# การกำจัด 2,4-ไดคลอโรฟีนอลด้วยกระบวนการฟลูอิดไดซ์เบดเฟนตัน

นางสาว อิศรา ม่วงไทย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมสิ่งแวดล้อม ภาควิชาวิศวกรรมสิ่งแวดล้อม
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

# REMOVAL OF 2,4-DICHLOROPHENOL BY FLUIDIZED-BED FENTON PROCESS

Miss Isara Muangthai

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Environmental Engineering
Department of Environmental Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2009

| | |
|---|---|
| Thesis Title | REMOVAL OF 2,4-DICHLOROPHENOL BY FLUIDIZED-BED FENTON PROCESS. |
| By | Miss Isara Muangthai |
| Field of Study | Environmental Engineering |
| Thesis Advisor | Associate Professor Chavalit Ratanatamskul, Ph.D. |
| Thesis Co-Advisor | Professor Ming Chun Lu, Ph.D. |

---

Accepted by the Faculty of Environmental Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.................................................................. Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong,Dr. Ing. )

THESIS COMMITTEE

Petchporn . C
.................................................................. Chairman
(Associate Professor Petchporn Chawakitchareon,Ph.D.)

Chavalit
.................................................................. Thesis Advisor
(Associate Professor Chavalit Ratanatamskul,Ph.D.)

Ming Chun Lu
.................................................................. Thesis Co-Advisor
(Professor Ming Chun Lu, Ph.D.)

K. Osathaph
.................................................................. Examiner
(Assistant Professor Khemarath Osathaphan, Ph.D.)

.................................................................. External Examiner
(Associate Professor Jin Anotai, Ph.D.)

อิศรา ม่วงไทย : การกำจัด2,4-ไดคลอโรฟีนอล ด้วยกระบวนการฟลูอิดไดซ์เบดเฟนตัน.(REMOVAL OF 2,4-DICHLOROPHENOL BY FLUIDIZED-BED FENTON PROCESS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.ชวลิต รัตนธรรมสกุล, อาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม : Prof. Ming-Chun Lu, Ph.D., 155 หน้า.

สาร 2,4-ไดคลอโรฟีนอล เป็นสารที่ใช้อย่างแพร่หลายในอุตสาหกรรมยา สีย้อมผ้า ยาฆ่าแมลง และ น้ำยารักษาเนื้อไม้ ซึ่งสารนี้เป็นสารมีพิษและเป็นสารที่ก่อให้เกิดมะเร็ง ดังนั้น มีควาจำเป็นที่ต้องทำการบำบัดน้ำเสียจากโรงงานอุตสาหกรรมที่ปนเปื้อนด้วยสารนี้ ก่อนการปล่อยทิ้งสูสิ่งแวดล้อม งานวิจัยนี้ทำศึกษาการย่อยสลายสาร2,4-ไดคลอโรฟีนอล ด้วยกระบวนการฟลูอิดไดซ์เบดเฟนตัน โปรแกรมบอกซ์เบนเคนถูกนำมาใช้ในการประเมินหาผลกระทบของปัจจัยต่างๆ และสภาวะที่เหมาะสมจากการทดลอง พบว่า ความเข้มข้นเริ่มต้นของไฮโดรเจนเปอร์ออกไซค์ จัดเป็นปัจจัยหลักในการบำบัดสาร2,4-ไดคลอโรฟีนอล ในขณะที่พีเอช ความเข้มข้นเริ่มต้นของเฟอร์รัสไอออน และปริมาณของตัวกลาง เป็นปัจจัยที่สำคัญน้อยกว่า ผลจากการประเมินแบบจำลอง พบว่าสภาวะเหมาะสมในการย่อยสลายสาร 2,4-ไดคลอโรฟีนอล ที่ความเข้มข้น 1 มิลลิโมลาร์ คือ พีเอช 3 ปริมาณของซิลิกาไดออกไซค์ เท่ากับ 100 กรัม ความเข้มข้นเริ่มต้นของเฟอร์รัสไอออน เท่ากับ 0.25 มิลลิโมลาร์ และความเข้มข้นเริ่มต้นของไฮโดรเจนเปอร์ออกไซค์เท่ากับ 10 มิลลิโมลาร์ ซึ่งสามารถประเมิน ประสิทธิภาพการกำจัดได้ 99.86 % 60.49 % และ 14.38% สำหรับสาร2,4-ไดคลอโรฟีนอล ซีโอดี และ ปริมาณเหล็กทั้งหมด ตามลำดับ จากการเปรียบเทียบประสิทธิภาพการบำบัดระหว่างกระบวนการเฟนตันและฟลูอิดไดซ์เบดเฟนตัน ที่สภาวะเหมาะสม พบว่าประสิทธิภาพในการย่อยสลายสาร2,4-ไดคลอโรฟีนอลของทั้งสองกระบวนการมีค่าใกล้เคียงกัน แต่ในกระบวนการฟลูอิดไดซ์เบดเฟนสามารถลดปริมาณเหล็กทั้งหมดได้มากกว่า เนื่องจากข้อดีของฟลูอิดไดซ์เบดเฟนตัน คือ สามารถลดปริมาณสลัดจ์ที่เกิดขึ้นโดยผ่านกระบวนการคริสตัลไรซ์เซชั่น นอกจากนี้เมื่อศึกษาจลนพลศาตร์ของการย่อยสลายสาร2,4-ไดคลอโรฟีนอล ภายใน 5 นาทีแรก ภายใต้สภาวะการทดลองที่พีเอช 3 ปริมาณซิลิกาไดออกไซค์ 100 กรัม ความเข้มข้นของเฟอร์รัสไอออน ไฮโดรเจนเปอร์ออกไซค์ และ 2,4-ไดคลอโรฟีนอล เท่ากับ 0.1-1, 1-10 และ 0.5-5 มิลลิโมลาร์ ตามลำดับ สามารถอธิบายได้ด้วยสมการ

