CUMENE HYDROPEROXIDE TREATMENT BY FENTON AND ELECTRO-FENTON PROCESS

Miss Kamonreuthai Tudthiam

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2012

การบำบัดคูมีนไฮโดรเปอร์ออกไซด์ด้วยกระบวนการเฟนตอนและอิเล็คโทรเฟนตอน

นางสาวกมลฤทัย ทัดเทียม

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2555

Thesis Title	Cumene Hydroperoxide Treatment by Fenton and Electro-Fenton Process
By	Miss Kamonreuthai Tudthiam
Field of Study	Environmental management
Thesis Advisor	Associate Professor Jin Anotai, 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

(Associate Professor Amorn Petsom, Ph.D.)

THESIS COMMITTEE

.... Chairman
(Assistant Professor Chantra Tongcumpou, Ph.D.)

.... Thesis Advisor
(Associate Professor Jin Anotai, Ph.D.)

.... Examiner
(Associate Professor Nurak Grisdanurak, Ph.D.)

.... Examiner
(Nonglak Boonrattanakij, Ph.D.)

.... External Examiner
(Chalermchai Ruangchainikom, Ph.D.)

กมลฤทัย ทัดเทียม: การบำบัดคูมีนไฮโดรเปอร์ออกไซด์ด้วยกระบวนการเฟนตอนและอิเล็คโทรเฟนตอน. (CUMENE HYDROPEROXIDE TREATMENT BY FENTON AND ELECTRO-FENTON PROCESS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร. จินต์ อโณทัย, 81 หน้า

งานวิจัยนี้ศึกษาความเป็นไปได้ของการบำบัดน้ำเสียจากการผลิตฟีนอลด้วยรูปแบบการบำบัดแบบผสมผสานระหว่างกระบวนการเฟนตอน กระบวนการอิเล็คโทรเฟนตอน และกระบวนการชีวภาพแบบใช้อากาศ น้ำเสียที่ใช้ในการทดลองมาจากโรงงานผลิตสารฟีนอลซึ่งพบว่ามีความเป็นพิษสูงและย่อยสลายทางชีวภาพได้ยาก โดยมีสารมลพิษหลักคือคูมีนไฮโดรเปอร์ออกไซด์ที่ระดับความเข้มข้น 250-550 มิลลิกรัมต่อลิตร และมีพีเอชและซีโอดีอยู่ในช่วง 12-13 และ 3,000-6,000 มิลลิกรัมต่อลิตรตามลำดับ

ผลการศึกษาพบว่าคูมีนไฮโดรเปอร์ออกไซด์สามารถทำปฏิกิริยาอย่างรวดเร็วกับอนุมูลเฟอร์รัสเกิดเป็นอะซีโตฟีโนนและสามารถย่อยสลายได้ทางชีวภาพได้โดยง่าย ชี้ให้เห็นว่าความเป็นพิษและความคงทนต่อการย่อยสลายทางชีวภาพของน้ำเสียนี้น่าจะเป็นผลมาจากสารมลพิษอื่นที่ปนเปื้อนอยู่นอกเหนือจากคูมีนไฮโดรเปอร์ออกไซด์ งานวิจัยชิ้นนี้จึงมุ่งเน้นที่จะกำจัดสารมลพิษอินทรีย์ที่ย่อยสลายทางชีวภาพได้ยากในรูปของซีโอดีแทน สภาวะที่เหมาะสมของกระบวนการเฟนตอนในการกำจัดซีโอดีคือที่พีเอช 3.0 และสัดส่วนไฮโดรเจนเปอร์ออกไซด์ต่อเฟอร์รัสโดยโมลเท่ากับ 1:0.2 ประสิทธิภาพในการกำจัดซีโอดีสูงขึ้นตามปริมาณของสารเฟนตอน อย่างไรก็ดีซีโอดีที่ผ่านการบำบัดด้วยกระบวนเฟนตอนยังคงมีค่าอยู่ในช่วง 700-1,000 มิลลิกรัมต่อลิตรซึ่งสูงกว่าเกณฑ์มาตรฐานน้ำทิ้งอุตสาหกรรมที่ 120 มิลลิกรัมต่อลิตรมาก การป้อนกระแสไฟฟ้าเพื่อปรับกระบวนการเป็นอิเล็คโทรเฟนตอนไม่สามารถบำบัดซีโอดีได้สูงขึ้นอย่างมีนัยสำคัญ อย่างไรก็ดีสามารถเพิ่มสัดส่วนบีโอดีต่อซีโอดีได้อย่างเห็นได้ชัด บีโอดีต่อซีโอดีของน้ำเสียก่อนบำบัด น้ำทิ้งที่ผ่านกระบวนการเฟนตอนและอิเล็คโทรเฟนตอนมีค่าเท่ากับ 0.4, 0.5 และ 0.8 ตามลำดับ เป็นผลให้น้ำทิ้งที่ผ่านกระบวนการอิเล็คโทรเฟนตอนมีแนวโน้มที่จะบำบัดต่อได้ด้วยกระบวนการชีวภาพแบบใช้อากาศ ผลการศึกษาการย่อยสลายทางชีวภาพด้วยระบบแอกทิเว-เต็ดสลัดจ์แบบเอสบีอาร์พบว่าสามารถลดซีโอดีให้ต่ำกว่า 40 มิลลิกรัมต่อลิตรได้ที่ระยะเวลากักพักชลศาสตร์ 2 วัน ดังนั้นการบำบัดแบบบูรณาการที่มีประสิทธิภาพสำหรับน้ำเสียจากการผลิตฟีนอลคือกระบวนการอิเล็คโทร เฟนตอนแล้วตามด้วยกระบวนการชีวภาพแบบใช้อากาศ

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต...

ปีการศึกษา 2555 ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก.......................................

5487505820: MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS: ACTIVATED SLUDGE, ELECTRO-FENTON, FENTON

KAMONREUTHAI TUDTHIAM: CUMENE HYDROPEROXIDE TREATMENT BY FENTON AND ELECTRO-FENTON PROCESS. ADVISOR: ASSOSC. PROF. JIN ANOTAI, Ph.D., 81 pp.

This research investigated the feasibility of treating phenol-production wastewater by treatment combination among Fenton, electro-Fenton and aerobic biological processes. Wastewater used in this study was obtained from a phenol-production plant and found to be highly toxic and refractory. Major pollutant was cumene hydroperoxide within the range of 250-550 mg/l with the pH and COD of 12-13 and 3,000-6,000 mg/l, respectively.

It was found that cumene hydroperoxide could rapidly react with ferrous ion to form acetophenone and was easily biodegraded. This implies that the toxicity and biological stability of this wastewater are derived from other pollutants rather than cumene hydroperoxide. As a result, this research was focused on the removal of refractory organic pollutants in term of COD. Optimum conditions for DOD removal of Fenton process were at pH 3.0 and the hydrogen peroxide to ferrous molar ratio of 1:0.2. Removal efficiency increased with increasing Fenton's reagent concentrations; however, the COD of the Fenton-treated effluent were in between 700-1,000 mg/l which were still much higher than the industrial effluent standard of 120 mg/l. Electric current discharge to transform the process to electro-Fenton could not significantly improve the COD removal. Nonetheless, it could obviously increase the BOD to COD ratio. The BOD to COD ratios of the raw wastewater, Fenton-treated and electro-Fenton treated effluents were 0.4, 0.5, and 0.8, respectively. As a result, the effluent from electro-Fenton process had high potential to be further treated by aerobic biological process. Biodegradation study revealed that the activated sludge SBR system could reduce the COD to be lower than 40 mg/l with the hydraulic retention time of 2 days. Thus, the effective integrated treatment scheme for phenol-production wastewater is the electro-Fenton process followed by aerobic biodegradation process.

Field of Study: Environmental Management	Student's Signature..............................
Academic Year: 2012	Advisor's Signature..............................

ACHNOWLEDGEMENTS

I would like to express my sincere appreciation to my advisor, Assoc. Prof. Dr. Jin Anotai for advice, guidance, and support. I am grateful for his suggestion and teaching. This research would not have been completed without his support.

Gratefully thanks go to the chairman of the committee, Asst. Prof Dr. Chantra Tongcumpou for giving suggestions and comments. I would also like to acknowledge my thesis committee, Assoc. Prof. Dr. Nurak Grisdanurak, Dr. Nonglak Boonrattanakij, and Dr. Chalermchai Ruangchainikom, for their valuable remarks and supports.

I would also like to thank the Department of Environmental Engineering, King Mongkut's University of Technology Thonburi (KMUTT) for laboratory supports. Also staffs and friends at the KMUTT and EHWM for their help and encouragement.

CONTENTS

Page

Page

Page

Page

LIST OF TABLES

Table **Page**

Table **Page**

LIST OF FIGURES

Figure **Page**

NOMENCLATURES

AOPs = Advanced Oxidation Processes

SBR = Sequencing Batch Reactors

COD = Chemical Oxygen Demand

CHP = Cumene Hydroperoxide

AP = Acetophenone

DMPC = Dimethyl Phenyl Carbinol

M = molar

mM = millimolar

ml = milliliter

min = minute

µm = micrometer

mg/l = milligram/liter

CHAPTER I
INTRODUCTION

1.1 Rational

Phenol is a key raw material in many industries. It is very useful in petrochemical and plastic industries. Phenol requirement has been increasing every year, so the improvement in the production technology to get a higher yield is necessary. However, phenol-production plants generate significant amount of wastewater, i.e., a ton of phenol produced generates 0.6 ton of wastewater (Kujawski et al., 2004). Phenol production wastewater is highly toxic even at low concentration because it contains phenol, acetone, aromatic hydrocarbons and especially cumene hydroperoxide (CHP). The US Environmental Protection Agency regulates the phenol in the discharge to be 0.1 mg/l (USEPA, 1985) but no data were found regarding of CHP in the discharge.

Activated carbon adsorption is typically used to reduce the toxicity of phenol-production wastewater before discharging to biological treatment process for biodegradable organic pollutant removal. Major disadvantages of this adsorption technique are its high carbon-replacement cost and disposal of toxic spent-carbon. Insufficient pre-treatment will cause failure to the biological process leading to unacceptable effluent quality.

Nowadays, there are several methods which can be used to remove toxic organic pollutants efficiently from wastewater. Advanced oxidation processes (AOPs) are widely applied for highly toxic wastewaters. Although complete mineralization of organic pollutants is rarely achieved for wastewater treatment, the AOPs are found to be very effectively for detoxification and biodegradable enhancement. However, the performance of AOPs is very sensitive to wastewater characteristics and normally has to evaluate on a case-by-case basis. This research focused on Fenton family since it does not require sophisticated and expensive equipment like other AOPs. Ordinary Fenton and electro-Fenton were used to treat highly-toxic phenol-production wastewater together with activated sludge process to access the degree of detoxification and biodegradation. Targeted pollutants are CHP and COD.

1.2 Objectives

To determine the feasibility of treating cumene hydroperoxide and COD of phenol-production wastewater by Fenton, Electro-Fenton, and activated sludge processes

1.3 Hypotheses

1. Cumene hydroperoxide can be oxidized by hydroxyl radicals generated by Fenton and Electro-Fenton processes.
2. Hydroxyl radicals can enhance the biodegradability of phenol-production wastewater

1.4 Scope of the Research

1. Chemical experiments were conducted in lab-scale reactors of 0.5 liter for Fenton and 5 liters for the Electro-Fenton.
2. Biodegradation studies were conducted in a lab-scale sequencing batch reactor (SBR) of 2 liters for Fenton effluent and in a bench-scale SBR of 100 liters for real phenol-production wastewater.
3. Controlled variables were temperature (25°C) and pressure (1 atm).
4. Studied variables included Fenton reagent dose, pH, CHP concentration, current density, and hydraulic retention time for activated sludge SBR.

1.5 Expected Outcomes

1. Cumene hydroperoxide would be completely removed from wastewater by Fenton reaction.
2. Hydroxyl radicals should be able to effectively detoxify the phenol-production wastewater so that the chemical oxygen demand in Fenton-treated wastewater would be in the acceptable range and did not cause failure to the biological treatment system.

CHAPTER II

THEORIES AND LITERATURE REVIEWS

Phenol is an important raw material and an additive in several organic chemical industries. Almost phenol available in the market is commonly produced by the Hock process as shown in Figure 2.1 (Yadav et al., 2002). It is based on the decomposition of cumene hydroperoxide (CHP) which is the product from the acid-catalytic reaction between benzene and propylene (Cao, 1983). Cumene is oxidized to cumene hydroperoxide by air and sequentially decomposed into phenol and acetone under acid catalysis (Huang et al., 2002). However, the decomposition of cumene hydroperoxide typically does not totally complete. Hence, the residuals will contaminate in the wastewater.

2.1 Cumene Hydroperoxide

2.1.1 General Information

Cumene hydroperoxide ($C_9H_{12}O_2$) has molecular weight of 152.19 g/mole with the molecular structure as shown in Figure 2.2. The National Institute of Environmental Health Sciences (NIEHS) identified CHP as a possible candidate for toxicity and carcinogenicity testing. CHP reacts aggressively with reducing agents (HSDB, 1997). It is used primarily in the phenol production as the intermediate and is also used in styrene, acrylic monomer polymerization (Lewis, 1993).

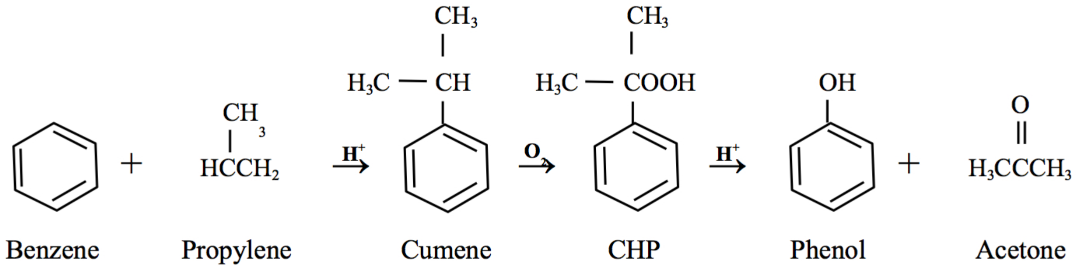


Figure 2.1 Phenol production by Hock process

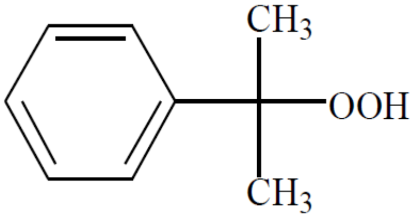


Figure 2.2 Cumene hydroperoxide molecular structure.

CHP decomposes rapidly when heated at the temperature higher than 150ºC via the oxidation of cumene (HSDB, 1997). Approximately 95% of the CHP was produced in the United States.

2.1.2 Physical and Chemical Properties

Important physical and chemical properties of CHP are shown in Table 2.1. It can be seen that CHP is a liquid under room conditions. Density is slightly higher than those of water. CHP can moderately dissolve in water.

Table 2.1 Physical and chemical properties of cumene hydroperoxide.

Property	Information	Reference
Physical state	Colorless to slight yellow liquid	Lewis (1993)
Odor	Strong odor	Radian Corporation (1991)
pH	~4	Radian Corporation (1991)
Melting point (ºC)	<-40	Radian Corporation (1991)
Boiling point (ºC)	100-101 @ 8 mm Hg	Radian Corporation (1991)
Density	1.024 g/ml @ 20 ºC 1.03g/ml @ 25 ºC	Radian Corporation (1991)
Vapor pressure	0.24 mm Hg @ 20 ºC	HSDB (1997)
Solubility (mg/ml @18 ºC)	Water < 0.1 95% ethanol:≥100 acetone:≥100	HSDB (1997)

2.1.3 Toxicological Information

No data on the humanity toxicity and the chemical disposition of CHP were reported. CHP can exposure to the workers in the phenol industry via dermal, causing skin rashes. It also affects human adenocarcinoma cells. CHP is highly toxic to animals and microorganisms. As a result, it severely interferes with the biological treatment process. Without proper treatment, CHP will enter the environment via industrial discharges and spills. Regarding to its environmental toxicity, CHP can cause acute toxic impact to animals via oral, dermal and inhalation routes, typically 2 to 4 days after exposure, resulting in death. Chronic impacts include shortened life span, reproductive and fertility problems, and behavioral effects (EPA, 1988). CHP can cause growth inhibition in plants. It is genotoxic, DNA damage and mutation in prokaryote and eukaryote systems. Despite of insufficient data to predict the extent of environmental persistence, data suggest that CHP is moderately persistent in water, with an estimated half-life of 20 to 200 days (EPA, 1988). Therefore, chemical treatment approach is required for complete removal or transformation of CHP to less toxic intermediates in order to prevent it from contaminating the environment.

2.1.4 Regulatory

According to the US Environmental Protection Agency (USEPA) and the US Department of Transportation (DOT), several considerations and rules related to CHP are regulated as follows:

- CHP is a volatile organic compound (VOC).
- When CHP is a commercial chemical product or a manufacturing chemical intermediate, it must be managed as a hazardous waste.
- CHP is listed as a hazardous material with the code number of UN 2116.

2.1.5 Decomposition Pathways

Apart from the main reaction pathway in which CHP catalytically decomposes to form phenol and acetone in the presence of strong mineral acid, CHP is also transformed via other major routes as shown in Figure 2.3 (Levin et al., 2005). In the presence of cumene and at high temperature, CHP can exothermically decompose to form dimethylphenyl carbinol (DMPC) or dimethyl benzyl alcohol (DMBA) which simultaneously transform to alpha-methylstyrene (AMS). In addition, CHP can also decompose thermally to form acetophenone (AP) and methanol (Schmidt, 2004). Actually, there are still many other minor reaction pathways of CHP decomposition which are complex but less favorable than previous routes.

