the toxicity reduction of these toxic chemicals.

The results of formaldehyde degradation by UV/TiO_2 process can be concluded in several aspects as following:

- The best optimum conditions for formaldhyde degradation of UV/TiO_2 photocatalysis process was at 0.1 g/l of TiO_2 dosage in acidic solution.

- In comparative study on an optimum TiO_2 dosage, at the level lower than that optimum condition present less amount of adsorption reaction, on the contrary, at the higher than that inhibit of UV-photocatalysis transmission was presented and formaldehyde degradation was reduced.

- At the optimum condition, effects of pH on formaldehyde removal efficiency were investigated. As compared to optimum pH, the results show that experiments conducted in acidic solution give a favorable oxidation rate than that in basic solution.

- The higher the initial formaldehyde concentrations, the longer time required to attain the completely formaldehyde removal. It could be implied that the oxidation rate by UV/TiO_2 was decreased significantly when the initial concentration formaldehyde concentration increased.

- Even though the residual formaldehyde had been decreased obviously, the reduction of toxicity still remained significantly as seen at the sample with initial concentration of 8,000 and 10,000 mg/l. This may due to the by product of formaldehyde after UV-TiO_2 process done still has some severe toxicity. Accordingly, it was strongly recommended that in the case of handling with the mixture solution at which the initial concentration over beyond than 5,000 mg/l, the application of UV/TiO_2 should be considered.

5.2 Recommendations

The recommendations are oriented towards improvement of the laboratory scale of reactor to the practical scale in order to apply to real wastewater contained formaldehyde solution. It is necessary to optimize of the dimensions of the reactor as to permit optimum utilization. Besides, the chemical modification of the titanium dioxide surface can provide the enhancement in the photocatalytic destruction of pollutants. A simple and effective method to affect the charge carrier recombination dynamics is by introducing suitable dopants, such as platimun, to the semiconductor. This modified process may increase the photocatalytic oxidation rate. The bottom line of the suggestion obtained from this study was shown as follows:

1. The optimum conditions for formaldehyde degradation by UV/TiO_2 process obtained from this work could be applicable for further research development and / or

for real situation. It is also provide an alternative treatment method for wastewater containing formaldehyde.

2. The dimension of experimental reactor in lab scale affected to the efficiency of formaldehyde degradation. For application to the industry scale, the dimension of reactor strongly recommended to investigate.

3. In application of UV/TiO_2 process in the real situations which has various variables of formaldehyde concentration containing, the reaction rate constant obtained from this work is beneficial for forecast of degradation behavior.

4. From the results specified in the study of toxicity reduction, it is suggested that the well considertion of UV/TiO_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 seriously considered as unsafe level for microorganism.

5. Eventually, to achieve the highest formaldehyde attenuation dealt with the real medical wastewater, the results of factors that affect formaldehyde degradation such as several hydroxyl radical scavenger species, carbonate, bicarbonate and chloride etc. would also be considered for those application.

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APPENDICES

APPENDIX A

Table A-1 Degradation of Formaldehyde by Volatilization process
($[CH_2O]o$ = 10,000 mg/l, pH 7, and variations in oxygen and temperature)

Time	**Residual Fraction (C/Co)**			
	NONE, atp.	**NONE, 34 c**	**O_2, atp.**	**O_2, 34 c**
0 hr	1.000	1.000	1.000	1.000
0.5 hr	0.999	0.999	0.999	0.997
1.0 hr	0.998	0.997	0.997	0.995
1.5 hr	0.996	0.995	0.994	0.992
2.0 hr	0.995	0.993	0.992	0.990
2.5 hr	0.994	0.992	0.991	0.989
3.0 hr	0.994	0.992	0.991	0.989

Table A-2 Degradation of Formaldehyde by UV Photolysis process
($[CH_2O]o$ = 10,000 mg/l, pH 7, and variations in oxygen and temperature)