$$-d[2,4\text{-DCP}]/dt = 1.84\times 10^{-1}[\text{Fe}^{2+}]^{0.51}[\text{H}_2\text{O}_2]^{0.19}[2,4\text{-DCP}]^{0.68}$$

ภาควิชา วิศวกรรมสิ่งแวดล้อม.................. ลายมือชื่อนิสิต อิศรา ม่วงไทย
สาขาวิชา วิศวกรรมสิ่งแวดล้อม.............. ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา 2552...................................... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

## 5070648621 : MAJOR ENVIRONMENTAL ENGINEERING
KEYWORDS : 2,4-DICHLOROPHENOL / FENTON PROCESS / FLUIDIZED-BED FENTON PROCESS/ BOX-BEHNKEN STATISCAL DESIGN

ISARA MUANGTHAI : REMOVAL OF 2,4-DICHLOROPHENOL BY FLUIDIZED-BED FENTON PROCESS. THESIS ADVISOR: ASSOC. PROF. CHAVALIT RATANATAMSKUL, Ph.D. THESIS CO-ADVISOR: PROF. MING-CHUN LU, Ph.D., 155 pp.

2,4-dichlorophenol has been widely used in the industries of dyes, pharmaceutical, pesticides and wood preservative. It is considered as a toxic and carcinogenic chemical. Therefore, the industrial wastewater contaminated with this chemical need to be treated before release to the environment. This research aims to investigate the degradation of 2,4-dichlorophenol by fluidized-bed Fenton process. In this study, Box-Behnken experiment design was applied to assess the effects of variables and determine the optimum condition. The result reveals that the initial $H_2O_2$ concentration was the main factor affecting the degradation of 2,4-dichlorophenol whereas pH, $Fe^{2+}$ and the amount of carrier were consider as less significant factors. The optimum condition for removal of 1 mM of 2,4-dichlorophenol was at pH 3, 100 grams of $SiO_2$, 0.25 mM of $Fe^{2+}$ and 10 mM of $H_2O_2$ which could be predicted to obtain the removal efficiencies of 99.86%, 60.49% and 14.38 % for 2,4-dichlorophenol, COD and total iron, respectively. With comparison between Fenton and fluidized-bed Fenton process at the optimum condition, the removal efficiency of 2,4-dichlorophenol from both processes were almost the same while the higher total iron removal was found in fluidized-bed Fenton process. Since the advantage of fluidized-bed Fenton can reduce the amount of sludge via crystallization process. Moreover, the kinetic study was also investigated. The overall kinetic equation, under the studied ranges of 0.1 to 1 mM of $Fe^{2+}$, 1 to 20 mM of $H_2O_2$, 0.5 to 5 mM of 2,4-dichlorophenol , 100 grams of $SiO_2$ and pH 3 can be described as follows : $d[2,4\text{-DCP}]/dt = 1.84 \times 10^{-1}[Fe^{2+}]^{0.51}[H_2O_2]^{0.19}[2,4\text{-DCP}]^{0.68}$

Department : Environmental Engineering Student's Signature อิศรา ม่วงไทย
Field of Study : Environmental Engineering Advisor's Signature
Academic Year : 2009 Co-Advisor's Signature

## ACKNOWLEDGEMENTS

I would like to express my gratitude to my advisor, Assoc. Prof. Dr. Chavalit Ratanamskul for his constant guidance, strong encouragement, kindness and support throughout this research. Most of all, I would like to express my sincere appreciation to Prof. Ming-Chun Lu., my co-advisor, for his attention, constant supervision , a valuable suggestion and extremely help in conducting this thesis. In addition, I am very deeply impressed for all of his support, his care and his motivation for me to deal with the problem and achieve this work.

Special gratitude is given to the chairman of the committee, Assoc. Petchporn Chawakitchareon for providing in valuable advice and examining my final work. I also would like to thanks Asst. Prof. Dr. Khemarath Osathaphan and Assoc. Prof. Dr. Jin Anotai for their valuable comments and insightful suggestions which significantly enhanced the quality of this work.