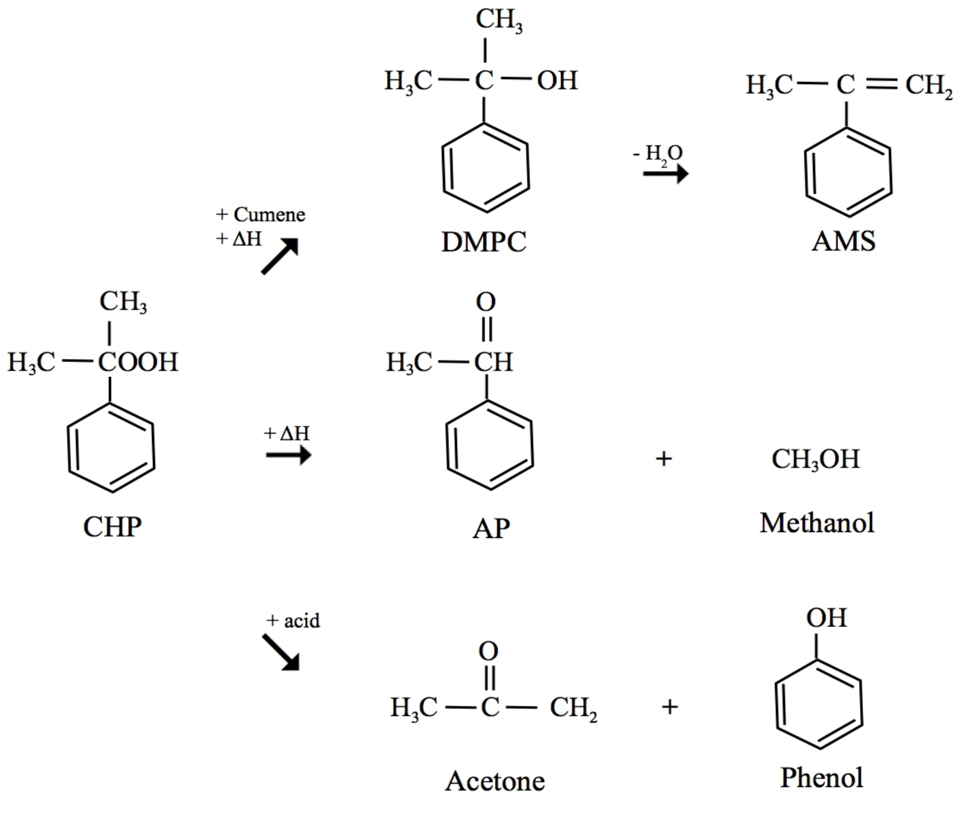


Figure 2.3 Main decomposition pathways of cumene hydroperoxide.

2.2 Advance Oxidation Processes

Advance oxidation processes (AOPs) are widely used for treating the resistant organic compounds such as pesticide, surfactant, pharmaceutical substances from industrial and municipal wastewaters. AOPs have been defined as those which involve the generation of hydroxyl radicals ($OH^{\bullet}$) in sufficient quantity to affect water purification (Tchobanoglous et al., 2003). Hydroxyl radicals are non-stable and highly reactive species; hence, they can oxidize many pollutants. AOPs normally provide a complete oxidation for water purification but not complete oxidation for wastewater treatment. Due to its unstable property, it is necessary to generate $OH^{\bullet}$ in situ. Several processes can be employed to generate the $OH^{\bullet}$ including ozone/hydrogen peroxide, hydrogen peroxide/UV, semiconductor photocatalysis, and Fenton process. This research project focused on the Fenton process which does not require sophisticated and expensive equipments.

2.3 Fenton Process

Fenton process is one of the AOPs widely used for treating the water and soil contaminated especially in industrial wastewater treatment because this process not only can effectively treat non-biodegradable, highly toxic and hazardous wastewaters but also requires no sophisticated and expensive equipment. Fenton process generates the $OH^{\bullet}$ via the reaction between Fenton's reagent consisting of hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}). After the combination of H_2O_2 and Fe^{2+}, the $OH^{\bullet}$ will be generated from H_2O_2 decomposition in the presence of Fe^{2+} and Fe^{2+} will be oxidized to ferric ion (Fe^{3+}) in less than a second. The typical optimum pH range is 2 to 4; however, Sakugawa et al., (2013) found that pH 2.8 to be the most efficient to generate $OH^{\bullet}$. Further reactions after the generation of $OH^{\bullet}$ are very complicated and consisting of several sequential reaction steps. Fenton process is one of most popular AOPs because of low capital cost, easy operation and non-toxic by-product. However, it has several drawbacks including the ferric hydroxide sludge production at the end of treatment after neutralization, and increasing the effluent TDS. Because the sensitivity and reactivity of Fenton reactions depends largely on the impurity of the wastewater, it is recommended that the reaction always be characterized through laboratory treat ability test before proceeding to the plant scale.

2.3.1 Hydrogen Peroxide

Hydrogen peroxide has a chemical formula of H_2O_2. It has a molecular weight of 34.015 g/mole. It is a weak colorless acid and non-flammable and has an acidic odor at high concentration.

Hydrogen peroxide is available as a solution in water and significantly decomposed into oxygen when temperature rises over 60 °C. For water and wastewater, H_2O_2 is mainly used for oxidation reaction in chemical syntheses. Hydrogen peroxide is used to pre-oxidize organic compounds and removed iron and manganese ion in drinking water purification.

2.3.2 Ferrous

Iron (Fe) has an atomic weight of 55.845. Iron is generally present in the nature in the form of ferrous and ferric ions. It is a plentiful element on the earth. Comparing the cost of necessary metals, iron is the cheapest that why it is widely used in many activities.

Iron found in the environment is ferrous (Fe^{2+}) and ferric (Fe^{3+}) even though its oxidation number varies from -2 to +6. Ferrous ion is not stable in the atmosphere because it is rapidly oxidized to ferric when exposed to oxidizing agents such as oxygen. Ferrous can catalyze the decomposition H_2O_2 to form $OH^{\bullet}$. Common form ferrous salt is $FeSO_4.7H_2O$ which is commercially available in the market. It is used as a fertilizer, a medicine in the treatment of iron deficiency, coagulant for coagulation, and especially a catalyst in the Fenton process.

2.3.3 Hydroxyl Radicals

Hydroxyl radicals ($OH^{\bullet}$) are strong oxidants, nonselective transient species, extremely reactive, short lived and a very low steady-state concentration in water.

An oxidation potential of $OH^\bullet$ is 2.8 volt which is only second to fluorine. However, fluorine is not commonly used because of its toxicity. The oxidation potential of hydroxyl radicals compared to others oxidants are shown in Table 2.2. (Parsons, 2004)

Table 2.2 Oxidation potential of common oxidation species.

Oxidant	Oxidation Potential (volt)
Fluorine	3.03
Hydroxyl radicals	2.8
Ozone	2.07
Hydrogen peroxide	1.78
Potassium permanganate	1.68
Chlorine dioxide	1.59
Chlorine	1.36

2.3.4 Fenton Reaction

Fenton process is one of AOPs using for treating water and soil contaminated. The conventional "dark" Fenton process involves the use of an oxidizing agent (usually H_2O_2) and a catalyst (a metal salt, usually iron) to generate hydroxyl radical. Once the Fenton's reagent is combined together, its sequential reactions are very complicated but well specified as shown in Eqs. (1) to (12) (Pignatello, 1992; Lu et al., 1999; Chen et al., 2001).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \qquad k_1 = 76\ M^{-1}s^{-1} \qquad (1)$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \qquad k_2 = 1.59\times10^{-12} \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet \qquad k_3 = 0.02\ M^{-1}s^{-1} \qquad (3)$$

$$HO_2^\bullet \leftrightarrow O_2^{\bullet-} + H^+ \qquad k_4 = 1.6\times10^{-5}\ M \qquad (4)$$

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \qquad k_5 = 4.3\times10^{6}\ M^{-1}s^{-1} \qquad (5)$$

$$Fe^{2+} + O_2^{\bullet-} \rightarrow Fe^{3+} + O_2^- \qquad k_6 = 1\times10^{7}\ M^{-1}s^{-1} \qquad (6)$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^\bullet \qquad k_7 = 1.2\times10^{6}\ M^{-1}s^{-1} \qquad (7)$$

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2^\bullet + H_2O \qquad k_8 = 2.7\times10^{7}\ M^{-1}s^{-1} \qquad (8)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad k_9 = 8.3\times10^{5}\ M^{-1}s^{-1} \qquad (9)$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad k_{10}=5.3\times10^{9}M^{-1}s^{-1} \qquad (10)$$

$$RH + {}^{\bullet}OH \rightarrow RH^{\bullet} + OH^{-} \rightarrow\rightarrow\rightarrow \text{products or } CO_2 + H_2O \qquad (11)$$

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_{3(s)} \qquad K_{sp} = 4\times10^{-38} \qquad (12)$$

Ferrous acts as a catalyst in the Fenton reaction, as illustrated in Eqs. (1) and (3) but the regeneration rate of Eq. (3) is almost 3,800 times slower than the consumption rate of Eq. (1). As a result, Fe^{2+} concentration will decrease rapidly after the initiation of Fenton reaction. Sufficient Fe^{2+} will lead to the $OH^{\bullet}$-excessive environment resulting in rapid degradation of the pollutants. In some specific cases, Fe^{3+} might be used instead of Fe^{2+} as a source of iron in Fenton process so called "Fenton-like process" (Lunar et al., 2000). A major disadvantage for conventional Fenton process as shown in Eq. (12) is ferric hydroxide sludge occurring at the end of process because of the neutralization. Table 2.3 summarizes the main advantages and disadvantages of Fenton process

Table 2.3 Advantages and disadvantages of the Fenton process.

Advantages	Disadvantages
Fenton reagent is inexpensive and a commercial available and the system operates easily.	Fe^{2+} are used rapidly than they can be regenerated resulting in deteriorating of oxidation rate.
No energy is needed to activate the H_2O_2 and catalyst.	Ferric hydroxide sludge needs to be disposed and the disposal cost is typically expensive.

2.4 Electro-Fenton Process

Electro-Fenton process (EF) is a modified version of conventional Fenton process. EF method has been found to be able to degrade non-biodegradable more. effectively than ordinary Fenton. It is widely used to remove many organic compounds including dyes, drugs, pesticides and phenolic compounds, etc. (Nidheesh, 2012). There are three main types of EF characterized by the use of electrochemical reaction to overcome the drawback of the ordinary Fenton process. Several reduction and oxidation reactions can occur at the cathode and anode as shown in Figure 2.4; however, principle transformation at the electrodes will depend on the system configuration and solution composition.

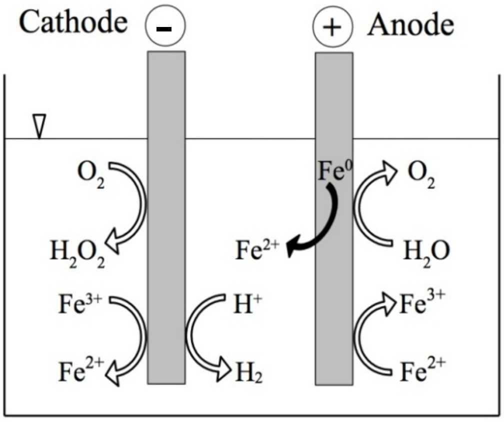


Figure 2.4 Oxidation and reduction reactions of Electro-Fenton process.

2.4.1 Cathodic Fenton Process (EF-H_2O_2)

Hydrogen peroxide can be generated in situ at the cathode by the reduction of oxygen, and Fe^{2+} is externally applied. This method needs to continuously supply oxygen at the cathode in order to generate H_2O_2 uninterruptedly according to Eq. (13). The anode is necessary made from inert material such as platinum or platinized titanium to protect corrosion at the anode.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (13)$$

2.4.2 Anodic Fenton Process (EF-FeOX)

In this case, the anode is an iron electrode which serves as a source of Fe^{2+} in the reactor. Ferrous can be generated at the anode by the reaction of metallic iron according to Eq. (14). Corrosion will progressively occur at the anode and H_2O_2 is externally applied in this case.

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (14)$$

2.4.3 Fenton Sludge Recycling System (FSR)

H_2O_2 and Fe^{2+} are both externally applied similar to ordinary Fenton process. However, in the FSR system, Fe^{2+} is electrochemically regenerate from Fe^{3+} reduction at the cathode as shown in Eq. (15). FSR has been developed to reduced ferric hydroxide sludge which is a major disadvantage of traditional Fenton process (Anotai et al., 2006).

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad \text{at cathode} \qquad (15)$$

2.5 Biological Treatment

Biological treatment plays an important role in contamination removal from both domestic industrial wastewaters by using bacteria and microorganisms. It is an economically feasible method for wastewater treatment, both in terms of capital and operating costs. All heterotrophic-biological treatment processes use organic pollutants in the wastewater as the substrates for microorganisms growth. There are three categories of heterotrophic biological treatment namely aerobic, anaerobic and anoxic as follows:

Aerobic biological treatment takes place in the presence of oxygen and microorganisms which require oxygen, the aerobes act to degrade the target pollutants convert them into carbon dioxide, water, and biomass as the by-products.

Anaerobic biological treatment takes place in the absence of oxygen and use microorganisms which do not require oxygen to convert the target pollutants to methane, carbon dioxide, and biomass.

Anoxic biological treatment can work in oxygen deficient and use microorganisms which do not require pure oxygen molecules but rather use nitrite and/or nitrate.

Hazardous wastewater can inhibit microorganisms and; thus, is difficult to be degraded due to its toxicity. Traditional biological treatment does not suitably treat the wastewater which contains high concentration aromatic compounds such as aniline, phenols, PAHs and pesticides without acclimatization of bacteria to the wastewater. Microbial acclimatization is necessary to effectively biodegrade toxic wastewater because microbes can be inhibited even at low concentrations. For example, bacteria growth is inhibited at concentration above 0.05 g/l of phenol and phenol is bactericidal at concentrations of about 2 g/l, if microorganism adaptation to phenol has not been provided (Bajai et al., 2008). For this result, biological treatment is common used as pre-treatment, post-treatment and/or combine with chemical treatment to treat hazardous wastewater.

Activated sludge is and aerobic process and widely acceptable for the biodegradation. It is extensively used to treat municipality and industrial wastewaters. It is a suspended-growth aerobic process in which the sludge age and hydraulic retention time can be varied independently from each other.

Sequencing batch reactor (SBR) is a modification of the conventional activated sludge system which widely used for treating industrial wastewater. There are many researches reported that the SBR system under aerobic condition is a good alternative to treat of heavy metals, resistible chemical compounds or non-degradable pollutants. The SBR has several advantages including easily operation, low cost, no sludge lost and no need to return activated sludge. It uses only a single aeration tank which contains a suspension of the wastewater and microorganisms, so this process is a complex ecosystem of competing organisms (Moussavi et al., 2009). In an SBR system, wastewater is added to a single batch reactor followed by five basis steps as shown in Figure 2.5.

(a) Fill: Adding the wastewater and substrate for microbial activity.

(b) React: Aeration is supplied to the tank for microbial use, no wastewater enters the tank and the organic removal rate increases significantly.

(c) Settle: No aeration and mixing. The activated sludge form biofloc and settle down so treated water and sludge are separated.

(d) Draw: Treated effluent and excess sludge were withdrawn from the reactor.

(e) Idle: Lag time to wait for new cycle.

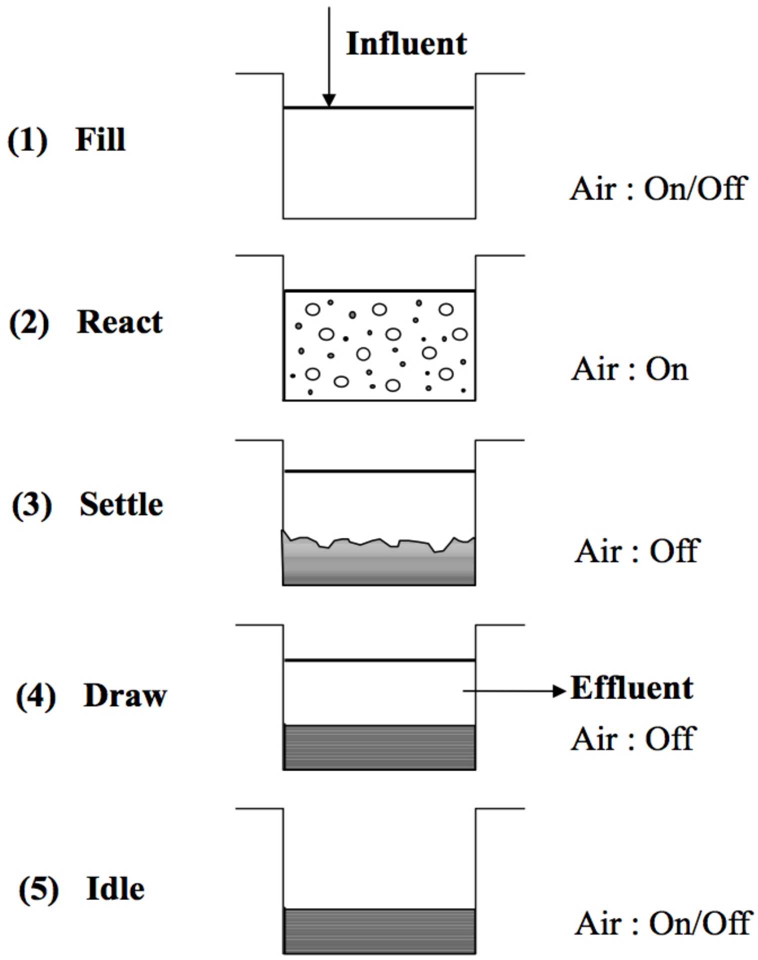


Figure 2.5 The SBR operation cycle

Although the SBR is good system and uses little area but it still has some operational problems, such as excess sludge generation and high sludge volume index (Moussavi et al., 2009).