Time	**pH**	**Residual Fraction (C/Co)**		
		UV	**UV + O_2**	**NONE**
0 hr	7.000	1.000	1.000	1.000
0.5 hr	6.990	0.998	0.998	0.999
1.0 hr	6.976	0.997	0.996	0.997
1.5 hr	6.970	0.994	0.99	0.995
2.0 hr	6.951	0.989	0.987	0.993
2.5 hr	6.936	0.988	0.98	0.992
3.0 hr	6.925	0.988	0.979	0.992

Table A-3 Degradation of Formaldehyde by Adsorption onto TiO_2 surface
($[CH_2O]o$ = 10,000 mg/l, pH 7)

Time	Residual Fraction (C/Co)								
	0	0.1	0.2	0.5	1.0	2.0	3.0	4.0	5.0
0 min	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
15 min	0.999	0.998	0.973	0.967	0.972	0.952	0.953	0.947	0.934
30 min	0.998	0.99	0.958	0.939	0.944	0.903	0.91	0.91	0.874
45 min	0.998	0.982	0.935	0.924	0.908	0.833	0.833	0.825	0.797
60 min	0.994	0.972	0.926	0.895	0.859	0.784	0.762	0.746	0.735
90 min	0.991	0.97	0.929	0.875	0.825	0.78	0.762	0.744	0.723
120 min	0.989	0.966	0.927	0.876	0.821	0.77	0.754	0.733	0.717
150 min	0.989	0.961	0.929	0.87	0.816	0.766	0.751	0.731	0.715
180 min	0.988	0.96	0.925	0.867	0.813	0.767	0.746	0.727	0.714

Table A-4 Degradation of Formaldehyde by UV/Ti_2 Process
($[CH_2O]o$ = 10,000 mg/l, neutral pH 7)

Time	Residual Fraction (C/Co)				
	0.05	0.1	0.2	0.5	1
0 hr	1.000	1.000	1.000	1.000	1.000
0.5 hr	0.999	0.998	0.975	0.952	0.920
1.0 hr	0.998	0.983	0.949	0.904	0.862
1.5 hr	0.997	0.974	0.936	0.881	0.836
2.0 hr	0.996	0.966	0.928	0.873	0.824
2.5 hr	0.956	0.906	0.874	0.847	0.803
3.0 hr	0.859	0.814	0.816	0.808	0.782
3.5 hr	0.748	0.712	0.762	0.771	0.756
4.0 hr	0.671	0.636	0.707	0.740	0.740
4.5 hr	0.605	0.570	0.645	0.707	0.729
5.0 hr	0.544	0.503	0.582	0.680	0.710
5.5 hr	0.497	0.451	0.534	0.659	0.690
6.0 hr	0.479	0.421	0.514	0.644	0.676
6.5 hr	0.470	0.405	0.504	0.632	0.669
7.0 hr	0.467	0.397	0.499	0.628	0.663
7.5 hr	0.468	0.400	0.500	0.629	0.662
8.0 hr	0.467	0.398	0.499	0.629	0.663

Table A-5 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, neutral pH 7, TiO_2 dosage = 0.05 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	6.60	27.5	1.000	1.000
0.5 hr	7.00	27.5	0.989	0.991
1.0 hr	7.00	27.5	0.986	0.988
1.5 hr	7.00	27.7	0.983	0.988
2.0 hr	7.00	27.9	0.975	0.988
2.5 hr	6.98	30.7	0.898	0.990
3.0 hr	6.92	34.5	0.812	0.981
3.5 hr	6.86	36.6	0.640	0.964
4.0 hr	6.79	33.9	0.593	0.966
4.5 hr	6.73	32.0	0.563	0.903
5.0 hr	6.66	33.2	0.524	0.884
5.5 hr	6.53	34.2	0.479	0.879
6.0 hr	6.50	36.2	0.466	0.866
6.5 hr	6.49	36.3	0.455	0.855
7.0 hr	6.40	36.5	0.452	0.852
7.5 hr	6.26	36.8	0.446	0.845
8.0 hr	6.20	36.8	0.444	0.854