I would like to thank all of staff and friends at Department of Environmental Engineering Chulalongkorn University, Thailand. Special thanks belongs to Chia Nan University of Pharmacy and Science, Tainan, Taiwan for giving me the worth opportunity to carry out my research there. Moreover, I am grateful to The National Science Council of Taiwan for supporting me to achieve this work .

Last but not least, I own big thanks to my Thai and Taiwan's friends whom always helped me and took care me while I was staying at Chia Nan University of Pharmacy and Science, Tainan, Taiwan, including my senior whom always gave me an advice, clarified my question and took care me as well. I want to especially thank Miss Nalinrut Masoonboon, Mr. Piyawat Tanvanit, Miss Mullika Teerakun, Mr. Piaw Phatai, Miss Sutthinee Narkwittaya, Mr. Pumis Thuptimdang, Mr. Sermporn Sairiam, Chien- Wei Chen, I-Hsuan Chen, Wei-Yu Lan and Yu-Lin Liu. Moreover, I also thank you every friend of mine in everywhere for our good friendship and being there whenever I need.

Finally, a very special thank you belongs to my beloved family for their unconditional love, a whole understanding, great patience and consistent support throughout my entire study.

# CONTENTS

page

page

page

# LIST OF TABLES

# LIST OF FIGURES

Figures page

## LIST OF ABBREVIATIONS

°C = Celsius degree

AOPs = Advanced oxidation processes

UV = ultraviolet

DI = De-ionized

2,4-DCP = 2,4-dichlorophenol

$H_2O_2$ = Hydrogen peroxide

$Fe^{2+}$ = Ferrous ion

$Fe^{3+}$ = Ferric ion

•OH = Hydroxyl radical

mol = mole

M = Molar

mM = Millimolar

$M\Omega/cm$ = Milliohm per centimeter

min = Minute

s = Second

g = Gram

L = Liter

mL = Milliliter

$\mu L$ = Microliter

k = Rate constant

UVV = Ultravacuum

# CHAPTER I

# INTRODUCTION

## 1.1 Rational

Nowadays, expansions in many industries are rapidly increased. There are various types of chemicals widely used as raw materials, staring materials and intermediates in several industrial processes. The effluent containing a chemical from those industries can cause pollution in the environmental. There are several hazardous chemicals which are environmentally persistent and cause serious health to all living organisms. Chlorophenols are one kind of the toxic organic compounds listed by Environmental Protection Agency (EPA) as priority pollutants (Wang, H. and Wang, J, 2008). 2,4-dichlorophenol (2,4-DCP) is an organic halogen hydrocarbon consisting of phenol and chlorine functional group. It has been widely used for production of dyes, herbicides, pesticides, fungicides, chemical, wood preservative, and pharmaceutical manufacturing. It can also be formed as by products from the paper industry, i.e. during the bleaching of paper pulp with chlorine (Doocey and Sharratt, 2004). There are released into the environment mainly by the chlorination of municipal water, the degradation of some chemicals and the manufacturing of various products such as pesticides, pharmaceuticals and dyes. However, this chemical is toxic to human. It is readily absorbed into the body by inhalation of its aerosal, through the skin and by ingestion which cause irritation symptoms of the nose, eyes, respiratory tract, and skin contact (Kintz et al.,1992). It was also a suspected mutagens and carcinogen to human. Moreover, the accumulation of chlorinated aromatic compounds in the environment has become a serious problem. Upon entering to environment, 2,4-dichlorophenols are toxic and persistent organic pollutants which cause considerable damage to aquatic ecosystem and human health also. Therefore, in this type of environment and conditions, measurement of chemical oxidation is needed and important for effective wastewater treatment (Bell et al., 2003).

Advanced oxidation processes (AOPs) are the alternative approach which provides the destruction of hazardous organic compounds. Advanced oxidation processes generate the high reactivity of hydroxyl radicals (•OH) in the degradation of toxic organic pollutants. Among various AOPs, Fenton process ($H_2O_2/Fe^{2+}$) has been effectively used to treat various organic contaminants including highly toxic compounds. In Fenton reaction, hydrogen peroxide ($H_2O_2$) is catalyzed by ferrous ions ($Fe^{2+}$) to produced hydroxyl radical (•OH). The reaction is performed under acidic conditions to keep the iron soluble and to enhance the oxidative character of the hydroxyl radicals. The process includes a neutralization step to allow the elimination of ferric ions by precipitation as hydroxide. The mainly limitation of the Fenton process is the production of substantial amount of sludge that required further separation and disposal. There are several new Fenton modifications, which can solve this problem. One of such alternative is the use of fluidized-bed Fenton reactor. The carriers in fluidized-bed Fenton reactor can reduce iron precipitate via crystallization process to from iron oxide species onto their surface (Chou et al., 2004). Moreover, the synthesized iron oxide can also serve as a catalyst for hydrogen peroxide decomposition in a heterogeneous reaction. Therefore, the precipitation in the puffy ferric hydroxide forms can reduce.