2.6 Literature Reviews

2.6.1 Cumene Hydroperoxide Degradation

From literature survey, it is very surprising that very few articles related to CHP decomposition have been published. Among those papers, all of them were focused on the product of phenol from CHP decomposition and attempted to improve the conversion efficiency of CHP to phenol and acetone. No paper up-to-date has been studied the removal of CHP in wastewater.

Huang et al. (2002) substituted the sulfuric acid catalyst with sulfonic resin catalyst which could increase the conversion and product selectivity of CHP to be over 99% and 98%, respectively.

Levin et al. (2006) determined the factors affecting the decomposition of CHP and found that increasing dose of sulfuric acid catalyst could lower the decomposition temperature. As the acid concentrations at or above 5,000 ppm, the exotherm could emerge at the temperature as low as 5°C.

Shin et al. (2001) investigated the photo-dissociation dynamics of CHP at 248 nm (UVC) and 193 nm (VUV). They concluded that the decomposition of CHP decomposed under 248-nm irradiation is through the direct impulsive dissociation whereas via indirect dissociation with the exit channel barrier at 193-nm irradiation.

2.6.2 Degradation of Hazardous Wastewater by AOPs

Chu et al. (2012) used a dual-cathode in electrochemical oxidation system and anodic oxidation system to degrade 4-nitrophenol. Gas diffusion cathode was used to generate H_2O_2 and Fe^{3+} was regenerated to Fe^{2+} at the graphite electrode. The mechanism of the dual-cathode oxidation system is shown in Figure 2.6. The experiment showed that the optimum concentration of Fe^{2+} was 0.10 mM while a single-cathode system used Fe^{2+} at 0.25 mM for 4-nitrophenol degradation. Moreover, 74.5% of TOC and 57.0% of the nitrogen were removed by the dual-cathode oxidation system

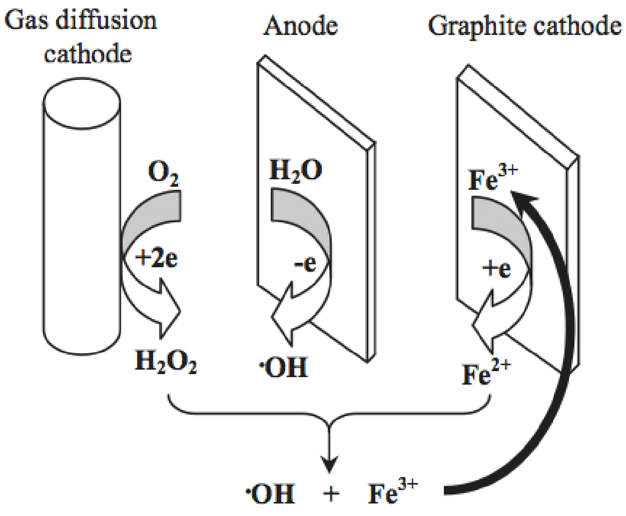


Figure 2.6 Mechanism of the dual-cathode oxidation system (Chu et al., 2012)

Li et al. (2009) investigated the optimal reaction condition of the Fenton reaction treating real industrial wastewater and synthesized wastewater containing triazophos pesticide. They found that the concentrations of 2.5 g/l of $FeSO_4.7H_2O$ and 100 ml/l of H_2O_2 were optimal for degrading the synthesized wastewater. COD removal efficiency of 96.3% was obtained. For the real wastewater, 5.0 g/l of $FeSO_4.7H_2O$ and 75 ml/l of H_2O_2 were used and the COD removal efficiency was 85.4%. For both synthetic and real wastewater, the optimum pH and reaction time were 4 and 90 minutes.

Hong et al. (2007) demonstrated methyl *t*-butyl ether (MTBE) degradation by using anodic Fenton treatment (AFT) and classic Fenton treatment (CFT). The AFT system has more efficient than CFT for MTBE. The optimized time was 4-8 min and 32 min for AFT and CFT systems, respectively.

2.6.3 Degradation of Hazardous Wastewater by Biological Treatment

Malakahmad et al. (2011) examined the removal a synthetic petrochemical wastewater containing mercury and cadmium by using a sequencing batch reactor (SBR). The SBR could remove 76-90% of Hg^{2+} and 96-98% of Cd^{2+} in 110 days with the microorganism acclimatization period of 60 day.

Va ́zquez et al. (2006) studied the biological treatment of coke wastewater containing phenol, ammonium and thiocyanate under aerobic condition. Without the addition of bicarbonate which is an inorganic carbon source to support nitrification, the COD, phenol and thiocyanate removal efficiencies were 75%, 98% and 90%, respectively. The ammonium removal efficiency increased to 71% when bicarbonate was added.

Shawaqfeh (2010) investigated the feasibility of pesticide removal from wastewater by using anaerobic and aerobic biological treatment. The experiment showed that more 96% of the pesticide was removed under aerobic and anaerobic conditions in 172 days and 230 days, respectively. The aerobic reactor was operated at 22±2 °C while the anaerobic reactor was controlled at 30±2°C.

2.6.4 Degradation of Hazardous Wastewater by AOPs Combined with Biological Treatment

Martins et al. (2010) applied Fenton's oxidation process as a pre-treatment for phenolic wastewater purification. $FeSO_4.7H_2O$ 271 mg/l and H_2O_2 488 mM were added into twelve aliquots at every 30 minutes during 6 hours of reaction. At the end of treatment, the TOC, COD, and BOD_5 were 123 mg/l, 180 mg/l, 146 mg/l, respectively. Moreover, the BOD_5/COD ratio has changed from 0.3 to 0.8 meaning that the Fenton reaction could significantly improve the biodegradability of the wastewater which is good for the biological treatment process.

Moussavi et al. (2012) studied the degradation and mineralization of formaldehyde wastewater by using an electro-Fenton process (EFP) combine with biodegradation. They concluded that 7,500 mg/l of formaldehyde was completely degraded in the EFP in 6 minutes and 51% mineralization of formaldehyde could be achieved. The treated wastewater from the EFP was transferred to biological process. The COD was reduced to below 50 mg/l after 16 days while it took 31 days to completely biodegrade formaldehyde in the raw wastewater. Hence, combining EFP with a biological process is an efficient for formaldehyde treatment.

Liu et al. (2011) investigated an individual photo-Fenton process, a single biological oxidation, and a combined Fenton-biological system for aniline wastewater treatment. The result showed that 62.5% H_2O_2 has been saved when combined both Fenton and biological processes as compared to the single photo-Fenton process. In addition, direct biological oxidation was inhabited due to aniline toxicity to microorganisms. They found that the toxicity of aniline was reduced after photo-Fenton treatment.

CHAPTER III
METHODOLOGY

3.1 Materials and Chemicals

Synthetic wastewater was prepared by adding cumene hydroperoxide at 80% purity into demineralized water at the concentration of 375 mg/l which was the average CHP concentration in the real wastewater sample. The COD value of the synthetic wastewater was 1,100 mg/l, and the pH value was 6.8. Real wastewater was collected from the storage tank after decanter of a phenol-production plant. The COD value of the real wastewater was 3,000-6,000 mg/l, and the pH value was 12-13.

Cumene hydroperoxide at 80% purity, hydrogen peroxide at 30% purity, ferrous sulfate heptahydrated, and all other chemicals were reagent grade. Demineralized water was used for all solutions preparation.

3.1.1 Fenton Reactor

A 0.5-liter Pyrex beaker with a stirrer and a magnetic stir bar was used. Temperature was controlled at 25°C by using a water bath.

3.1.2 Electro-Fenton Reactor

An acrylic reactor of $15 \times 21 \times 20$ cm^3 of 5 liters of working volume with three mixers was used. Three cathodes were made from stainless-steel nets and two anodes were special nets made from Ti/Pt or DSA. All electrodes were connected to a DC power supply which discharged constant current at 4 A. The reactor was placed in a waterbath for temperature control at 25°C as shown in Figure 3.1.

3.1.3 Biological Reactor

A 100-liter plastic container with an aquarium aerator and 6 diffusers was used as an SBR for real wastewater experiment. A 2-liter beaker with an aquarium aerator

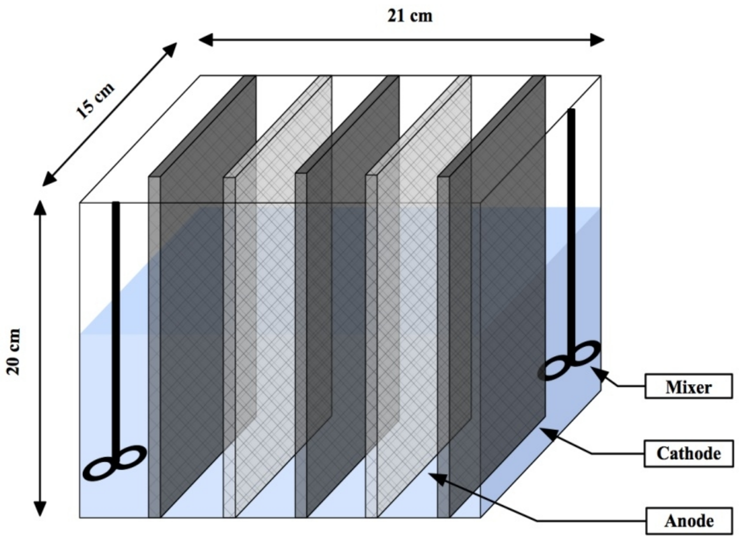


Figure 3.1 Electro-Fenton reactor.

And 2 diffusers were used as an SBR for post-treatment of electro-Fenton effluent.

3.2 Experimental Procedures

3.2.1 Fenton Experiment

From the preliminary study, it was found that CHP could readily react with Fe^{2+} whereas H_2O_2 alone could not oxidize CHP. As a result, predetermined volume of H_2O_2 was firstly added into the synthetic/real wastewaters. Solution pH was adjusted to the required value. Stock ferrous solution was prepared by dissolving $FeSO_4.7H_2O$ in demineralized water. To start the Fenton reaction, predetermined amount of Fe^{2+} standard solution was added into the mixture and then the Fenton reaction began. At predetermined time, a sample was collected using a syringe. Experimental steps were summarized in Figure 3.2.

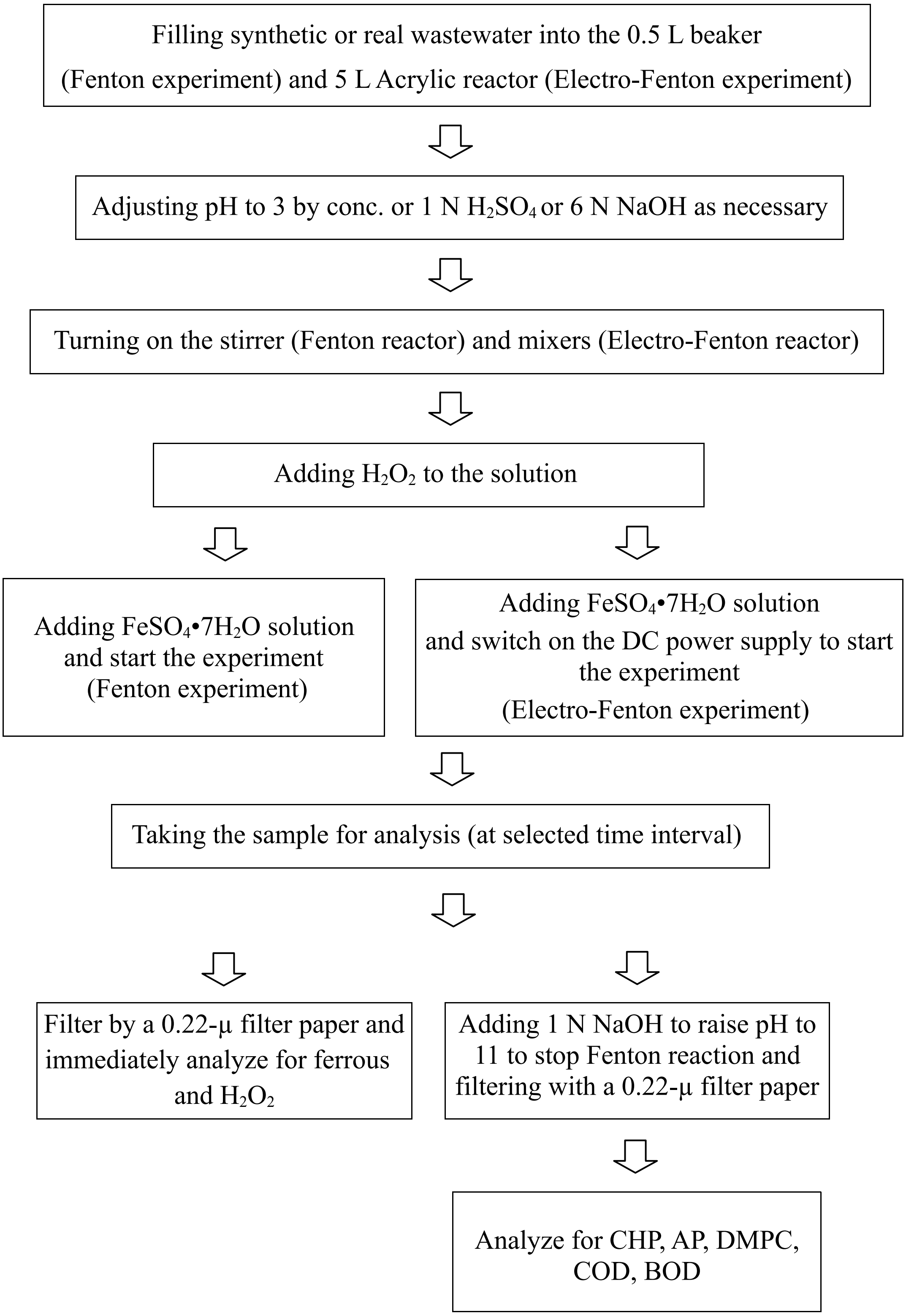


Figure 3.2 Experimental scheme for Fenton and Electro-Fenton processes.

3.2.2 Electro-Fenton Reactor

All procedures for electro-Fenton experiment were similar to those of Fenton experiment except the power supply was switched on when Fe^{2+} solution was added.

3.2.3 SBR Experiment

The biodegradation tests were conducted using acclimated biomass. During the acclimation, neutralized real wastewater from phenol production was added into the mixed liquor at the ratio of 10% to dilute and reduce the toxicity. Essential nutrients including nitrogen from NH_4Cl, phosphorus from NaH_2PO_4 and iron from $FeCl_3$ were supplied so that the BOD:N:P:Fe^{2+} ratio was 100:5:1:0.5. After 80% of the initial COD has been removed, fresh phenol-production wastewater was added at a gradually proportion until reaching 50% ratio. This acclimation step took 38 days. After acclimation, the mixed liquor was ready for biological experiments. The SBRs were operated with filling to idle volume of 1:1 and the settling time was controlled at 1 hour. Real wastewater and Fenton-treated effluent were neutralized to pH 7.0 before feeding. Sufficient nutrients were supplied to ensure suitable environment for microbial growth. The COD of filtered mixed liquor was monitored frequently until reaching a steady state; after which, a new SBR cycle began. At the end of each batch, the supernatant was analyzed for COD, BOD, CHP, AP, and DMPC.

3.3 Experimental Scenarios

3.3.1 Fenton Experiment

3.3.1.1 Effect of H_2O_2 or Fe^{2+}

This part investigated the effect of H_2O_2 or Fe^{2+} on the target compounds. The experiments were conducted using 1,000 mg/l H_2O_2 or 100 mg/l Fe^{2+} with both synthetic and real wastewaters.

3.3.1.2 Effect of H_2O_2 or Fe^{2+} Ratio

This experiment aimed to verify the proper H_2O_2:Fe^{2+} ratio for oxidizing target compounds and COD. Five experiments were set up under the conditions as shown in Table 3.1.

Table 3.1 Conditions for the determination of the optimal ratio of Fenton's reagent.

Wastewater	Ratio	H_2O_2 (mg/l)	Fe^{2+} (mg/l)	pH
Real wastewater	1 : 0.1	2435	400	3
	1 : 0.2		800	
	1 : 0.5		2,000	
	1 : 1		4,000	
	1 : 2		8,000	

3.3.1.3 Effect of pH

This experiment aimed to investigate the optimum pH for target compounds and COD removal by Fenton reaction. There experiments were set up by using optimum H_2O_2:Fe^{2+} ratio obtained from previous section (initial concentrations of Fenton's reagent are 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+}) and varied pH from 2.5 to 3.0 and 3.5.

3.3.1.4 Effect of Fenton's Reagent Concentration

This experiment aimed to determine the effect of Fenton's reagent dose on the organic compound degradation in both synthetic and real wastewaters. The optimum ratio of H_2O_2:Fe^{2+} was used in this scenario but the concentrations of H_2O_2 and Fe^{2+} were varied as shown in Table 3.2.

Table 3.2 Conditions for the determination of the effect of Fenton's reagent concentration.

Wastewater	Ratio	H_2O_2 (mg/l)	Fe^{2+} (mg/l)	pH
Synthetic wastewater	1 : 0.2	608	200	3
		1,217	400	
		2,435	800	
Real wastewater	1 : 0.2	608	200	3
		1,217	400	
		2,435	800	
		12,175	4,000	

3.3.1.5 Effect of Fenton's Reagent Adding Pattern

This experiment aimed to investigate the effect of Fenton's reagent adding pattern on the removal of target compounds and COD in real wastewater. Four experiments were examined under the conditions as shown in Table 3.3.