Table A-6 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, neutral pH 7, TiO_2 dosage = 0.1 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	6.67	28.0	1.000	1.000
0.5 hr	7.00	27.5	0.998	0.988
1.0 hr	7.00	27.5	0.983	0.983
1.5 hr	7.00	27.7	0.974	0.984
2.0 hr	7.00	27.9	0.966	0.979
2.5 hr	6.98	29.7	0.930	0.973
3.0 hr	6.90	32.0	0.877	0.967
3.5 hr	6.83	36.9	0.800	0.958
4.0 hr	6.74	32.0	0.684	0.944
4.5 hr	6.70	34.5	0.571	0.891
5.0 hr	6.61	36.0	0.503	0.834
5.5 hr	6.55	31.0	0.452	0.852
6.0 hr	6.48	34.0	0.421	0.841
6.5 hr	6.43	34.2	0.406	0.848
7.0 hr	6.39	36.2	0.398	0.840
7.5 hr	6.21	36.3	0.401	0.845
8.0 hr	6.12	36.5	0.398	0.838

Table A-7 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, neutral pH 7, TiO_2 dosage = 0.5 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	6.80	25.5	1.000	1.000
0.5 hr	7.00	25.5	0.953	0.993
1.0 hr	7.00	25.4	0.906	0.990
1.5 hr	7.00	25.5	0.882	0.989
2.0 hr	7.00	25.5	0.874	0.987
2.5 hr	6.99	27.7	0.848	0.985
3.0 hr	6.96	35.0	0.807	0.981
3.5 hr	6.89	36.9	0.772	0.977
4.0 hr	6.84	33.0	0.740	0.974
4.5 hr	6.78	35.0	0.708	0.951
5.0 hr	6.67	36.0	0.681	0.941
5.5 hr	6.60	31.0	0.656	0.936
6.0 hr	6.55	34.0	0.645	0.925
6.5 hr	6.51	36.9	0.628	0.918
7.0 hr	6.45	31.0	0.636	0.904
7.5 hr	6.39	33.0	0.628	0.903
8.0 hr	6.32	36.8	0.630	0.903

Table A-8 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, neutral pH 7, TiO_2 dosage = 1.0 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	6.71	28.0	1.000	1.000
0.5 hr	7.00	27.5	0.921	0.987
1.0 hr	7.00	27.5	0.863	0.986
1.5 hr	7.00	27.7	0.838	0.980
2.0 hr	7.00	27.9	0.824	0.982
2.5 hr	6.99	28.7	0.805	0.981
3.0 hr	6.95	32.0	0.783	0.978
3.5 hr	6.88	36.9	0.758	0.976
4.0 hr	6.85	32.0	0.740	0.974
4.5 hr	6.79	34.5	0.724	0.962
5.0 hr	6.70	36.0	0.711	0.951
5.5 hr	6.57	33.0	0.690	0.947
6.0 hr	6.53	34.0	0.672	0.932
6.5 hr	6.50	36.9	0.675	0.928
7.0 hr	6.49	31.0	0.665	0.917
7.5 hr	6.44	35.0	0.669	0.917
8.0 hr	6.30	36.5	0.664	0.916

Table A-9 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]_o$ = 10,000 mg/l, acidic pH 3, TiO_2 dosage = 0.05 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	3.00	27.0	1.000	1.000
0.5 hr	3.00	27.0	0.989	0.999
1.0 hr	3.00	27.5	0.986	0.986
1.5 hr	3.00	27.7	0.983	0.983
2.0 hr	3.00	27.9	0.975	0.980
2.5 hr	2.95	31.0	0.898	0.980
3.0 hr	2.89	34.5	0.812	0.962
3.5 hr	2.77	36.6	0.640	0.945
4.0 hr	2.69	34.0	0.563	0.926
4.5 hr	2.55	32.0	0.513	0.890
5.0 hr	2.39	33.2	0.472	0.844
5.5 hr	2.35	34.0	0.452	0.839
6.0 hr	2.33	35.5	0.449	0.826
6.5 hr	2.30	32.0	0.455	0.825
7.0 hr	2.24	34.0	0.452	0.825
7.5 hr	2.22	35.7	0.446	0.825
8.0 hr	2.21	35.7	0.444	0.824