Up to now, most studies have focused on the basic single-factor-at-a-time approach. Studying the effect of each experimental parameter while keeping all other conditions constant. However, this strategy does not take into account cross-effects from the factors considered and may lead to a poor optimization result. To over come this problem, the use of statically based strategies has proven to be quite advantageous, allowing the minimum number of experiments while simultaneously changing several variables (Montgomery, 2001). Indeed, the design of experiments methodology is a modern approach which has been widely used in several applications because it reduces the number of experiments to be performed, considers interactions among the variables and can be used for optimization on the operating parameters in multivariable systems (Ay et al., 2009). In order to find the effect of each variable factor on the process, to obtain the optimum conditions and to determined the kinetic information for 2,4-dichlorophenol degradation, the statistical design of experiments is a promising method to use. Consequently, this research investigated on the removal of 2,4-dichlorophenol in synthetic wastewater by fluidized-bed Fenton process by using the Box-Benhken statistical experimental design methodology.

## 1.2 Objectives

1. To investigate and compare the removal efficiency of 2,4-dichlorophenol in synthetic wastewater by Fenton and Fluidized-bed Fenton process.
2. To determine the effects of pH initial ferrous and hydrogen peroxide concentration on the removal efficiency of 2,4-dichlorophenol by Fluidized-bed Fenton process.
3. To determine the optimum conditions of 2,4-dichlorophenol by Fluidized-bed Fenton process using Box-Benhken statistical experiment.
4. To determine the kinetic information of 2,4-dichlorophenol by varying the conditions including initial ferrous concentration, initial hydrogen peroxide dosage and initial 2,4-dichlorophenol concentration.

## 1.3 Hypothesis

1. Efficiency of 2,4-dichlorophenol degradation in fluidized-bed Fenton process depends on pH, ferrous ions and hydrogen peroxide concentration.
2. Statistical experimental design is an accurate tool for optimization with a minimal run of experiments.

## 1.4 Scope of research

1. Using lab scale fluidized-bed reactor of 1.35 liters.
2. Using synthetic wastewater with 2,4-dichlorophenol.
3. Using silica dioxide ($SiO_2$) as the carriers for the fluidized-bed Fenton process.
4. The experiment conducts at room temperature.
5. The experiment operates in batch mode.
6. Working at laboratory of Chia Nan University of Pharmacy and Science, Tainan, Taiwan

### 1.5 Expected Results

1. Effect of pH, hydrogen peroxide, and ferrous ions concentration on the degradation of 2,4-dichlorophenol in fluidized-bed Fenton process.
2. The removal efficiency of 2,4-dichlorophenol in synthetic wastewater by Fenton and fluidized- bed Fenton processes.
3. The optimum conditions of 2,4-dichlorophenol removal in synthetic wastewater by fluidized-bed Fenton process regarding to using Box-Benhken statistical experiment
4. The kinetic equation for 2,4-dichlorophenol degradation by fluidized-bed Fenton process according to the initial ferrous concentration ,hydrogen peroxide dosage and initial 2,4-dichlorophenol concentration.

# CHAPTER II

# THEORIES AND LITERATURE REVIEWS

## 2.1 Properties of 2,4-Dichlorophenol

### 2.1.1 General Information

Chlorophenols are organic halogen compounds of cyclic aromatics formed by replacing hydrogen atoms in phenol by 1-5 atoms of chlorine. There are five basic types of chlorophenols: monochlorophenols, dichlorophenols, trichlorophenols, tetrachlorophenols and pentachlorophenols. There are 19 compounds of chlorophenols of three mono-, six isomeric substances each of di-, tri-, as well as three isomeric substances tetra-, and fully chlorinated pentachlorophenol. Chlorinated phenol compounds are solids at room temperature, except 2-Monochlorophenol which melts at 8 $^{o}$C. Chlorinated phenols are primarily used as antiseptics, disinfectants, herbicides, pesticides, and wood preservatives (Lauderdale et al., 2003). They are priority toxic pollutants listed in the US EPA Clean Water Act and are difficult to be removed from water bodies (Zhou et al., 2008). 2,4-Dichlorophenol is the one of interesting compounds. It has many synonym such as 2,4-DCP, 2,4-Dichlorohydroxyl- benzene, 4,6-Dichlorophenol, 1-Hydroxy-2,4-dichlorobenzene and 4-Hydoxy-1,3-dichlorobenzene. The molecular formula is $C_6H_4Cl_2O$ as show in figure 2.1. It is mainly used as intermediate in the preparation of the herbicide 2,4-dichlorophenoxy acetic acid (2,4-D) and propionic acid (2,4-DP). Industrially, 2,4-dichlorophenol can be obtained by chlorinating phenol, *p*-chlorophenol, *o*-chlorophenol, or a mixture of these compounds in cast-iron reactors.

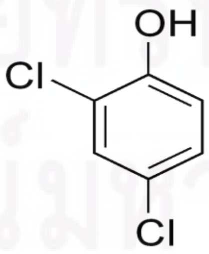


Figure 2.1 Structural of 2,4-Dichlorophenol (Lauderdale et al., 2003).