Table 3.3 Conditions for the study of the effect of Fenton's reagent adding pattern in real wastewater. (Fenton experiment)

Fenton's reagent (mg/l)	Adding Time (min)			
	0	15	30	45
H_2O_2	2,435	-	-	-
Fe^{2+}	800	-	-	-
H_2O_2	1,217	-	1,217	-
Fe^{2+}	400	-	400	-
H_2O_2	608	608	608	608
Fe^{2+}	200	200	200	200
H_2O_2	2,435	2,435	2,435	-
Fe^{2+}	800	-	-	-

3.3.1.6 Effect of Iron Interference

Since Fe^{3+} can interfere with Fenton reaction, this part was designed to determine the effect of Fe^{3+}. Two experiments were set up. The first run added 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+} every 60 minutes for 3 times (total experimental period was 3 hours). In the second experiment, prior to re-supplement of Fenton's reagent, the Fe^{3+} was removed by neutralization with NaOH to pH 7 to precipitate out the $Fe(OH)_3$ sludge.

3.3.2 Electro-Fenton Experiment

3.3.2.1 Effect of Electric Current on Fenton Reaction

This part aimed to study the effect of current discharge on Fenton reaction (becomes electro-Fenton process) and to study the feasibility of reducing Fe^{2+} which need to supply because the electro-Fenton reaction can regenerate Fe^{2+} from Fe^{3+}. Two experiments were conducted using real wastewater with the ratio 1:0.1 and 1:0.2 of $H_2O_2:Fe^{2+}$.

3.3.2.2 Effect of Fenton's Reagent Adding Pattern

This experiment aimed to investigate the effect of Fenton's reagent adding pattern on the removal of target compounds and COD in real wastewater. Three experiments were examined under the conditions as shown in Table 3.4.

Table 3.4 Conditions for the study of the effect of Fenton's reagent adding pattern in real wastewater. (Electro-Fenton experiment)

Fenton's reagent (mg/l)	Time (min)			
	0	15	30	45
H_2O_2 Fe^{2+}	2,435 800	- -	- -	- -
H_2O_2 Fe^{2+}	2,435 800	2,435 -	2,435 -	2,435 -
H_2O_2 Fe^{2+}	2,435 800	2,435 -	2,435 800	2,435 -

3.3.3 SBR Experiment

This experiment aimed to examine the feasibility of organic degradation by activated sludge SBR process. Two experiments were set up by using real wastewater and effluent from electro-Fenton process. To support the microbial activity, the pH was adjusted to 7 and nutrient was regulated at the desired level required for microbial metabolism by using the ratio 100:5:1:0.5 of BOD:N:P:Fe^{2+} (the nutrient contained of NH_4Cl, NaH_2PO_4 and $FeCl_3$).

3.4 Analytical Methods

3.4.1 Measurement of Cumene Hydroperoxide, Acetophenone, and Dimethyl-Phenyl-Carbinol

After raising the pH by adding 0.1 N NaOH and filtered by a 0.22-μ filter paper to separate precipitated iron, the sample was analyzed for residual organic compounds, i.e., CHP, AP, and DMPC by using a GC/FID gas chromatograph equipped with a flame ionization detector and HP-5 capillary column with inside diameter of 0.53 mm and column length of 15 m. One μl of the sample was injected into the injection port. The initial temperature of column was set at 50 °C for 1 minute and then increased by 65 °C per minute to 150 °C and maintained at this temperature for the final 5 minutes. The detector temperature was set at 250 °C.

3.4.2 Measurement of Iron

Concentration of iron species, Fe^{2+}, soluble and total iron were performed immediately after sampling without alkaline addition in order to prevent the precipitation of $Fe(OH)_2$. For ferrous analysis, the sample was analyzed by light absorbance measurement at 510 nm after being complexed with 1,10-phenanthroline using UV-vis spectrophotometer following the Standard Methods (APHA, 1992). For a blank, the DI water mixed with the sample without phenanthroline was used. For total and soluble iron analysis, the samples were digested by concentrated hydrochloric acid (HCl) and hydroxylamine as a reductant to transform Fe^{3+} to Fe^{2+}. Then, the samples were formed a colored complex with 1,10-phenanthroline following to the ferrous analysis.

3.4.3 Measurements of Hydrogen Peroxide Residual

Similar to Fe^{2+} analysis, the sample was analyzed for H_2O_2 immediately after sampling. Standard iodometric method was used to determine the concentration of hydrogen peroxide residual, the potassium iodide was used as the reactant and sodium thiosulfate was used as the titrant, respectively.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Standard Curves

Cumene hydroperoxide (CHP), cumene (CM), acetophenone (AP), dimethyl phenyl carbinol (DMPC) were purchased from Aldrich which have the purity of 80%, 98%, 99% and 97%, respectively, as shown in Figure 4.1. Because CHP is only 80% purity, several compounds are co-existing. Analysis by using a gas chromatograph (GC/FID) under the same conditions (one single injection can determine all of these four compounds) found that standard solution of CHP has several other compounds similar to those in the real wastewater. Figure 4.2 shown chromatograph of real wastewater and CHP standard solution. CM, AP, DMPC, and CHP were detected in both real wastewater and CHP standard solution with the time elapsed between injection and elution or retention time of 2.249, 4.185, 4.495, and 6.942 minutes, respectively. Since CM is highly volatile and is rather insoluble in water, its standard curve could not be prepared with high accuracy; thus, it was not considered in this study.

The standard curves for CHP, AP and DMPC were linear lines and have the R^2 values greater than 0.999 as shown in Figure 4.3. This means that the use of GC/FID with HP-5 capillary column under the analytical conditions employed in this study to determine these target compounds is accurate and reliable.

Cumene Hydroperoxide 80%

Cumee 98%

Acetophenone 99%

Dimethyl Phenyl Carbinol (2-Phenyl-2-Propanol) 97%

Figure 4.1 Analytical-grade chemicals used for standard curve and synthetic wastewater preparation

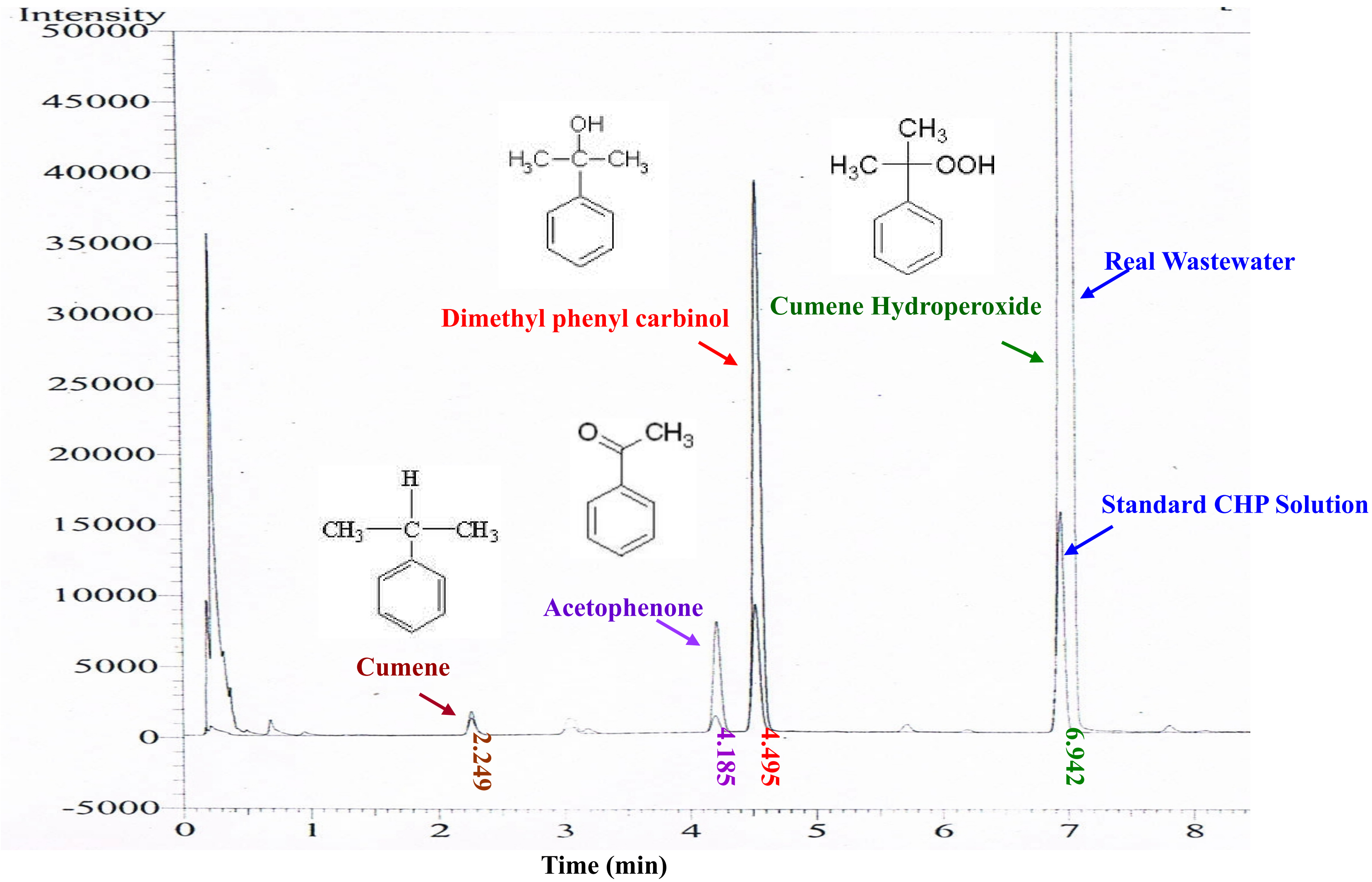
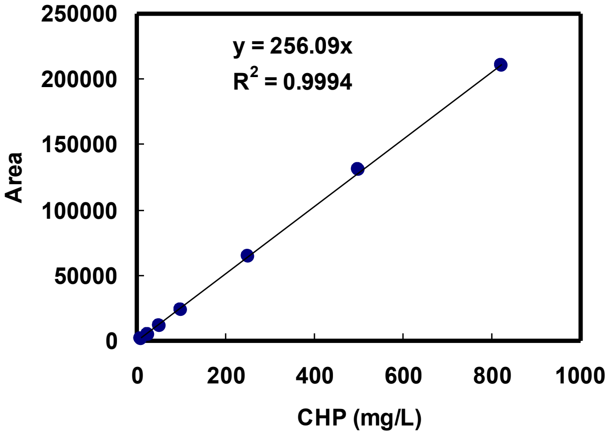
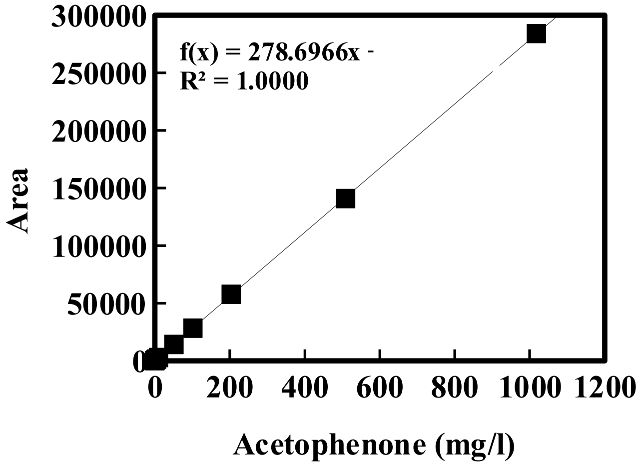


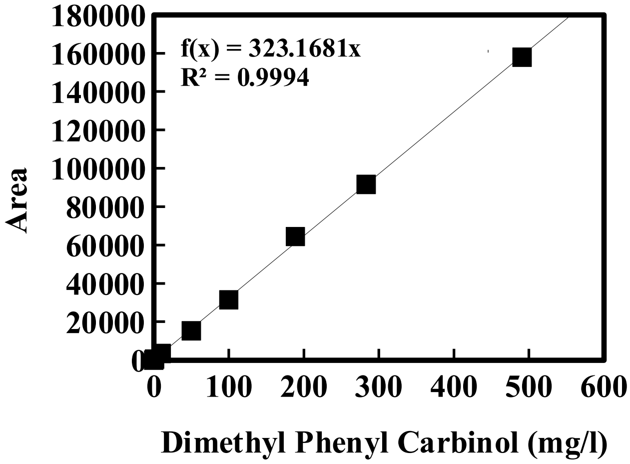
Figure 4.2 Gas chromatograph of standard CHP solution and real wastewater from phenol-production wastewater



(a) CHP



(b) AP



(c) DMPC

Figure 4.3 Standard curves of CHP, AP and DMPC

4.2 Wastewater Characteristic

Real wastewater characteristic varied tremendously from time to time of the sampling particularly for the COD, BOD, CHP, AP and DMPC as shown in Table 4.1. This was expected since the wastewater characteristic should be closely related to production activities. These analytical results were within the range of the plant data. Nonetheless, the BOD:COD ratio of each wastewater sample were within 0.3 to 0.6. This moderate to high BOD:COD ratios implied that the wastewater was relatively biodegradable and the biological treatment might be feasible. As a result, biological treatment approach was studied.

Table 4.1 Wastewater characteristic from a phenol-production factory

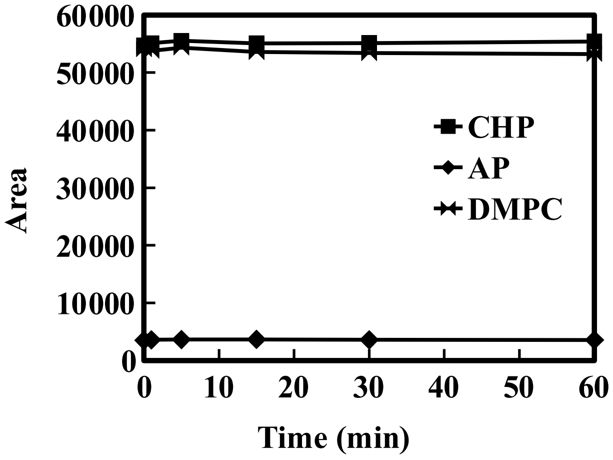
Parameter	Sample Date					Plant Data
	10 May 12	13 Jun 12	18 Jul 12	15 Oct 12	11 Jan 13	
pH	12.39	12.52	12.58	12.64	12.16	12-13
COD_{Total} (mg/l)	4419	4952	5913	5217	4394	3,000-6,000
$COD_{Soluble}$ (mg/l)	4114	4876	5391	4522	4183	na
BOD_{Total} (mg/l)	1882	2835	2231	2385	1982	na
$BOD_{Soluble}$ (mg/l)	162	2764	2163	2122	1769	na
BOD:COD	0.43	0.57	0.38	0.46	0.45	na
SS (mg/l)	4	6	20	27	25	na
TKN (mg/l)	3	2	0	12	2.6	na
Total Phosphorus(mg/l)	0.1	0	0	0.01	0	na
CHP (mg/l)	90	275	100	216	263	250-550
AP (mg/l)	74	14	16	13	24	<10
DMPC(mg/l)	362	279	146	230	229	50-150

remark: na = not analyzed

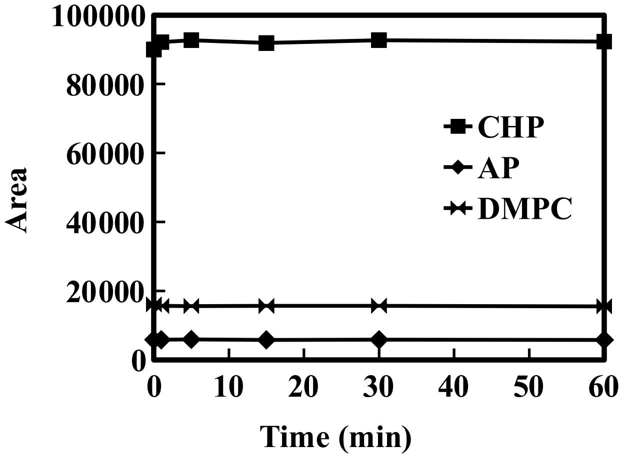
4.3 Control Experiments

4.3.1 Hydrogen Peroxide Control

To observe the effect of direct oxidation by H_2O_2, 1,000 mg/l of H_2O_2 was added to both real and synthetic wastewaters at pH 3. The results showed that CHP, AP and DMPC in both real and synthetic wastewaters were not significantly changed as illustrated in Figure 4.4. This indicates that the H_2O_2 alone was not powerful enough to oxidize CHP, AP and DMPC.



(a) Real wastewater



(b) Synthetic wastewater

Figure 4.4 Control experiment for direct H_2O_2 oxidation with real and synthetic wastewaters at pH 3 and 25°C

4.3.2 Ferrous Control

In this study, Fe^{2+} at 100 mg/l was added to the synthetic and real wastewaters to examine the impact of Fe^{2+} regarding on chemical reaction and coagulation which will occur after neutralization. The result from Fe^{2+} control experiment was very interesting because it was found that, in the presence of Fe^{2+}, CHP decreased whereas AP increased as shown in Figures 4.5 to 4.6. From these results, it suggested that Fe^{2+} might be able to react with CHP and AP was formed as the intermediate. According to Suppes and McHugh (1989), CHP could decompose to form free radicals via homolytic scission in the presence of metal catalyst and further transform via β-scission to form AP as shown in the following equations:

$$\text{Homolytic scission: } C_9H_{11}OOH \xleftrightarrow{\text{metal}} [C_9H_{11}O^{\bullet\bullet}OH] \longrightarrow C_9H_{11}O^{\bullet} + {}^{\bullet}OH \qquad (4.1)$$

$$\beta\text{-scission: } \quad C_9H_{11}O^{\bullet} \xrightarrow{\qquad} C_8H_8O + CH_3^{\bullet} \qquad (4.2)$$

The relation between CHP disappeared and AP formed was determined by varying Fe^{2+} concentrations from 50 to 100, 150 and 200 mg/l and using synthetic wastewater in order to eliminate any interference from other compounds present in real wastewater. The result showed that although the disappearing of CHP and the emerging of AP increased when Fe^{2+} concentration increased, the molar ratio of $CHP_{\text{disappeared}}:AP_{\text{appeared}}$ was not 1:1 as shown in Figure 4.7 indicaing that the occurred reactions were complicated and might contain several sequential steps. Direct redox reaction between CHP and Fe^{2+} was not the main reaction but free radicals might get involved in the reaction series. As a result from this part, in the Fenton experiments, H_2O_2 was added to the solution before Fe^{2+} addition to start the experiments.