Table A-10 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]_o$ = 10,000 mg/l, acidic pH 3, TiO_2 dosage = 0.1 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	3.00	28.0	1.000	1.000
0.5 hr	3.00	27.5	0.989	0.990
1.0 hr	3.00	27.5	0.973	0.987
1.5 hr	2.99	28.0	0.954	0.984
2.0 hr	2.98	27.9	0.931	0.976
2.5 hr	2.98	29.7	0.785	0.967
3.0 hr	2.88	32.7	0.639	0.957
3.5 hr	2.75	35.9	0.453	0.938
4.0 hr	2.52	32.0	0.339	0.914
4.5 hr	2.24	34.5	0.290	0.861
5.0 hr	2.15	35.0	0.246	0.834
5.5 hr	2.02	32.0	0.226	0.822
6.0 hr	2.05	34.0	0.224	0.811
6.5 hr	2.01	34.2	0.216	0.815
7.0 hr	2.03	35.6	0.223	0.814
7.5 hr	1.97	36.0	0.230	0.815
8.0 hr	1.98	36.0	0.226	0.814

Table A-11 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, acidic pH 3, TiO_2 dosage = 0.5 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	3.00	25.5	1.000	1.000
0.5 hr	3.00	26.0	0.964	0.989
1.0 hr	3.00	26.0	0.896	0.986
1.5 hr	3.00	27.5	0.888	0.985
2.0 hr	3.00	27.5	0.884	0.985
2.5 hr	2.98	27.7	0.820	0.982
3.0 hr	2.92	35.0	0.761	0.978
3.5 hr	2.79	33.0	0.705	0.967
4.0 hr	2.73	31.0	0.654	0.954
4.5 hr	2.66	35.0	0.610	0.931
5.0 hr	2.45	36.0	0.590	0.914
5.5 hr	2.41	31.0	0.577	0.894
6.0 hr	2.39	34.0	0.570	0.893
6.5 hr	2.36	35.9	0.563	0.892
7.0 hr	2.33	31.0	0.566	0.890
7.5 hr	2.27	33.0	0.559	0.890
8.0 hr	2.29	35.6	0.552	0.890

Table A-12 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, acidic pH 3, TiO_2 dosage = 1.0 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	3.00	28.0	1.000	1.000
0.5 hr	3.00	28.0	0.900	0.989
1.0 hr	3.00	28.5	0.859	0.986
1.5 hr	3.00	29.0	0.827	0.984
2.0 hr	3.00	29.0	0.824	0.982
2.5 hr	2.99	28.7	0.804	0.980
3.0 hr	2.94	32.0	0.728	0.976
3.5 hr	2.89	35.0	0.681	0.977
4.0 hr	2.75	32.0	0.660	0.974
4.5 hr	2.71	34.5	0.637	0.946
5.0 hr	2.68	31.0	0.617	0.931
5.5 hr	2.66	33.0	0.615	0.927
6.0 hr	2.55	35.0	0.614	0.913
6.5 hr	2.53	33.0	0.609	0.893
7.0 hr	2.46	31.0	0.600	0.892
7.5 hr	2.43	35.0	0.587	0.892
8.0 hr	2.42	36.0	0.585	0.892

Table A-13 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, alkaline pH 10, TiO_2 dosage = 0.05 g/l)