However, 2,4-D reverse to 2,4-DCP by solar photolysis or microbial activities in nearby soil or in natural water. It has been found in the effluent of disinfected water after chlorination, the flue gas of municipal waste incineration or, pulp and paper wastewater (Li et al., 2007). This chemical can be toxic to human health if inhale, ingest or absorb through the skin and contact with large amounts may be fatal. Moreover, it was suspected mutagens and carcinogen to human, also caused damage to aquatic eco-system.

### 2.1.2 Physical and Chemical Properties

2,4-Dichlorophenol is an organic halogen hydrocarbon which is mainly used as intermediate for production of 2,4-dichlorophenoxy acetic acid, other related herbicide, ingredient of antiseptics and starting material higher. 2,4-dichlorophenol is solid at ambient temperature (colorless crystals) and has a strong characteristic odor. It is slightly soluble in water, but highly soluble in alcohols. The physical and chemical properties of 2,4-Dichlorophenol are given in table 2.1.

Table 2.1 Physical and Chemical properties of 2,4-dichlorophenol (Lauderdale et al., 2003).

| Properties | Value |
|---|---|
| Molecular formula | $C_6H_4Cl_2O$ |
| Molecular weight | 163.00 g/mol |
| CAS NO. | 120-83-2 |
| Appearance | Colorless crystals, White or pale yellow solid |
| Odor | Strong medicinal |
| Melting point | 45 $^{o}$C |
| Boiling point | 210 $^{o}$C |
| Specific gravity | 1.383 |
| Solubility in water | 0.45 g/l at 20 $^{o}$C |
| Solubility in organic solvent | Soluble in carbon tetrachloride, ethyl ether,<br>Soluble in aqueous alkali |
| Vapor density | 5.62 |
| Vapor pressure | 133 kPa @53 $^{o}$C |

| Properties | Value |
|---|---|
| Density | 1.388 g/ml @ 50 $^{o}$C |
| Specific heat | 190 J.mol$^{-1}$.K$^{-1}$ @ 20 $^{o}$C |
| Viscosity | 2.65 mPa.s @ 50 $^{o}$C |
| Flash point | 113 $^{o}$C |
| Stability | Stable under ordinary conditions |

### 2.1.3 Toxicology

In chlorophenol production, irritation symptoms of the nose, eyes, respiratory tract, and skin resulting in chloroacne have been observed. The results of epidemiology studies on the long-term effects of chlorophenols are quite contradictory and have not allowed the experts to reach any firm conclusions (Kintz et al.,1992).

The substance can be absorbed into the body by inhalation of its aerosol, through the skin and by ingestion (International Chemical Safety Cards, 1997). TLV (Threshold Limit Value) has not been established. Lethal dose ($LD_{50}$) for rats has been found to be 580 mg.kg$^{-1}$(oral) and 1730 mg.kg$^{-1}$ (percutaneous). Insufficient data are available on the effect of this substance on human health, therefore utmost must be taken. Increasing attention is devoted at the present time to the risks of 2,4-dichlorophenol in relation to skin adsorption under the EPA’s testing program for high-production-volume chemicals. EPA recommends that drinking water containing this chemical no more than 0.03 mg.L$^{-1}$ (US.EPA, 2008).

#### 2.1.3.1 Acute Toxicity

**Routes of exposure** : The substance can be absorbed into the body by inhalation of its aerosol, through the skin and by ingestion.

**Affected organs** : skin, eyes, center nervous system (CNS)

Table 2.2 Symptoms, prevention and first aid of 2,4-dichlorophenol (International Chemical Safety Cards, 1993).

| Route of Exposure | Symptoms | Prevention | First aid |
|---|---|---|---|
| Inhalation | Burning sensation. Cough. Shortness of breath. Sore throat. | Local exhaust or breathing protection. | Fresh air, rest. Artificial respiration if indicated. Refer for medical attention. |
| Skin | Redness. Pain. Blisters. | Protective gloves. Protective clothing. | Remove contaminated clothes. Rinse and then wash skin with water and soap. |
| Eyes | Redness. Pain. Severe deep burns. | Face shield, or eye protection in combination with breathing protection. | First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor. |
| Ingestion | Burning sensation. Abdominal pain. Tremor. Weakness. Labored breathing. Shock or collapse. | Do not eat, drink, or smoke during work. | Rinse mouth. Do not induce vomiting. Refer for medical attention. |