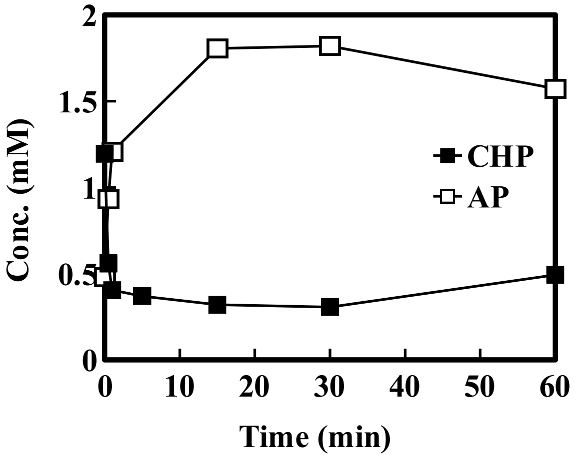
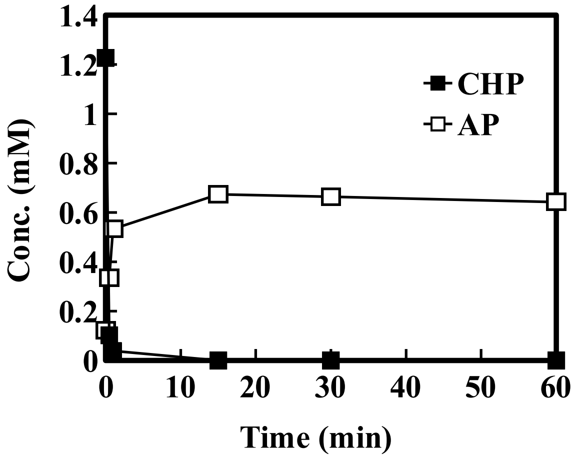
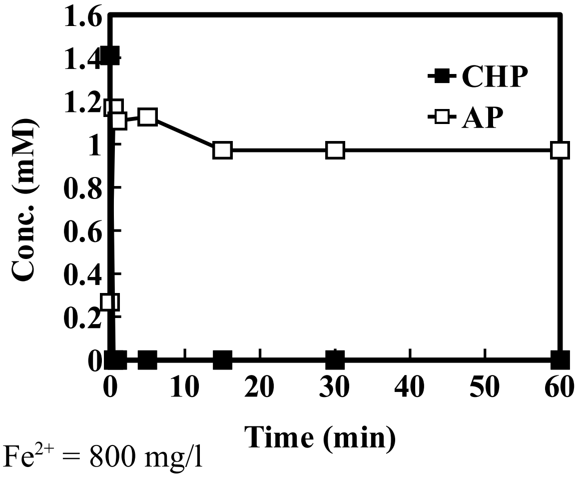


Figure 4.5 Effect of ferrous on CHP and AP concentration in synthetic wastewater (conditions: Fe^{2+} = 100 mg/l, pH 3, and 25°C)



(a) Fe^{2+} = 100 mg/l



(b) Fe^{2+} = 800 mg/l

Figure 4.6 Effect of ferrous on CHP and AP concentration in real wastewater (conditions: Fe^{2+} = 100 or 800 mg/l, pH 3, and 25°C)

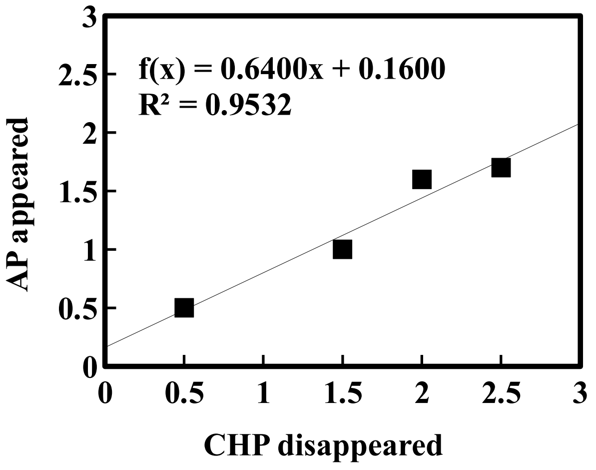


Figure 4.7 Relation of CHP disappeared and AP formed under various Fe^{2+} concentrations

4.4 Fenton Experiments

4.4.1 Effect of $H_2O_2:Fe^{2+}$ Ratio by Mole

In this experiment, real wastewater was used to study the optimum of $H_2O_2:Fe^{2+}$ ratio which can be adapted in real situation. The result showed that CHP was easily oxidized within 15 minutes after initiation as shown in Figure 4.8. AP and DMPC were also decomposed rapidly in the presence of $OH^{\bullet}$. As a result, the initially targeted compounds, i.e., CHP, AP, and DMPC, were not a problem for Fenton treatment. Consequently, COD was selected as a target pollutant for phenol-production wastewater treatment instead of CHP. In this part, the concentration of H_2O_2 was fixed at 2,435 mg/l whereas the concentrations of Fe^{2+} varied from 400 mg/l to 800, 2,000, 4,000, and 8,000 mg/l which corresponding to the molar ratio of $H_2O_2:Fe^{2+}$ of 1:0.1, 1:0.2, 1:0.5, 1:1 and 1:2, respectively. Figure 4.9 shows that, when $H_2O_2:Fe^{2+}$ ratio increased from 1:0.1 to 1:0.2, the COD reduction increased obviously; however, further increase of $H_2O_2:Fe^{2+}$ ratio did not have any significant effect on COD removal. It is well documented that both H_2O_2 and Fe^{2+} can act as a scavenger of $OH^{\bullet}$ if they are present in an excess amount. Hence, the ratio of 1:0.2 was chosen as the optimum ratio since it required the least ferrous salt and sequentially generated the least $Fe(OH)_3$ sludge.

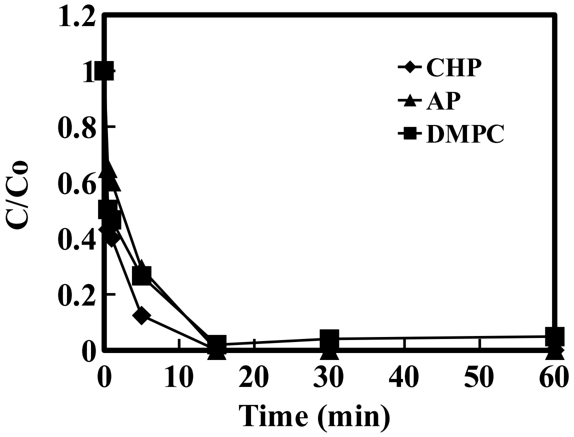


Figure 4.8 Fenton reaction on real wastewater at the ratio 1:0.2, pH 3 and 25°C

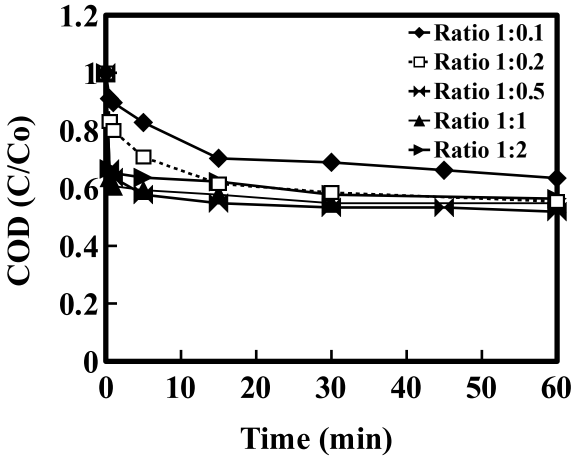


Figure 4.9 The COD removal of Fenton reaction on real wastewater at pH 3 and 25°C

4.4.2 Effect of pH

Optimum pH for Fenton process is reported to be between 2 and 4. Thus, this study selected pH of 2.5, 3.0, and 3.5 for investigation. The results are shown in Figure 4.10. It was found that COD removals at all these three pH did not have any significant difference. Nonetheless, pH 3.0 which is the median of the studied range was selected as the optimum point.

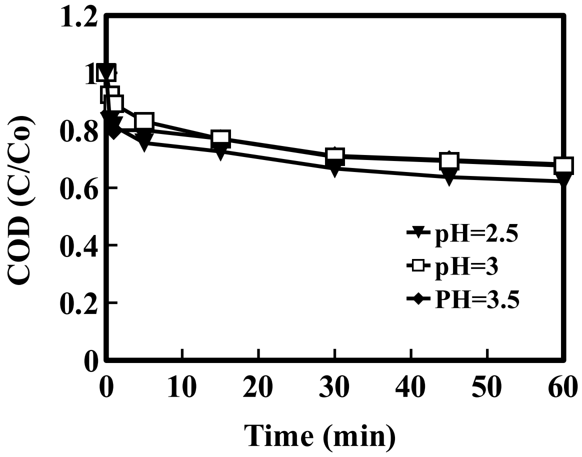
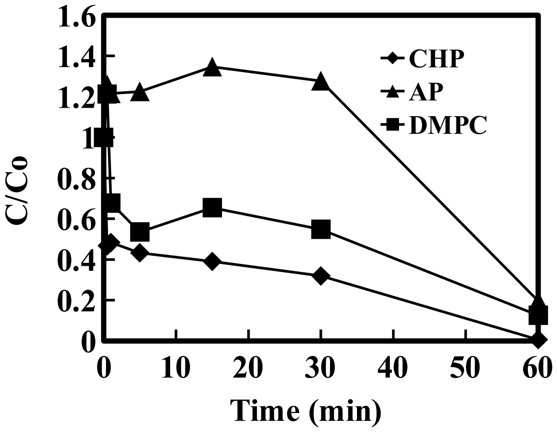


Figure 4.10 Effect of pH on the COD removal of Fenton reaction on real wastewater, 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+} at 25°C

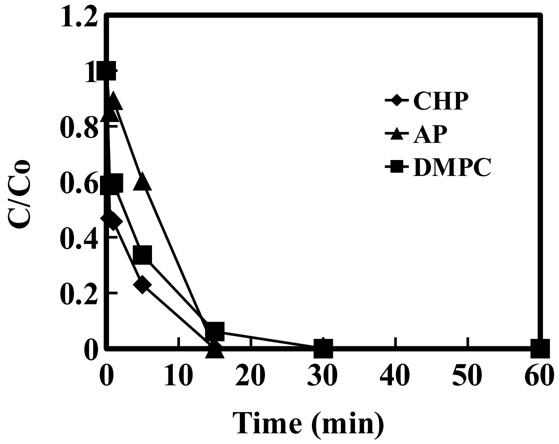
4.4.3 Effect of Fenton's Reagent Concentration

4.4.3.1 Synthetic Wastewater

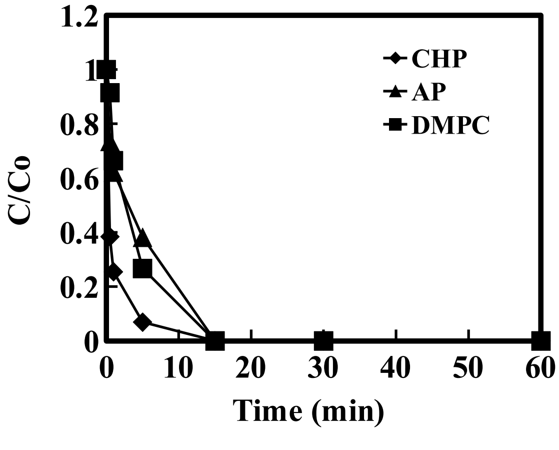
Optimum molar H_2O_2:Fe^{2+} ratio of 1:0.2 and pH 3.0 were used to investigate the effect of Fenton's reagent concentration on COD removal. Ferrous was varied from 200 mg/l to 400 and 800 mg/l while H_2O_2 was varied correspondingly to the optimum molar ratio. The results showed that when increased the Fenton's reagent concentrations, CHP, AP, DMPC and COD were removed more rapidly and more efficiently. At Fe^{2+} of 400 and 800 mg/l, CHP, AP, and DMPC could be totally removed within 30 and 15 minutes, respectively. Figure 4.11 shows the effect of Fenton's reagent concentration in synthetic wastewater. It was found that CHP, AP and DMPC were removed more rapidly as the Fenton's reagent concentration increased. Profile of COD also showed the similar trend as shown in Figure 4.12; however, complete mineralization could not be achieved under the studied conditions.



(a) H_2O_2:Fe^{2+} = 608 mg/l: 200 mg/l



(b) H_2O_2:Fe^{2+} = 1,217 mg/l: 400 mg/l



(c) H_2O_2:Fe^{2+} = 2,435 mg/l: 800 mg/l

Figure 4.11 Effect of Fenton's reagent concentrations on CHP, AP, and DMPC removal in synthetic wastewater at pH 3

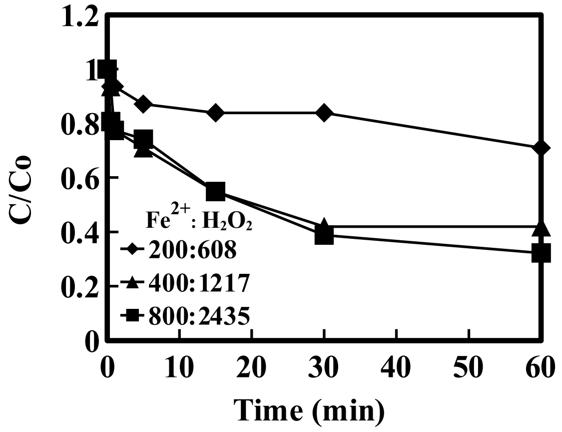
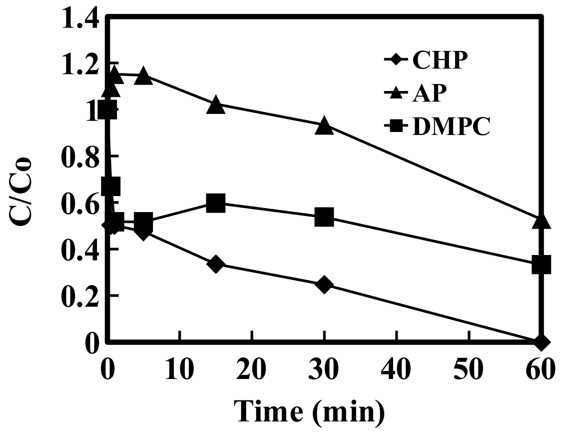


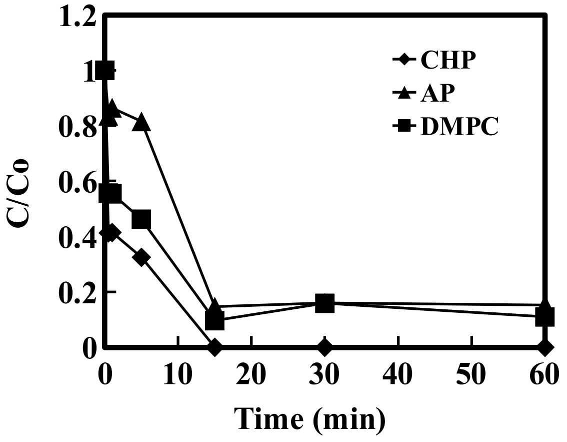
Figure 4.12 Effect of Fenton's reagent concentrations on COD removal in synthetic wastewater at pH 3

4.4.3.2 Real Wastewater

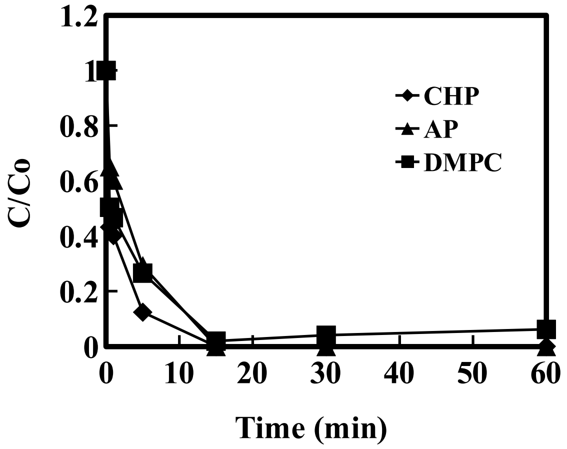
Under the similar conditions, i.e., H_2O_2:Fe^{2+} molar ratio of 1:0.2 and pH 3.0, increasing Fe^{2+} from 200 mg/l to 400, 800, and 4,000 mg/l could improve the removal efficiency similar to synthetic wastewater study as shown in Figure 4.13. Compared to Figure 4.12, it can be seen that the removal efficiencies in real wastewater were lower than those obtained from synthetic wastewater. This was due to the presence of other organic pollutants in the real wastewater which competed with CHP, AP, and DMPC or $OH^{\bullet}$. However, when Fe^{2+} was increased 10 times to 4,000 mg/l, all CHP, AP, and DMPC were removed.