Time	**pH**	**Temp**	**Residual Fraction (C/Co)**	
			CH_2O	**TOC**
0 hr	10.00	27.1	1.000	1.000
0.5 hr	10.00	27.2	0.989	0.999
1.0 hr	10.00	27.5	0.972	0.986
1.5 hr	9.98	27.7	0.960	0.983
2.0 hr	9.97	27.7	0.950	0.975
2.5 hr	9.97	32.0	0.871	0.967
3.0 hr	9.89	34.5	0.782	0.957
3.5 hr	9.88	35.6	0.616	0.943
4.0 hr	9.88	34.0	0.546	0.934
4.5 hr	9.74	32.0	0.497	0.898
5.0 hr	9.67	33.7	0.456	0.852
5.5 hr	9.54	34.0	0.432	0.847
6.0 hr	9.45	35.5	0.437	0.834
6.5 hr	9.43	32.0	0.434	0.833
7.0 hr	9.33	33.0	0.445	0.827
7.5 hr	9.21	35.7	0.434	0.832
8.0 hr	9.19	36.0	0.437	0.832

Table A-14 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, alkaline pH 10, TiO_2 dosage = 0.1 g/l)

Time	**pH**	**Temp**	**Residual Fraction (C/Co)**	
			CH_2O	**TOC**
0 hr	10.0	26.0	1.000	1.000
0.5 hr	10.0	27.5	0.980	0.990
1.0 hr	10.0	27.5	0.948	0.983
1.5 hr	10.0	28.0	0.915	0.980
2.0 hr	10.0	27.9	0.910	0.976
2.5 hr	10.0	29.7	0.757	0.964
3.0 hr	10.0	32.7	0.611	0.952
3.5 hr	9.8	35.9	0.459	0.930
4.0 hr	9.8	32.0	0.353	0.909
4.5 hr	9.8	34.5	0.280	0.861
5.0 hr	9.7	35.0	0.271	0.839
5.5 hr	9.6	32.0	0.244	0.822
6.0 hr	9.4	34.0	0.250	0.811
6.5 hr	9.4	34.2	0.236	0.826
7.0 hr	9.2	35.6	0.240	0.818
7.5 hr	9.1	36.0	0.236	0.819
8.0 hr	9.1	36.0	0.233	0.818

Table A-15 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, alkaline pH 10, TiO_2 dosage = 0.5 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	10.00	25.5	1.000	1.000
0.5 hr	9.98	27.0	0.964	0.987
1.0 hr	9.97	27.0	0.896	0.985
1.5 hr	9.97	27.5	0.863	0.979
2.0 hr	9.96	27.5	0.850	0.984
2.5 hr	9.96	27.7	0.795	0.980
3.0 hr	9.85	35.0	0.730	0.971
3.5 hr	9.84	32.0	0.681	0.967
4.0 hr	9.80	34.0	0.652	0.954
4.5 hr	9.79	35.0	0.619	0.948
5.0 hr	9.76	36.0	0.603	0.924
5.5 hr	9.66	32.0	0.584	0.903
6.0 hr	9.55	34.0	0.570	0.905
6.5 hr	9.52	36.0	0.573	0.908
7.0 hr	9.46	32.0	0.554	0.904
7.5 hr	9.33	33.0	0.570	0.903
8.0 hr	9.20	35.0	0.573	0.903

Table A-16 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, alkaline pH 10, TiO_2 dosage = 1.0 g/l)

Time	pH	Temp	Residual Fraction (C/Co)	
			CH_2O	TOC
0 hr	10.01	28.0	1.000	1.000
0.5 hr	10.00	28.0	0.900	0.982
1.0 hr	9.99	28.5	0.859	0.980
1.5 hr	9.99	29.0	0.804	0.978
2.0 hr	9.99	29.5	0.804	0.974
2.5 hr	9.98	29.7	0.774	0.970
3.0 hr	9.97	33.0	0.752	0.967
3.5 hr	9.92	35.6	0.711	0.963
4.0 hr	9.67	32.0	0.680	0.954
4.5 hr	9.52	34.5	0.662	0.946
5.0 hr	9.48	32.1	0.646	0.931
5.5 hr	9.45	33.7	0.622	0.927
6.0 hr	9.43	36.0	0.624	0.913
6.5 hr	9.42	33.0	0.619	0.928
7.0 hr	9.43	35.6	0.619	0.917
7.5 hr	9.41	34.0	0.630	0.917
8.0 hr	9.42	36.0	0.633	0.916