#### 2.1.3.2 Chronic Toxicity

#### Carcinogenicity

**- Human carcinogenicity data**

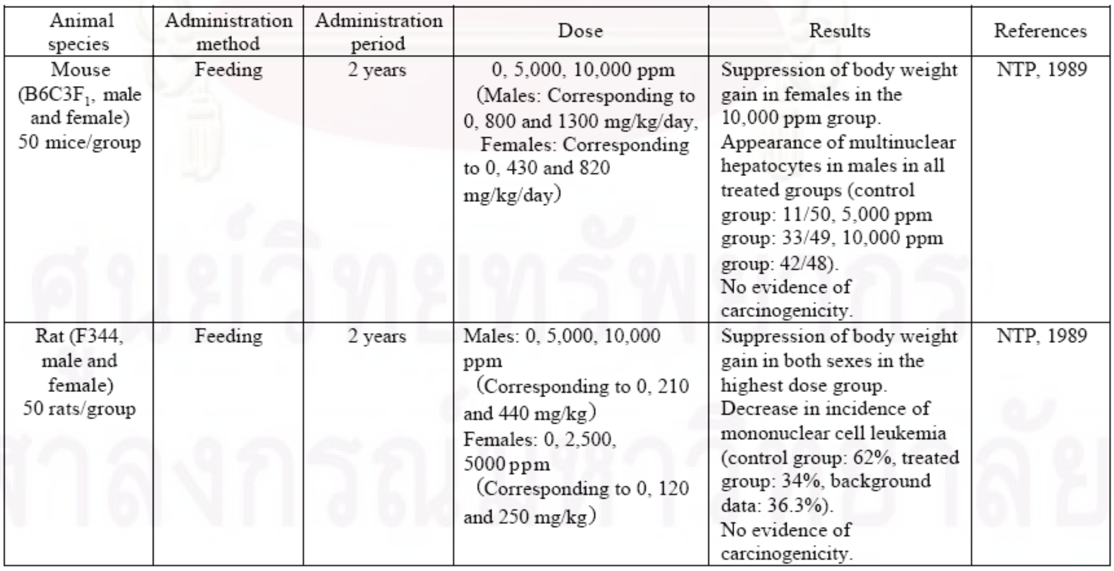
Mortality and/or cancer incidence has been analyzed in several cohort studies of chemical manufacturers, almost all of which have been incorporated within a multicentre international collaborative study, and also in a case–control study nested within this cohort. Two other cohort studies have focused on leather tanneries in Sweden and sawmills in Canada where chlorophenols were used. In addition, case–control studies have examined the association of chlorophenols with soft-tissue sarcoma, non-Hodgkin lymphoma, thyroid cancer, nasal and nasopharyngeal cancer, colon cancer and liver cancer (ATSDR, 1999).

These investigations have shown significant associations with several types of cancer, but the most consistent findings have been for soft-tissue sarcoma and non-Hodgkin lymphoma. Although the odds ratios in some case–control studies may have been inflated by recall bias, this cannot explain all of the findings. Nor are they likely to have arisen by chance. It is not possible, however, to exclude a confounding effect of polychlorinated dibenzo-*para*-dioxins which occur as contaminants in chlorophenols (IRAC, 1999).

- **Animal carcinogenicity data**

Animals that were given food or drinking water containing chlorophenols at high levels developed adverse or negative health effects. The major effects with exposure to high levels of chlorophenols were on the liver and the immune system. Also, the animals that ate or drank chlorophenols did not gain as much weight as the animals that ate food and drank water not containing chlorophenols (IRAC, 1999).

Table 2.3 Results of carcinogenicity studies of 2,4-dichlorophenol (National Toxicology Program, 1989).



| Animal species | Administration method | Administration period | Dose | Results | References |
|---|---|---|---|---|---|
| Mouse ($B6C3F_1$, male and female) 50 mice/group | Feeding | 2 years | 0, 5,000, 10,000 ppm (Males: Corresponding to 0, 800 and 1300 mg/kg/day, Females: Corresponding to 0, 430 and 820 mg/kg/day) | Suppression of body weight gain in females in the 10,000 ppm group.<br>Appearance of multinuclear hepatocytes in males in all treated groups (control group: 11/50, 5,000 ppm group: 33/49, 10,000 ppm group: 42/48).<br>No evidence of carcinogenicity. | NTP, 1989 |
| Rat (F344, male and female) 50 rats/group | Feeding | 2 years | Males: 0, 5,000, 10,000 ppm (Corresponding to 0, 210 and 440 mg/kg)<br>Females: 0, 2,500, 5000 ppm (Corresponding to 0, 120 and 250 mg/kg) | Suppression of body weight gain in both sexes in the highest dose group.<br>Decrease in incidence of mononuclear cell leukemia (control group: 62%, treated group: 34%, background data: 36.3%).<br>No evidence of carcinogenicity. | NTP, 1989 |

From table 2.3, feeding rats and mice high doses of 2,4-dichlorophenol for a long time did not cause cancer because no increase in the incidence of tumors was found. However, long-term treatment of rats and mice with high doses of 2,4,6-trichlorophenol by oral administration caused leukemia in rats and liver cancer in mice. In one study in mice in a screening test for lung tumours. In mice, it increased the incidences of benign and malignant tumours of the liver and In rats mononuclear cell leukaemia. It did not induce lung adenomas in mice. Suggesting that 2,4,6-trichlorophenol may be a carcinogen (ATSDR, 1999).