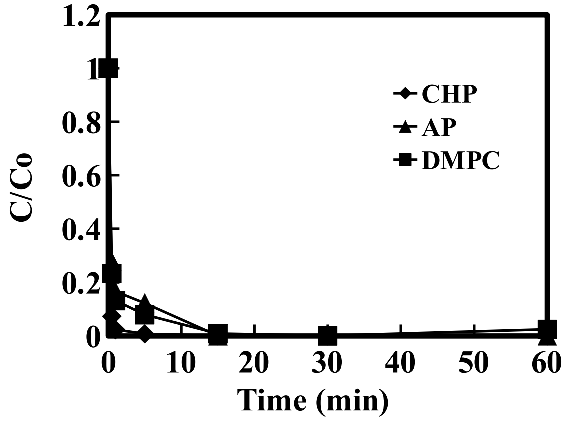
(a) H_2O_2:Fe^{2+} = 608 mg/l: 200 mg/l



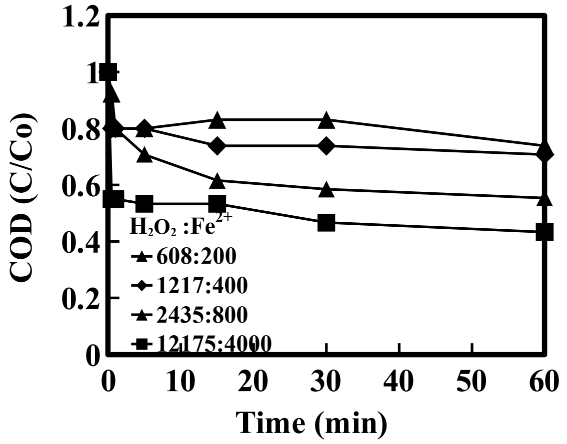
(b) H_2O_2:Fe^{2+} = 1,217 mg/l: 400 mg/l



(c) H_2O_2:Fe^{2+} = 2,435 mg/l: 800 mg/l



(d) H_2O_2:Fe^{2+} = 12,175 mg/l: 4,000 mg/l



(e) The COD removal

Figure 4.13 Effect of Fenton's reagent concentrations on CHP, AP, DMPC and COD removals in real wastewater at pH 3 and 25°C

4.4.4 Effect of Fenton's Reagent Adding Pattern

In this experimental part, several supplying schemes of Fenton's reagent into real wastewater were investigated and the results are summarized in Figure 4.14. It was found that, at the same total Fenton's reagent mass, single addition at the beginning was better than 4-time intermittent addition but worse than 2-time intermittent addition. This observation is possible since wastewater composition is the main factor affecting the performance of Fenton process and other AOPs. With single addition, $OH^{\bullet}$ is generated intensively at the beginning. Excess $OH^{\bullet}$ can react with each other to form H_2O_2; hence, reduces the process performance. On the other hand, when Fenton's reagent was intermittently added for 4 times, the amount of $OH^{\bullet}$ being formed is too little to have significant impact on water quality. In addition, it was found that H_2O_2 was consumed quickly under the studied conditions and exhausted after 15 minutes which would cease the Fenton reaction even though iron was still present. Hence, another experiment was conducted to evaluate the effect of H_2O_2 re-supplementation. H_2O_2 was re-supplied whenever it was exhausted and the result revealed that COD removal was better than without re-supplement of H_2O_2.

This implies that H_2O_2 plays an important role in removing COD from phenol-production wastewater. However, the effect of Fenton's reagent adding pattern depended largely on properties of wastewater. Further study with treated effluent from the activated sludge process receiving phenol-production wastewater showed that adding pattern of Fenton’s reagent did not have any significant effect on the COD removal. This is different from the case of raw wastewater because the type of organic pollutant has been changed after biodegradation as shown in Figure 4.15.

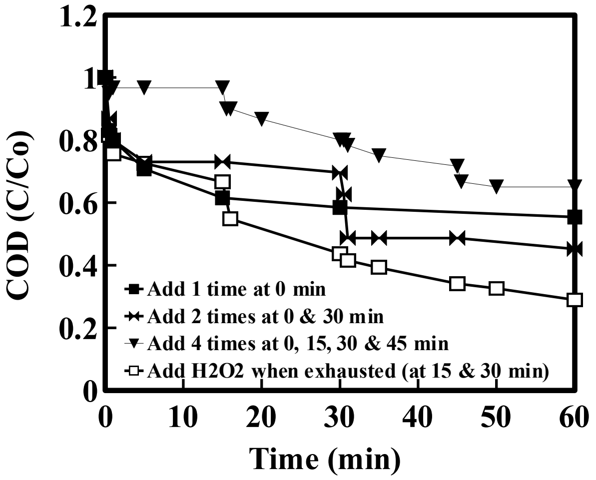


Figure 4.14 Effect of Fenton's reagent adding pattern on COD removal in real wastewater at pH 3 and 25°C

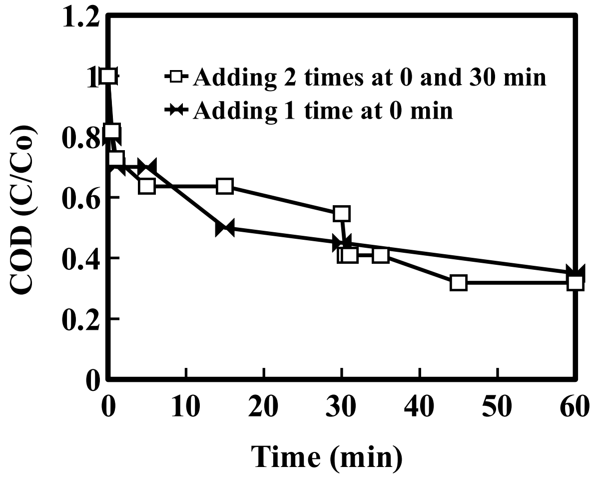


Figure 4.15 Effect of Fenton's reagent adding pattern on COD removal in activated sludge effluent at pH 3 and 25°C

4.4.5 Effect of Iron Interference

Fe^{2+} added into the Fenton reactor will be converted to Fe^{3+} simultaneously and remains in the solution while H_2O_2 will be consumed and finally exhausted. Therefore, adding Fenton's reagent many times can cause Fe^{3+} to accumulate in the mixture and could interfere with the overall process performance due to scavenging effect. This part aimed to investigate the effect of iron interference by supplying 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+} every 60 minutes for 3 times. In another parallel experiment to the control run, the $Fe(OH)_3$ was precipitated and separated from the solution before re-supplement of Fenton’s reagent. The results show that $Fe(OH)_3$ precipitation and separation before re-supplement of Fenton’s reagent could just slightly increase the COD removal as shown in Figure 4.16 indicating that Fe^{3+} did not severely interfere with Fenton reaction under that studied conditions.

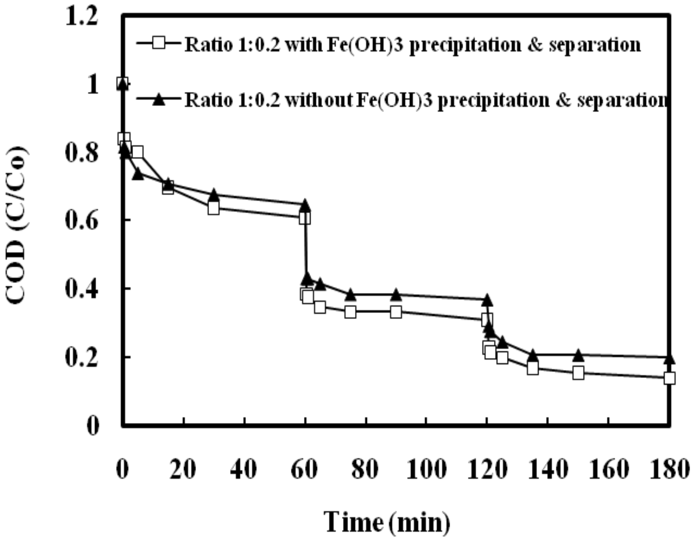


Figure 4.16 Effect of Fe^{3+} on Fenton reaction (conditions: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+}, pH 3 and 25°C)

4.5 Electro-Fenton Experiment

4.5.1 Effect of Electric Current on Fenton Reaction

Results from previous Fenton experiments revealed that high concentration of Fenton's reagent was required in order to achieve high COD removal leading to high chemical and iron sludge disposal costs. Electro-Fenton which can electrochemically regenerate Fe^{2+} from Fe^{3+} is another alternative that can reduce Fe^{2+} addition. This experimental part was set up to determine the effect of electric current on Fenton reaction. Figure 4.17 shows the comparison between Fenton and Electro-Fenton experiments using synthetic wastewater. It can see that electric discharge could enhance the performance of Fenton reaction immediately from the beginning, i.e., electro-Fenton could reduce COD from 1113 mg/l to 209 mg/l within the first 30 minutes whereas Fenton could only reduce to 419 mg/l during the same period. This enhancement was mainly due to the acceleration of Fe^{2+} regeneration. After 30 minutes, H_2O_2 was re-supplied in the electro-Fenton reactor since it was exhausted. However, the COD removal did not change much implying that the remaining organic pollutants were not susceptible to $OH^{\bullet}$ under the studied conditions. Although the results with synthetic wastewater were very satisfied, the outcome with real wastewater was frustrated as shown in Figure 4.18. In this case, electrical discharge could not improve the degradation of COD. Nonetheless, comparing between the H_2O_2:Fe^{2+} ratios of 1:0.2 and 1:0.1, there were no significant difference in COD removal efficiency. This implies that electric current did regenerate the Fe^{2+} from Fe^{3+}.

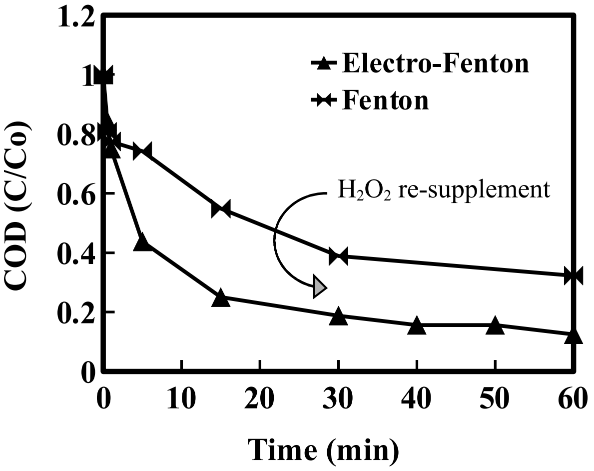


Figure 4.17 Comparison the COD removal in synthetic wastewater between Fenton and Electro-Fenton process at pH 3 and 25°C

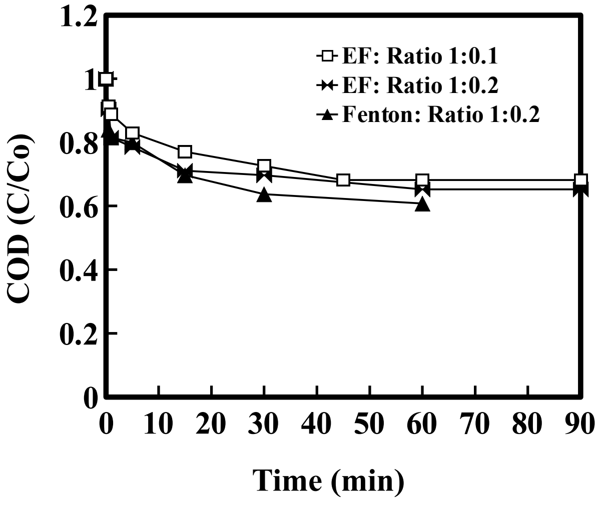


Figure 4.18 Comparison the COD removal in real wastewater between Fenton and Electro-Fenton process at pH 3 and 25°C

4.5.2 Effect of Fenton's Reagent Adding Pattern

It was found that H_2O_2 disappeared rapidly in the presence of electric current; therefore, re-supplement of H_2O_2 and/or Fe^{2+} was provided. The results as shown in Figure 4.19 indicated that addition of H_2O_2 when exhausted could increase the efficiency of the process. This is expected since the configuration of the electro-Fenton reactor used in this study could not significantly generate H_2O_2 in situ. In addition, in order to verify the role of electric current in the electro-Fenton reactor, another experiment was set up with the re-supplement of Fe^{2+} at 30 minutes. The result revealed that it could not significantly increase the COD removal. This is because the electro-Fenton reaction could effectively regenerate Fe^{2+} from Fe^{3+}. So, the re-supplement of Fe^{2+} was not necessary. Re-supplement of H_2O_2 in the electro-Fenton experiment could decrease the COD from 4,350 mg/l to 450 mg/l which was comparable to the efficiency obtained from the Fenton experiment with re-supplement of Fe^{2+} (Figure 4.16, the ratio 1:0.2 with $Fe(OH)_3$ precipitation and separation). Nonetheless, the electro-Fenton process could save a huge amount of Fe^{2+} as compared to ordinary Fenton process.

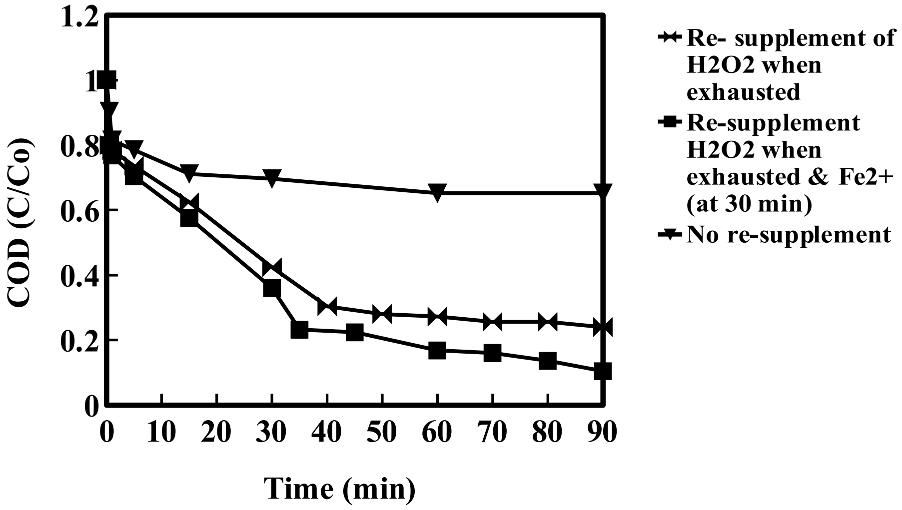


Figure 4.19 Effect of re-supplement of H_2O_2 and/or Fe^{2+} at 4 A, pH 3 and 25°C

4.6 Biological Treatment

4.6.1 Raw Wastewater Treatment

Since the BOD:COD ratio of phenol-production wastewater varied between 0.38 and 0.67, it implies that this phenol-production wastewater is somewhat biodegradable. Hence, it is possible to be treated by the biological process. The SBR activated sludge was used in this experimental part. After microbial acclimation for 40 days (the initial period of Figure 4.20), the SBR was set up and the biodegradability test was begun. The reacting period of the SBR was not maintained constantly. The aeration period was extent until the treated COD became constant. Figure 4.20 shows that the biological process could remove COD effectively and the final COD was below 600 mg/l although the reacting period was quite long depending on the wastewater characteristics. From microscopic observation, the sludge was healthy and several high-class microorganisms were detected including swimming ciliates, stalked ciliates and rotifers as shown in Figure 4.21. Treated effluent was analyzed by GC and found that CHP and AP were completely removed whereas DMPC was still detected at low concentration indicating that DMPC was the most refractory organic among these three target pollutants. Therefore, biological process can effectively treat phenol-production wastewater if very long hydraulic retention time is provided. Aerobic ponds or large aerated lagoons are highly potential for phenol-production wastewater treatment.