Table A-17 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]_o$ = 1,000 mg/l, acidic pH 3, TiO_2 dosage = 0.1 g/l)

Time	pH	Temp	Residual Fraction (C/Co)		ln C/C_0
			CH_2O	TOC	
0 hr	3.00	28.0	1.000	1.000	0.000
0.5 hr	3.00	27.5	0.872	0.972	-0.137
1.0 hr	3.00	27.5	0.721	0.950	-0.327
1.5 hr	3.00	27.7	0.650	0.940	-0.431
2.0 hr	3.00	27.9	0.542	0.919	-0.612
2.5 hr	2.98	28.7	0.210	0.911	-1.561
3.0 hr	2.92	35.0	0.017	0.829	-4.075
3.5 hr	2.79	36.9	0.000	0.808	#NUM!
4.0 hr	2.73	33.0	0.000	0.742	#NUM!
4.5 hr	2.66	35.0	0.000	0.667	#NUM!
5.0 hr	2.39	36.0	0.000	0.633	#NUM!

Table A-18 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]_o$ = 3,000 mg/l, acidic pH 3, TiO_2 dosage = 0.1 g/l)

Time	pH	Temp	Residual Fraction (C/Co)		ln C/C_0
			CH_2O	TOC	
0 hr	3.00	25.5	1.000	1.000	0.000
0.5 hr	3.00	25.5	0.891	0.980	-0.115
1.0 hr	3.00	25.4	0.856	0.970	-0.155
1.5 hr	2.99	25.5	0.813	0.959	-0.207
2.0 hr	2.98	25.5	0.786	0.938	-0.241
2.5 hr	2.98	27.7	0.462	0.930	-0.772
3.0 hr	2.94	34.0	0.243	0.921	-1.415
3.5 hr	2.89	35.7	0.042	0.911	-3.170
4.0 hr	2.75	32.0	0.006	0.842	-5.116
4.5 hr	2.71	31.0	0.006	0.792	-5.116
5.0 hr	2.68	34.0	0.005	0.738	-5.298

Table A-19 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 5,000 mg/l, acidic pH 3, TiO_2 dosage = 0.1 g/l)

Time	pH	Temp	Residual Fraction (C/Co)		ln C/C_0
			CH_2O	TOC	
0 hr	3.00	27.5	1.000	1.000	0.000
0.5 hr	3.00	27.5	0.925	0.985	-0.078
1.0 hr	3.00	27.5	0.909	0.978	-0.095
1.5 hr	3.00	27.7	0.868	0.968	-0.142
2.0 hr	3.00	27.9	0.838	0.970	-0.177
2.5 hr	2.95	30.7	0.603	0.979	-0.506
3.0 hr	2.89	34.5	0.423	0.951	-0.860
3.5 hr	2.77	36.6	0.273	0.912	-1.298
4.0 hr	2.69	33.9	0.144	0.884	-1.938
4.5 hr	2.55	32.0	0.108	0.818	-2.226
5.0 hr	2.39	33.2	0.063	0.786	-2.765

Table A-20 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 8,000 mg/l, acidic pH 3, TiO_2 dosage = 0.1 g/l)

Time	pH	Temp	Residual Fraction (C/Co)		ln C/C_0
			CH_2O	TOC	
0 hr	3.00	25.0	1.000	1.000	0.000
0.5 hr	3.00	25.7	0.974	0.992	-0.026
1.0 hr	3.00	26.0	0.954	0.989	-0.047
1.5 hr	2.99	26.0	0.920	0.978	-0.083
2.0 hr	2.98	27.5	0.908	0.968	-0.097
2.5 hr	2.98	30.7	0.741	0.960	-0.300
3.0 hr	2.88	34.5	0.564	0.956	-0.573
3.5 hr	2.75	35.0	0.420	0.918	-0.868
4.0 hr	2.52	33.9	0.301	0.896	-1.201
4.5 hr	2.24	31.0	0.234	0.844	-1.452
5.0 hr	2.15	33.2	0.177	0.821	-1.732