There is limited evidence in humans for the carcinogenicity of combined exposures to polychlorophenols. There is evidence suggesting lack of carcinogenicity of 2,4-dichlorophenol in experimental animals. In contrast, There is limited evidence in experimental animals for the carcinogenicity of 2,4,6-trichlorophenol and there is sufficient evidence in experimental animals for the carcinogenicity of pentachlorophenol. So, combined exposures to polychlorophenols are possibly carcinogenic to humans (Group 2B).

The Department of Health and Human Services has determined that 2,4,6-trichlorophenol may reasonably be anticipated to be a carcinogen. The International Agency for Research on Cancer (IARC) has determined that the chlorophenols as a group, are possibly carcinogenic to man (Group 2B). The Environmental Protection Agency (EPA) has determined that 2,4,6-trichlorophenol is a probable carcinogen.

### 2.1.4 Exposure

Chlorophenols can enter the environment while they are being made or used as pesticides. Most of the chlorophenols released into the environment go into water, with very little entering the air. The compounds that are most likely to go into the air are the mono- and dichlorophenols because they are the most volatile. Once in the air, sunlight helps destroy these compounds and rain washes them out of the air. Chlorophenols stick to soil and to sediments at the bottom of lakes, rivers, or streams. However, low levels of chlorophenols in water, soil, or sediment are broken down by microorganisms and are removed from the environment within a few days or weeks (ATSDR, 1999).

Most people are exposed to very low levels of chlorophenols in drinking water that has been disinfected with chlorine (chlorinated drinking water). Chlorophenols have been measured in chlorinated drinking water at parts per trillion concentrations. In lakes, rivers, and streams, chlorophenols were found in less than 1 percent of the water that was tested. Chlorophenols have been measured in city air at concentrations of less than a part per trillion. It has been estimated during the National Occupational Exposure Survey (NOES) from 1981-1983 that about 5,000 people in the United States are exposed to 4-chlorophenol, 2,4,5-trichlorophenol, or 2,4,6-trichlorophenol at work (NOES 1990). It has not been estimated how many people are exposed at work to the other chlorophenols. People who make chlorophenols or use them as pesticides are most likely to have high exposure to these chemicals. For example, mixtures of tetrachlorophenols are used at sawmills as wood preservatives. Skin contact while treating wood with the tetrachlorophenols is the most likely route of exposure. Another likely route of exposure is breathing air contaminated by mono- and dichlorophenols (OSHA, 2002).

### 2.1.5 Environmental levels

Residues of all chlorophenol isomers have been detected in aquatic systems. Generally, residues are present at measurable concentrations in discharges from such sources as manufacturing plants, wood-treatment facilities, municipal waste discharges, and in the receiving waters adjacent to these sources.

Chlorophenols in sewage, stream water and tap water in the vicinity of Seoul, Korea from Jan to Sept, 1979 was studied. Chlorinated phenols can be produced by the chlorination of phenol with hyperchlorite in water. Chlorophenols identified from tap water in Seoul during the summer of 1979 were: O-Chlorophenol 0.042 ppb; 2,6-Dichlorophenol 0.033 ppb; 2,4-Dichlorophenol 0.003 ppb.

Drinking water: Based on federal studies of finished drinking waters, 2,4-Dichlorophenol has been found in 17.2% of the ground water supplies. 2,4-Dichlorophenol was detected in 8 raw water samples and 26 treated water samples (out of a total of 480 samples) collected at 40 potable water treatment facilities in Canada between Oct 1984 and July 1985; max concentration of 17 and 72 ng/l were found in raw and treated water, respectively.

Surface water: An analysis of the USEPA STORET Database determined that 2,4-dichlorophenol was positively detected in 0.4% of 876 effluent reporting stations at a median level below 10 ppb . 2,4-Dichlorophenol (plus 2,5-dichlorophenol) levels of 1.8 ug/kg were detected in water samples taken from the Weser estuary in Germany on Aug 21, 1978 . A 2,4-

dichlorophenol level of 0.45 ppb was found in the Rhine River in 1978 . Max levels of 0.59 and 0.35 ppb were detected in the Rhine at Lobith, Netherlands in 1976 and 1977, respectively.

Ground water: 2,4-dichlorophenol was detected in 6 of 10 groundwater samples (concentration of 3.2-79.7 ppb) taken from two wells (between Oct 1981 and Mar 1983) in the vicinity of an abandoned creosote facility in Conroe, TX. 2,4-Dichlorophenol was detected in groundwater associated with an Australian quarry receiving organic waste dumping .

Seawater: Seawater from the Gulf of Bothnia (Sweden) was found to contain 2,4-dichlorophenol levels of 2-400 ng/l from samples collected on Sept 13, 1982 and Nov 3, 1983; the presence of chlorophenols in the seawater was attributed to effluent discharges from a sulfate pulp mill .

Rain/Snow: An average 2,4-dichlorophenol concentration of 1.3 ng/l (range of 0.56-2.5 ng/l) was detected in rainwater of Portland, OR during monitoring between Feb and Apr 1984. Levels of 0.55-20 ng/l were detected in rainwater collected in suburban Beaverton, OR in Feb and Apr 1982.