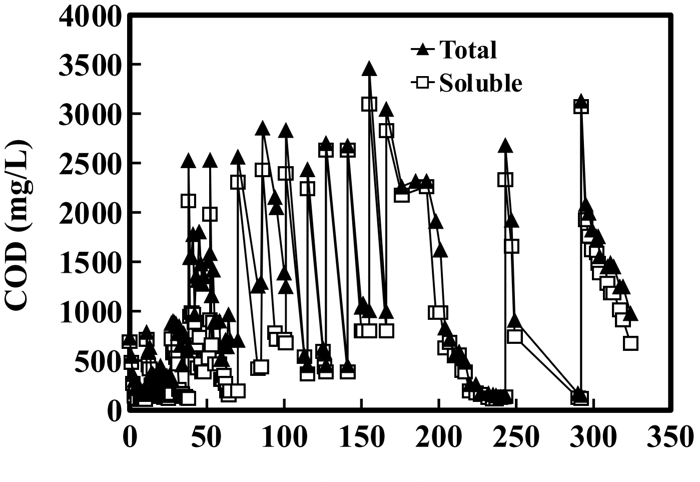


Figure 4.20 Phenol-production wastewater treating by activated sludge SBR

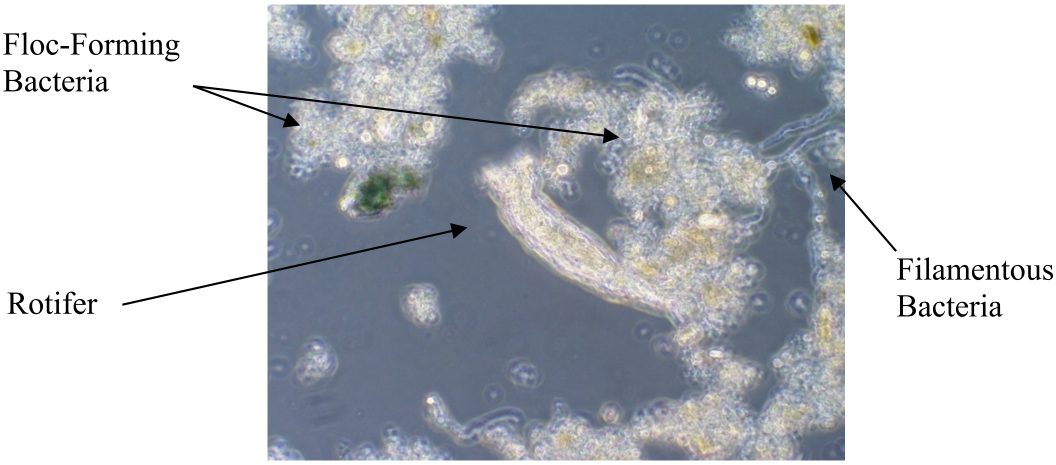


Figure 4.21 Microorganisms in the sludge of the SBR receiving phenol-production wastewater

4.6.2 Electro-Fenton Effluent Treatment

According to electro-Fenton study, it was found that COD of the treated effluent from electro-Fenton process was still high and did not comply with the industrial effluent standard of 120 mg/l. However, it was found that the BOD:COD ratio of the treated effluent increased to more than 0.8 indicating readily biodegradable organics. As a result, further investigation was made to treat the electro-Fenton effluent with biological process. Effluent of electro-Fenton process supplied with 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+} which had the COD between 700-1,000 mg/l was fed to the activated sludge SBR. The Figure 4.22 showed that it could decrease COD to less than 100 mg/l within 2 days. It means that the electro-Fenton process could effectively transform non-biodegradable COD to BOD. So, aerobic process could perform better and faster. Biomass in the SBR was healthy, i.e., swimming ciliates, stalked ciliates, crawling ciliates and rotifers can be detected as shown in Figure 4.23.

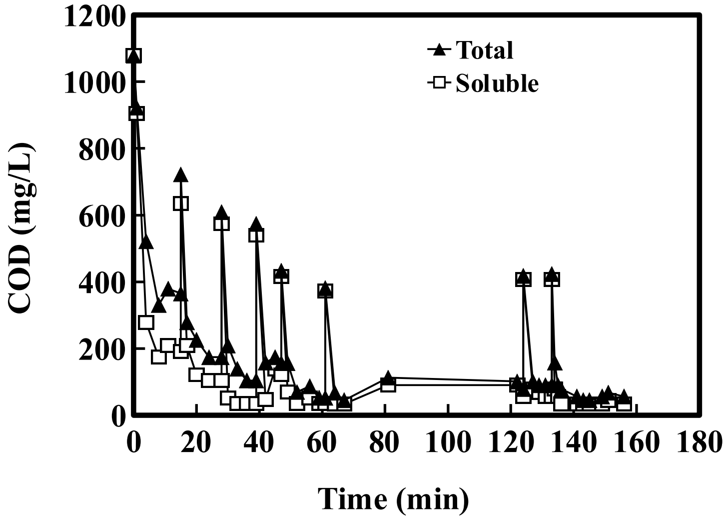


Figure 4.22 Performance of the activated sludge SBR receiving treated effluent from electro-Fenton process

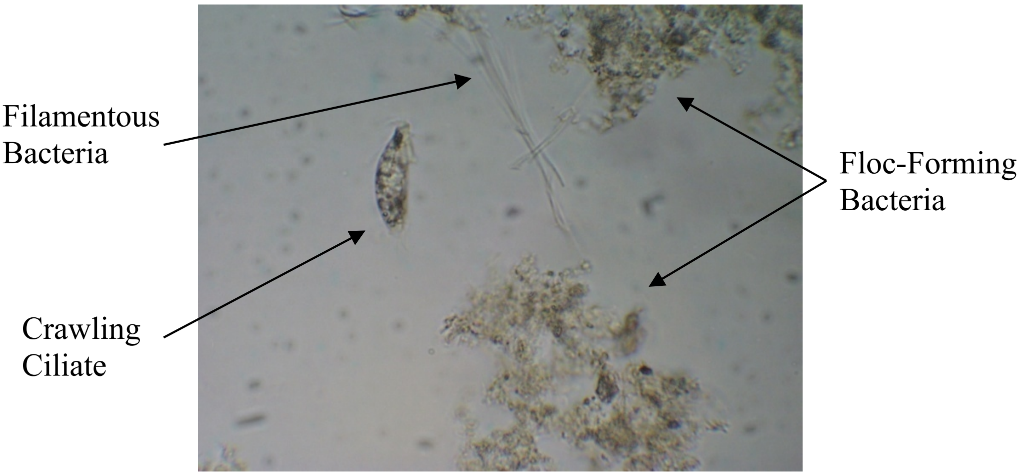


Figure 4.23 Microorganisms in the sludge of the SBR receiving treated effluent from electro-Fenton process

CHAPTER V
CONCLUSIONS

5.1 Conclusions

Effect of $OH^{\bullet}$ on phenol-production wastewater containing CHP, AP and DMPC as well as COD has been investigated by using Fenton and electro-Fenton reactions under various conditions including Fenton's reagent dose and adding pattern. Biological treatment was also studied to determine the biodegradability of the wastewater. The results can be concluded as follows:

- CHP could be rapidly transformed to AP in the presence of Fe^{2+} due to its oxidation potential.
- CHP, AP, and DMPC could be easily oxidized by $OH^{\bullet}$ but its intermediates were less susceptible to $OH^{\bullet}$; thus, not completely oxidized.
- Optimum conditions for Fenton process treating phenol-production wastewater were pH 3 and H_2O_2:Fe^{2+} ratio of 1:0.2.
- Electro-Fenton process could reduce the COD better than ordinary Fenton process if H_2O_2 was sufficient.
- Phenol-production wastewater contained highly refractory organic pollutants; hence, very long hydraulic retention time was required for the activated sludge process to reduce the COD from higher than 4,000 mg/l to less than 600 mg/l. Products from biodegradation were resistant to $OH^{\bullet}$ oxidation.
- $OH^{\bullet}$ could effectively transform refractory organic pollutants present in phenol-production wastewater to more-biodegradable intermediates.
- Pre-Fenton treatment followed by aerobic degradation is a promising combination for phenol-production wastewater treatment.

5.2 Recommendations for Further Studies

1. Determine the intermediates from CHP, AP and DMPC oxidation by $OH^\bullet$.
2. Determine the feasibility of treating phenol-production wastewater by other AOPs and compared to the results obtained from this study.

REFERENCES

Ahmad T. Shawaqfeh (2010) Removal of pesticides from water using anaerobic-aerobic biological treatment. Chinese Journal of Chemical Engineering 18(4): 672-680

Anotai, J., Lu, M., Chewpreecha, P. (2006) Kinetics of aniline degradation by Fenton and electro-Fenton processes. Water Research 40: 1841-1847

APHA (1992) Standard methods for the examination of water and wastewater, 18th Edition, Washington D.C.: American Public Health Association.

Bajaj, M., Gallert, C., Winter, J. (2008) Biodegradation of high phenol containing synthetic wastewater by an aerobic fixed bed reactor. Bioresource Technology 99: 8376-8381.

Cao, G. (1983) Production of phenol/acetone using cumene process. The Chemical Industry Press, Beijing.

Chen, G., Hoag, G.E., Chedda, P., Nadim, F., Woody, B.A. and Dobbs, G.M. (2001) The mechanism and applicability of in situ oxidation of trichloroethelene with Fenton's reagent. Journal of Hazardous Materials B87: 171-186.

Chu, Y. Y., Qian, Y., Wang, W. J., Deng, X. L. (2012) A dual-cathode electro-Fenton oxidation coupled with anodic oxidation system used for 4-nitrophenol degradation. Journal of Hazardous Materials 199-200: 179-185.

EPA. (1988) Factsheet on cumene hydroperoxide (January 1988) AQUIRE Database, ERL-Duluth, U.S. Environmental Protection Agency.

Hong, S., Zhang, H., Duttweiler, C. M., Lemley, A. T. (2007) Degradation of methyl *tertiary-butyl* ether (MTBE) by anodic Fenton treatment. Journal of Hazardous Materials 144: 29-40.

HSDB/Hazardous Substances Data Bank. (1997) In: Tomes plus. Environmental Health and Safety Series I. Vol 32. National Library of Medicine.

Huang, D., Han, M., Wang, J., Jin, Y. (2002) Catalytic decomposition process of cumene hydroperoxide using sulfonic resins as catalyst. Chemical Engineering Journal 88: 215-223.

Kujawski, W., Warszawski, A., Ratajczak, W., Porebski, T., Capala, W., Ostrowaka, I. (2004) Applcation of pervaporation and adsorption to the phenol removal from wastewater. Separation and Purification Technology 40: 123-132

Levin, M.E., Gonzales, N.O., Zimmerman, L.W., Yang, J. (2005) Kinetics of acid-catalyzed cleavage of cumene hydroperoxide. Journal of Hazardous Materials 130: 88-106.

Lewis, R. J. (1993) Hawley's Condensed Chemical Dictionary. New York: Van Nostrand Reinhold.

Li, R., Yang, C., Chen, H., Zeng, G., Yu, G., Guo, J. (2009) Removal of triazophos pesticide from wastewater with Fenton reagent. Journal of Hazardous Materials 167: 1028-1032.

Liu, Q. Y., Liu, Y. X., LU X. J. (2011) Combined photo-Fenton and biological oxidation for the treatment of aniline wastewater. Procedia Environmental Sciences 12: 341-348.

Lunar, L., Sicilia, D., Rubio, S., Perez-Bendito, D. and Nickel, U. (2000) Degradation of photographic developers by Fenton's reagent: condition optimization and kinetics for metal oxidation. Water Research 34, 6: 1791-1802.

Malakahmad, A., Hasani, A., Eisakhani, M., Isa, M. H. (2011) Sequencing Batch Reactor (SBR) for the removal of Hg2+ and Cd2+ from synthetic petrochemical factory wastewater. Journal of Hazardous Materials 191:118-125.

Martins, R. C., Rossi, A. F., Quinta-Ferreira, R. M. (2010) Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement. Journal of Hazardous Materials 180: 716-721.

Moussavi, G., Bagheri, A., Khavanin, A. (2012) The investigation of degradation and mineralization of high concentrations of formaldehyde in an electro-Fenton process combined with the biodegradation. Journal of Hazardous Materials 237-238: 147-152.

Nidheesh, P. (2012) Trends in electro-Fenton process for water and wastewater treatment: An overview. Desalination 299: 1-15

Nonglak Boonrattanakij. Kinetics of 2,6-Dimethyl-aniline Degradation and Iron Crystallization in Fluidized-bed Fenton Process. Doctoral dissertation, Inter-Department of Environmental Management, Chulalongkorn University, 2009.

Parsons, S. (2004) Advance oxidation processes for water and wastewater treatment, No.1, IWA Publishing, USA 130-145.

Pignatello, J.J. (1992) Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environmental Science and Technology 26: 944-951.

Radian Corporation (1991) Cumene hydroperoxide, NTP Chemical Repository Fact Sheet. Industrial catalytic processes-phenol production 280: 89-103.

Sakugawa H., Hasan N., Olasehinde E. F., Takeda K., Kondo H., Applicability of solar photo-Fenton process to the remediation of water polluted with pesticides. Nature and Science 11(1)

Schmidt, R. (2004) Industrail catalytic process-phenol production. Applied Catalysis A: General 280: 89-103

Shin, S., Park, S., Choi, Y., Kim, H. (2001) Photodissociation Dynamics of Cumene Hydroperoxide at 248 and 193 nm. The Journal of Physical Chemistry A: 105: 10018-10024

Tchobanoglous, G., Burton, F.L. and Stensel, H.D. (2003) Wastewater engineering treatment and reuse. 4th edition. New York: McGraw-Hill.

USEPA (1985) Technical Support Document for Water Quality Base Toxic Control, EPA/440/485032, United States Environment Protection Agency, Washington, DC, USA.

Vazquez, I., Rodrıguez, J., Maranon, E., Castrillon, L., Fernandez, Y. (2006). Simultaneous removal of phenol, ammonium and thiocyanate from coke wastewater by aerobic biodegradation. Journal of Hazardous Materials B137: 1773-1780.

Yadav, G., Asthana, N. (2002) Selective decomposition of cumene hydroperoxide into phenol and acetone by a novel cesium substituted heteropolyacid on clay. Applied Catalysis A: General 244: 341-357

Zeiger, E. (1998) Cumene hydroperoxide. Review of Toxicological Literature. Research Triangle Park, North Carolina 27709.

APPENDICES

APPENDIX A

Experimental Figures

Figure A.1 Fenton experiment

Figure A.2 Electro-Fenton experiment

Figure A.3 Gas chromatograph (GC-FID)

APPENDIX B

Analytical Hydrogen Peroxide by Means Standard Iodometric

B.1 Principle

Hydrogen peroxide reacted with potassium iodide and acid to oxidize potassium iodide to iodine by using molybdate as a catalyst. The iodine formed is titrated with thiosulfate solution, incorporating a starch indicator as demonstrated in the following equation:

$$H_2O_2 + 2KI + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2H_2O \qquad (C.1)$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI \qquad (C.2)$$

B.2 Interferences

Other oxidizing agents will also produce iodine, whereas reducing agents (and unsaturated organics) will react with the liberated iodine. The contribution from other oxidizing agents can be determined by omitting the acid and molybdate catalyst.

B.3 Reagents

1. Potassium iodine solution (1% w/v):dissolve 10 g of KI into 1 liter of DI water
2. Ammonium molybdate solution: dissolve 9 g of ammonium molybdate in 10 ml of 6 N NH_4OH, add 24 g of NH_4NO_3 and dilute to 100 ml with DI water.
3. Sulfuric acid solution (1+3 H_2SO_4): carefully add one part H_2SO_4 98% to three parts DI water.
4. Starch indicator: 2 g of starch and dilute to 100 ml by DI water.
5. Sodium thiosulfate solution (0.0125 N)

B.4 Apparatus

1. Analytical balance
2. Small weighing bottle
3. 250 Erlenmeyer flask
4. 50 ml burette

B.5 Procedure

1. Transfer sample to 250 Erlenmeyer flask.
2. Add DI water 50 ml to 250 Erlenmeyer flask. And add sulfuric acid solution 10 ml and potassium iodide 15 ml. Then two drops ammonium molybdate solution was added.
3. Titrate with 0.0125 N sodium thiosulfate to faint yellow or straw color. Swirl or stir gently during titration to minimize iodine loss
4. Add 1 ml starch indicator, and titration until the blue color just disappears.
5. Repeat steps 2-4 on a blank sample of water.
6. Note ml of 0.0125 N $Na_2S_2O_3$ for samples and blank analysis.

B.6 Calculation

$$H_2O_2\text{, mg/l} \quad = \quad \frac{(A-B)\times N\times 17\times 1000}{\text{ml. sample}}$$

Where:

A = ml of ml of $Na_2S_2O_3$ for sample

B = ml of $Na_2S_2O_3$ for blank

C = Normality of $Na_2S_2O_3$ for sample

APPENDIX C

Raw Data

C.1 Fenton Experiment

C.1.1 Effect of H_2O_2:Fe^{2+} Ratio

Table C.1 CHP, AP and DMPC oxidation of Fenton reaction on real wastewater

Time (min)	**Organic concentration (mM)**		
	CHP	**AP**	**DMPC**
0	0.371	0.552	2.870
0.5	0.160	0.359	1.446
1	0.149	0.333	1.338
5	0.046	0.161	0.763
15	0.000	0.000	0.055
30	0.000	0.000	0.116
60	0.000	0.000	0.140

Note: 2,435 mg/l H_2O_2 and 800 mg/l at pH 3 and 25°C

Table C.2 The COD removal of Fenton reaction on real wastewater at pH 3 and 25°C

Time (min)	**COD (C/Co)**				
	Ratio 1:0.1	**Ratio 1:0.2**	**Ratio 1:0.5**	**Ratio 1:1**	**Ratio 1:2**
0	1.000	1.000	1.000	1.000	1.000
0.5	0.91	0.831	0.67	0.64	0.667
1	0.897	0.800	0.637	0.607	0.652
5	0.828	0.708	0.578	0.593	0.637
15	0.703	0.615	0.548	0.578	0.622
30	0.690	0.585	0.533	0.548	0.578
45	0.662	-	0.53	-	-
60	0.634	0.554	0.519	0.548	0.563

Note: 2,435 mg/l H_2O_2 and varying Fe^{2+} concentrations = 400, 800, 2,000, 4,000 and 8,000 mg/l compared to the ratio of H_2O_2:Fe^{2+} by mole = 1:0.1, 1:0.2, 1:0.5, 1:1 and 1:2, respectively at pH 3 and 25°C

C.1.2 Effect of pH

Table C.3 Effect of pH on the COD removal of Fenton reaction on real wastewater.

Time (min)	**COD (C/Co)**		
	pH = 2.5	**pH = 3**	**pH = 3.5**
0	1.000	1.000	1.000
0.5	0.830	0.923	0.859
1	0.815	0.892	0.800
5	0.756	0.831	0.800
15	0.726	0.769	0.770
30	0.667	0.708	0.711
45	0.637	0.692	0.696
60	0.622	0.677	0.681

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+} at pH 3 and 25°C

C.1.3 Effect of Fenton's Reagent Concentrations

C.1.3.1 Synthetic Wastewater

Table C.4 Fenton's reagent concentrations effect on Fenton reaction (No.1)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	2.467	0.070	0.438	3.581	17.905	1.000
0.5	1.152	0.088	0.531	0.155	9.009	0.935
1	1.191	0.085	0.296	0.227	11.261	0.935
5	1.068	0.086	0.234	0.068	9.572	0.871
15	0.963	0.094	0.286	0.263	8.446	0.839
30	0.787	0.089	0.240	0.092	7.320	0.839
60	0.015	0.014	0.055	0.442	2.252	0.710

Note: 608 mg/l H_2O_2, 200 mg/l Fe^{2+} at pH 3.5 and 25 °C.