Table A-21 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 10,000 mg/l, acidic pH 3, TiO_2 dosage = 0.1 g/l)

Time	pH	Temp	Residual Fraction (C/Co)		ln C/C_0
			CH_2O	TOC	
0 hr	3.00	28.0	1.000	1.000	0.000
0.5 hr	3.00	27.5	0.989	0.998	-0.011
1.0 hr	3.00	27.5	0.973	0.998	-0.027
1.5 hr	3.00	27.7	0.954	0.998	-0.047
2.0 hr	3.00	27.9	0.931	0.997	-0.071
2.5 hr	2.98	29.7	0.785	0.973	-0.242
3.0 hr	2.92	32.0	0.639	0.967	-0.448
3.5 hr	2.79	36.9	0.453	0.938	-0.792
4.0 hr	2.73	32.0	0.339	0.914	-1.082
4.5 hr	2.66	34.5	0.290	0.860	-1.238
5.0 hr	2.45	36.0	0.246	0.834	-1.402

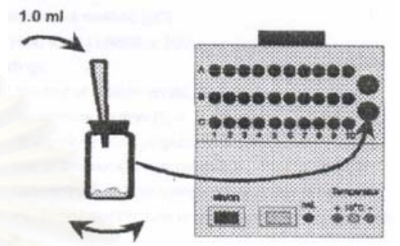
Table A-22 Degradation of Formaldehyde by UV/TiO_2 Process
($[CH_2O]o$ = 30,000 mg/l, acidic pH 3, TiO_2 dosage = 0.1 g/l)

Time	pH	Temp	Residual Fraction (C/Co)		ln C/C_0
			CH_2O	TOC	
0 hr	3.00	26.0	1.000	1.000	0.000
0.5 hr	3.00	27.0	0.990	0.998	-0.010
1.0 hr	3.00	28.0	0.986	0.998	-0.014
1.5 hr	3.00	27.7	0.983	0.998	-0.017
2.0 hr	3.00	28.0	0.982	0.997	-0.018
2.5 hr	2.99	29.0	0.937	0.996	-0.065
3.0 hr	2.94	32.0	0.871	0.989	-0.138
3.5 hr	2.89	36.9	0.805	0.980	-0.217
4.0 hr	2.75	32.0	0.736	0.976	-0.307
4.5 hr	2.71	34.5	0.699	0.959	-0.358
5.0 hr	2.68	36.0	0.649	0.936	-0.432

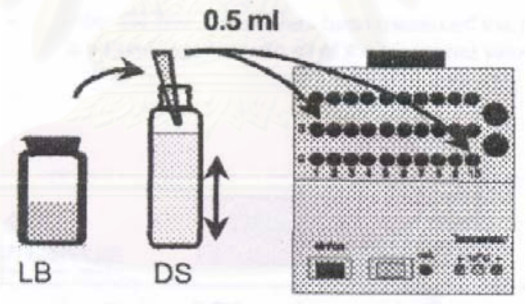
APPENDIX B

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.

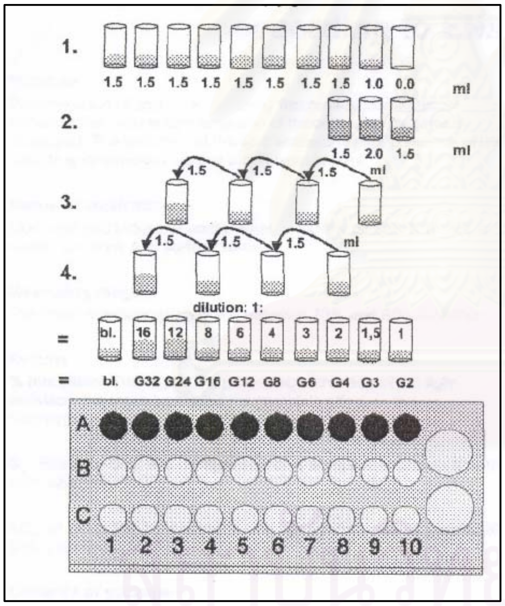
* Add solid NaCI until the concentration in the sample is 2% (wlv) (e.g.: weigh out 0.3 g NaCl and dissolve it in 15 ml sample).