Table C.5 Fenton's reagent concentrations effect on Fenton reaction (No.2)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	2.467	0.106	0.329	7.162	35.810	1.000
0.5	0.946	0.078	0.301	0.310	23.148	0.935
1	0.628	0.066	0.219	0.267	20.833	0.774
5	0.169	0.040	0.088	0.263	16.204	0.710
15	0.000	0.000	0.000	0.660	0.000	0.548
30	0.000	0.000	0.000	0.645	0.000	0.419
60	0.000	0.000	0.000	0.660	0.000	0.419

Note: 1,217 mg/l H_2O_2, 400 mg/l Fe^{2+} at pH 3.5 and 25 °C.

Table C.6 Fenton's reagent concentrations effect on Fenton reaction (No.3)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	2.467	0.074	0.473	14.324	71.621	1.000
0.5	1.156	0.063	0.278	0.298	45.607	0.806
1	1.128	0.066	0.282	0.322	44.481	0.774
5	0.567	0.045	0.159	0.167	42.792	0.742
15	0.000	0.000	0.029	0.426	30.968	0.548
30	0.000	0.000	0.000	0.187	10.135	0.388
60	0.000	0.000	0.051	0.167	0.000	0.323

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+} at pH 3.5 and 25 °C.

C.1.3.2 Real Wastewater

Table C.7 Fenton's reagent concentrations effect on Fenton reaction (No.4)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	0.534	0.554	2.685	3.581	17.905	1.000
0.5	0.269	0.607	1.799	0.183	5.953	0.923
1	0.268	0.639	0.482	0.159	5.953	0.800
5	0.254	0.636	0.480	0.147	5.357	0.800
15	0.179	0.567	1.605	0.191	4.762	0.831
30	0.132	0.518	1.443	0.267	2.976	0.831
60	0.000	0.293	0.894	0.533	0.000	0.738

Note: 608 mg/l of H_2O_2, 200 mg/l of Fe^{2+} at pH 3 and 25 °C.

Table C.8 Fenton's reagent concentrations effect on Fenton reaction (No.5)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	0.541	0.560	2.690	7.162	35.810	1.000
0.5	0.224	0.468	1.498	0.358	20.834	0.800
1	0.224	0.484	1.490	0.362	19.048	0.800
5	0.176	0.457	1.242	0.386	14.881	0.800
15	0.000	0.082	0.259	1.420	1.191	0.738
30	0.000	0.090	0.427	1.707	0.000	0.738
60	0.000	0.085	0.295	2.017	0.000	0.708

Note: 1,217 mg/l H_2O_2, 400 mg/l Fe^{2+} at pH 3 and 25 °C.

Table C.9 Fenton's reagent concentrations effect on Fenton reaction (No.6)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	0.371	0.552	2.870	14.324	71.620	1.000
0.5	0.160	0.359	1.446	0.979	47.758	0.831
1	0.149	0.333	1.338	0.999	45.989	0.800
5	0.046	0.161	0.763	1.464	31.838	0.708
15	0.000	0.000	0.055	1.536	0.000	0.615
30	0.000	0.000	0.116	1.480	0.000	0.585
60	0.000	0.000	0.359	2.379	0.000	0.554

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+} at pH 3 and 25 °C.

Table C.10 Fenton's reagent concentrations effect on Fenton reaction (No.7)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	1.879	0.209	1.278	71.620	358.103	1.000
0.5	0.137	0.058	0.297	0.032	70.652	0.550
1	0.043	0.035	0.168	0.030	67.391	0.550
5	0.013	0.025	0.101	0.042	62.500	0.533
15	0.000	0.000	0.010	0.006	59.239	0.533
30	0.000	0.000	0.000	0.018	38.587	0.467
60	0.000	0.000	0.030	0.012	0.000	0.433

Note: 12,175 mg/l H_2O_2, 4,000 mg/l Fe^{2+} at pH 3 and 25 °C.

C.1.4 Effect of Fenton's Reagent Adding Pattern

C.1.4.1 Real Wastewater

Table C.11 Fenton's reagent adding pattern effect on Fenton reaction (No.1)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	1.333	0.272	2.258	14.324	71.621	1.000
0.5	1.249	0.056	0.161	12.335	0.000	0.667
1	0.000	0.057	0.160	12.414	0.000	0.652
5	0.000	0.053	0.167	12.331	0.000	0.637
15	0.000	0.048	0.154	12.231	0.000	0.622
30	0.000	0.041	0.150	12.247	0.000	0.578
60	0.000	0.023	0.148	12.255	0.000	0.563

Note: 2,435 mg/l H_2O_2, 8,000 mg/l Fe^{2+} at pH 3 and 25 °C.

Table C.12 Fenton's reagent adding pattern effect on Fenton reaction (No.2)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	0.128	0.516	2.339	7.161	35.794	1.000
0.5	0.032	0.365	0.942	1.031	23.364	0.870
1	0.030	0.369	0.896	1.038	21.028	0.800
5	0.013	0.217	0.545	1.532	12.860	0.730
15	0.000	0.086	0.142	2.753	0.000	0.730
30	0.000	0.096	0.154	3.080	0.000	0.696
30.5	0.000	0.018	0.010	3.020	1.168	0.626
31	0.000	0.000	0.000	3.139	0.000	0.487
35	0.000	0.021	0.000	3.183	0.000	0.487
45	0.000	0.000	0.000	1.974	0.000	0.487
60	0.000	0.000	0.012	3.159	0.000	0.452
75	0.000	0.000	0.000	3.175	0.000	0.452
90	0.000	0.000	0.000	2.710	0.000	0.452

Note: 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+} were added 2 times at 0 min and 30 min at pH 3 and 25 °C.

Table C.13 Fenton's reagent adding pattern effect on Fenton reaction (No.3)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	0.255	0.568	1.608	3.581	17.905	1.000
0.5	0.114	0.542	1.004	0.422	6.977	0.950
1	0.118	0.628	1.014	0.406	5.233	0.967
5	0.113	0.656	0.994	0.458	5.233	0.967
15	0.107	0.646	0.948	0.637	4.070	0.967
15.5	0.034	0.477	0.512	0.914	11.628	0.900
16	0.033	0.474	0.485	1.521	9.884	0.900
20	0.000	0.135	0.182	1.982	2.907	0.867
30	0.000	0.091	0.118	2.328	0.000	0.800
30.5	0.000	0.020	0.017	2.577	1.907	0.800
31	0.000	0.027	0.026	2.724	1.744	0.783
35	0.000	0.019	0.029	2.818	0.000	0.750
45	0.000	0.017	0.085	3.176	0.000	0.717
45.5	0.000	0.000	0.000	3.202	0.000	0.667
46	0.000	0.000	0.000	3.590	0.000	0.583
50	0.000	0.000	0.000	3.871	0.000	0.650
60	0.000	0.000	0.000	3.959	0.000	0.650

Note: 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+} were added 4 times at 0, 15, 30 and 45 min at pH 3 and 25 °C.

Table C.14 Fenton's reagent adding pattern effect on Fenton reaction (No.4)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	0.266	0.360	2.405	14.324	71.621	1.000
0.5	0.240	0.260	1.190	1.592	33.830	0.815
1	0.222	0.238	1.052	1.520	30.963	0.756
5	0.119	0.192	0.689	1.727	21.789	0.726
15	0.000	0.018	0.176	2.137	0.000	0.667
16	0.000	0.019	0.026	1.962	40.137	0.548
30	0.000	0.000	0.018	1.102	0.000	0.437
31	0.000	0.000	0.000	0.919	68.806	0.415
35	0.000	0.000	0.000	0.788	47.017	0.393
45	0.000	0.000	0.000	0.788	40.137	0.341
50	0.000	0.000	0.000	0.657	33.830	0.326
60	0.000	0.000	0.000	0.629	22.936	0.289

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+}, 2,435 mg/l H_2O_2 were re-supplied when exhausted at pH 3 and 25 °C.

C.1.4.2 Treated wastewater from biological process

Table C.15 Fenton's reagent adding pattern effect on Fenton reaction (No.5)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	0.1	0.020	0.108	14.324	71.621	1.000
0.5	0.000	0.025	0.175	0.080	47.304	0.800
1	0.000	0.019	0.133	0.034	44.384	0.700
5	0.000	0.000	0.025	0.062	37.376	0.700
15	0.000	0.000	0.000	0.076	23.360	0.500
30	0.000	0.000	0.000	0.034	11.680	0.450
60	0.000	0.000	0.000	0.018	0.000	0.350

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+} at pH 3 and 25 °C.

Table C.16 Fenton's reagent adding pattern effect on Fenton reaction (No.6)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	0.1	0.047	1.356	14.324	7.162	1.000
0.5	0.000	0.016	0.049	0.080	0.117	0.818
1	0.000	0.012	0.030	0.034	0.133	0.727
5	0.000	0.000	0.000	0.062	0.072	0.636
15	0.000	0.000	0.008	0.076	0.076	0.636
30	0.000	0.000	0.033	0.034	0.084	0.545
60	0.000	0.000	0.000	0.018	0.074	0.318

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+} were added 2 times at 0 and 30 minutes at pH 3 and 25 °C.

C.1.5 Effect of Iron Interference

Table C.17 Effect of Iron interference on Fenton reaction in real wastewater (No.1)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	0.961	0.270	2.405	14.324	71.621	1.000
0.5	0.381	0.298	1.686	0.927	47.093	0.840
1	0.333	0.294	1.611	0.947	43.024	0.815
5	0.152	0.251	1.181	0.776	36.047	0.800
15	0.018	0.124	0.331	0.804	13.954	0.696
30	0.000	0.027	0.052	1.011	0.000	0.637
60	0.000	0.026	0.033	1.727	0.000	0.607
60.5	0.000	0.018	0.013	1.607	33.140	0.385
61	0.000	0.020	0.035	1.683	29.070	0.378
65	0.000	0.000	0.085	1.496	22.675	0.348
75	0.000	0.000	0.000	1.046	4.070	0.333
90	0.000	0.000	0.000	0.704	0.000	0.333
120	0.000	0.000	0.000	0.477	0.000	0.311
120.5	0.000	0.000	0.000	0.883	30.233	0.230
121	0.000	0.000	0.000	0.708	23.256	0.215
125	0.000	0.000	0.000	0.549	21.512	0.200
135	0.000	0.000	0.000	0.517	15.116	0.170
150	0.000	0.000	0.000	0.298	9.302	0.156
180	0.000	0.000	0.000	0.159	0.000	0.141

Note: 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+}, $Fe(OH)_3$ was precipitated and separated before started new experiment, 3 cycle, at pH 3 and 25 °C.

Table C.18 Effect of Iron interference on Fenton reaction in real wastewater (No.2)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	0.961	0.270	2.405	14.324	71.621	1.000
0.5	0.381	0.298	1.686	1.094	47.093	0.815
1	0.333	0.294	1.611	1.031	43.024	0.800
5	0.152	0.251	1.181	0.915	36.047	0.738
15	0.018	0.124	0.331	2.161	13.954	0.708
30	0.000	0.027	0.052	2.176	0.000	0.677
60	0.000	0.026	0.033	2.025	0.000	0.646
60.5	0.000	0.000	0.000	1.349	0.000	0.431
61	0.000	0.000	0.000	2.137	0.000	0.431
65	0.000	0.000	0.000	1.460	0.000	0.415
75	0.000	0.000	0.000	1.007	0.000	0.385
90	0.000	0.000	0.000	0.987	0.000	0.385
120	0.000	0.000	0.000	1.054	0.000	0.369
120.5	0.000	0.000	0.000	0.557	0.000	0.292
121	0.000	0.000	0.000	0.660	0.000	0.277
125	0.000	0.000	0.000	0.279	0.000	0.246
135	0.000	0.000	0.000	0.267	0.000	0.208
150	0.000	0.000	0.000	0.247	0.000	0.208
180	0.000	0.000	0.000	0.191	0.000	0.200

Note: 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+}, without $Fe(OH)_3$ precipitation and separation before started new experiment, 3 cycle, at pH 3 and 25 °C.

C.2 Electro-Fenton Experiment

C.2.1 Effect of Electric current on Fenton Reaction

Table C.19 The COD removal in synthetic wastewater between Fenton and Electro-Fenton process

Time (min)	COD (C/C_0)	
	Electro-Fenton	Fenton
0	1.000	1.000
0.5	0.844	0.806
1	0.750	0.774
5	0.438	0.742
15	0.250	0.548
30	0.188	0.388
40	0.156	-
50	0.156	-
60	0.125	0.323

Note: 2,435 mg/l H_2O_2 and 800 mg/l Fe^{2+} at pH 3 and 25 °C.

Table C.20 Electro-Fenton reaction in real wastewater (No.1)

Time (min)	Organic concentration (mM)			Fe^{2+} (mM)	H_2O_2 (mM)	COD (C/C_0)
	CHP	AP	DMPC			
0	0.827	0.195	2.630	14.324	71.621	1.000
0.5	0.508	0.190	2.348	0.609	46.024	0.904
1	0.380	0.180	1.734	1.524	17.259	0.815
5	0.027	0.178	0.593	2.192	12.029	0.785
15	0.000	0.031	0.351	6.171	0.000	0.711
30	0.000	0.022	0.068	7.628	0.000	0.696
60	0.000	0.035	0.105	8.256	0.000	0.652
90	0.000	0.000	0.222	7.357	0.000	0.652

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+}at pH 3 and 25 °C

Table C.21 Electro-Fenton reaction in real wastewater (No.2)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	0.723	0.195	2.192	7.162	71.261	1.000
0.5	0.397	0.279	1.863	0.664	48.639	0.914
1	0.359	0.260	1.649	0.521	48.116	0.889
5	0.324	0.258	1.370	0.633	41.840	0.830
15	0.143	0.208	1.163	0.776	24.581	0.770
30	0.047	0.149	0.688	0.979	4.707	0.726
45	0.000	0.071	0.313	1.305	0.000	0.681
60	0.000	0.067	0.239	2.228	0.000	0.681
90	0.000	0.060	0.207	2.033	0.000	0.681

Note: 2,435 mg/l H_2O_2, 400 mg/l Fe^{2+}at pH 3 and 25 °C.

C.2.2 Effect of Fenton's Reagent Adding Pattern

Table C.22 Effect of Fenton's Reagent adding pattern on Electro-Fenton reaction in real wastewater (No.1)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	0.137	0.534	2.583	14.324	71.620	1.000
0.5	0.074	0.324	1.672	0.418	58.335	0.800
1	0.074	0.368	1.720	1.265	47.620	0.784
5	0.025	0.253	0.835	2.109	29.167	0.736
15	0.000	0.047	0.047	4.409	0.000	0.624
30	0.000	0.057	0.044	3.748	0.000	0.424
40	0.000	0.015	0.000	0.923	0.000	0.304
50	0.000	0.000	0.000	0.649	36.906	0.280
60	0.000	0.000	0.000	0.553	5.953	0.272
70	0.000	0.000	0.000	0.434	0.000	0.256
80	0.000	0.000	0.000	0.219	15.477	0.256
90	0.000	0.000	0.016	0.215	13.691	0.240

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+}, 2435 mg/l H_2O_2 were re-supplied when exhausted at pH 3 and 25 °C.

Table C.23 Effect of Fenton's Reagent adding pattern on Electro-Fenton reaction in real wastewater (No.2)

Time (min)	**Organic concentration (mM)**			**Fe^{2+} (mM)**	**H_2O_2 (mM)**	**COD (C/C_0)**
	CHP	**AP**	**DMPC**			
0	0.177	0.530	2.972	14.324	71.621	1.000
0.5	0.086	0.349	1.994	2.113	56.470	0.800
1	0.070	0.283	1.631	2.606	31.25	0.768
5	0.017	0.130	0.575	3.000	22.478	0.704
15	0.000	0.000	0.014	3.895	0.000	0.576
30	0.000	0.000	0.000	1.444	0.000	0.360
35	0.000	0.000	0.015	0.991	3.290	0.232
45	0.000	0.000	0.034	0.859	0.000	0.224
60	0.000	0.000	0.000	0.840	15.351	0.168
70	0.000	0.000	0.000	0.645	0.000	0.160
80	0.000	0.000	0.000	0.410	43.312	0.136
90	0.000	0.000	0.007	0.223	16.448	0.104

Note: 2,435 mg/l H_2O_2, 800 mg/l Fe^{2+}, 2,435 mg/l H_2O_2 were re-supplied when exhausted, 800 mg/l Fe^{2+} were added 2 times at 0, 30 min at pH 3 and 25 °C.

BIOGRAPHY

NAME	Miss Kamonreuthai Tudthiam
DATE OD BIRTH	21th November 1988
PLACE OF BIRTH	Chantaburi, Thailand
HOME ADDRESS	222/39 Sukhumvit road, Makham, Chantaburi 22150
PHONE	+66 (0) 867670693
E-MAIL	kamonreuthai.t@hotmail.com
EDUCATIONAL RECORD	
Bachelor Degree	Bachelor of Engineering (Environmental Engineering) King Mongkut's University of Technology Thonburi, Bangkok, Thailand, 2010
Master Degree	Master of Science program (Environmental Management) International Postgraduate Program in Environmental Management (Hazardous Waste Management), Inter-Department of Environmental Management Chulalongkorn University, Bangkok, Thailand, 2012