* 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.

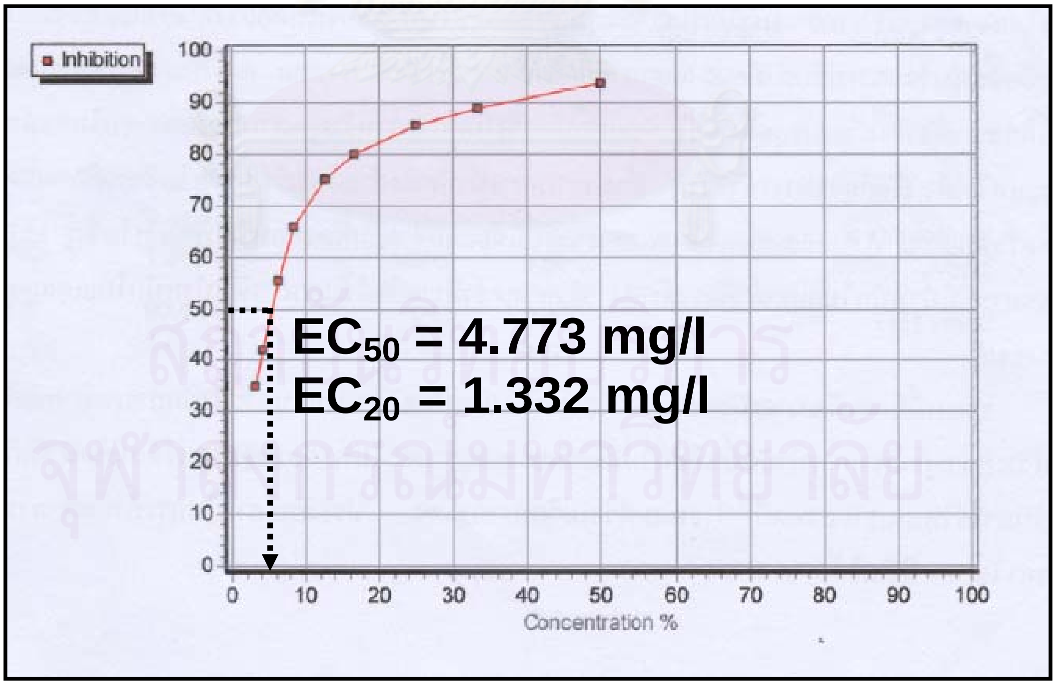


Figure B-1 Toxicity profile of Formaldehyde (10,000 mg/l of CH_2O with 10 fold pre dilution)

APPENDIX C.

PHYSICO-CHEMICAL PROPERTIES FOR DEGUSSA TITANIUM DIOXIDE P25[69]

Description	Units	Value
BET surface area	M^2/g	50±15
Averageprimary particle size	Nm	30
Moisture at leavng plant site (2 hours at 105 °C)	%	<1.5
Ignition loss (2 hours at 100 °C)	%	<1.5
pH in 4% aqueous suspension	-	3-4
X-Ray structure	-	primary anatase
Isoelectric point at pH value	-	6.6
Density	g/cm^3	3.98
Titanium dioxide	%	>99.5
Aluminum oxide	%	<0.3
Silica	%	<0.01
Iron oxide	%	<0.01
HCL	%	<0.3

BIOGHAPHY

Mr. Ratchata Titayanurak was born on July 13, 1974 in Bangkok, Thailand. He attended Assumption Bangkok School and graduated in 1990. He received his Bachelor’s degree in Environmental Engineering from faculty of Engineering, King Mongkut’s University of Technology Thonburi (KMUTT) in 1994. He therefore worked in the field of engineering for five years. After that he pursued his 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.