Effluent: 2,4-dichlorophenol is a major component of pulp mill effluents formed during the multi-step bleaching of cellulose to remove colored lignin constituents. An analysis of the US EPA STORET Database determined that 2,4-dichlorophenol was positively detected in 3.0% of 1319 effluent reporting stations at a median level below 10 ppb. 2,4-Dichlorophenol levels of 2-11 ng/l were detected in waste liquors from Finnish pulp mills in 1983 ; levels of 234 and 570 ng/g were found in combustion ash from two municipal refuge incinerators. A 2,4-dichlorophenol concentration of 0.1 ng/g was detected in particle effluents from coal-fired power plants. Combustion effluents from the combustion of municipal solid waste, wood wastes, and peat have been found to contain 2,4-dichlorophenol (Lauderdale et al., 2003 and U.S. National Library of Medicine, 2001).

### 2.1.6 Environmental considerations of chlorophenols

Chlorophenols constitute a group of organic substances that are introduced into the environ-ment as a result of several man-made activities, such as waste incineration, uncontrolled use of wood preservatives, pesticides, fungicides and herbicides, etc, as well as by-products formed during bleaching of pulp with chlorine and in the disinfection by chlorination to get drinking water (Ahlborg and Victorin, 1987).

All chlorophenol possess bactericidal activities that increase with the degree of chlorination. Chlorophenols are highly toxic to algae. Most of plants are very sensitive to the phytotoxicity of chlorophenols. As for aquatic organisms, fish and other aquatic organisms absorb chlorophenols through their gills, gastrointestinal tract or skin. The EPA recommends that a maximum average 2,4-dichlorophenol concentration in surface waters not exceed 2.02 mg/L.

Chlorophenols may be present in the aquatic environment in many forms. They may be dissolved in free or complexes form, adsorbed on suspended inert solid or benthic sediments, or carried in biological tissues. Volatilization transfers the chlorophenol from the water to the air but does not otherwise affect it. Biodegradation is the principal means by which chlorophenols are removed. It must be induced because the antimicrobial activities of these products require that the bacteria adapt (Lelesias, 2002).

## 2.2 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) have shown a potential for treating biorefractory compounds in water. Common processes involved in AOPs are Fenton's reagent, Ozone, Ozone/$H_2O_2$, and UV/$H_2O_2$ of which the primary intermediate is the hydroxyl radicals (•OH).

Advanced oxidation processed (AOPs) are chemical oxidation techniques able to produce in situ reactive free radicals, mainly the hydroxyl radical (•OH), by means of different reacting systems (Olalla, 2007). The concept was originally established by Glaze et al.,1987 as "oxidation processes which generate hydroxyl radical in sufficient quantity to affect water treatment" AOPs have been viewed with the great interest as a promising method for the removal organic contaminants from water. They involve the generation of highly reactive radicals (especially hydroxyl radicals) in sufficient quantity to effect water purification. •OH radicals are extraordinarily reactive species, that attack most of the organic molecules.

The hydroxyl radical is one of the most reactive free radical, a short-lived, high reactive, and one of strongest oxidants. The kinetics of reaction is generally first order with respect to the concentration of hydroxyl radicals and to the concentration of the specie to be oxidized. Rate constants are usually in the range of 108 – 1011 $M^{-1}.s^{-1}$,whereas the concentration of hydroxyl radicals lays between $10^{-10}$and $10^{-12}$ M, thus a pseudo-first order constant 20 between 1 and $10^{-4}$ $s^{-1}$ is obtained (Glaze et al., 1987).

Table 2.4 Oxidation Power of several oxidant species (Munter, 2001 and US. Peroxide, 2008)

| Oxidant | Oxidation Potential, V |
|---|---|
| Fluorine | 3.06 |
| Hydroxyl radical | 2.80 |
| Ozone | 2.07 |
| Atomic oxygen | 2.42 |
| Hydrogen peroxide | 1.77 |
| Potassium permanganate | 1.67 |
| Hypobromous acid | 1.59 |
| Chlorine dioxide | 1.50 |
| Hypochlorous acid | 1.49 |
| Hypoiodous acid | 1.45 |
| Chlorine | 1.36 |
| Bromide | 1.09 |
| Iodine | 0.54 |

As it can be seen from Table 2.4, hydroxyl radicals are more powerful oxidants than the chemical agents used in traditional chemical processes

AOPs can be classified by considering the phase where the process takes place. Hence, homogenous or heterogeneous processes can be differentiated. AOPs classification can also consider the different possible ways of hydroxyl radical production. In this way, photochemical and non-photochemical processes can be distinguished. Table 2.5 classifies some of the most important AOPs into photochemical and non-photochemical processes.

The hydroxyl radical can be produced in a homogenous system by two ways (Munter, 2001). The first is "non-photochemical"; this method is well known method for generating hydroxyl radicals without using light energy. This method includes ozonation at elevated values of pH up to 8.5, combining ozone with hydrogen peroxide, combining ozone and catalyst, and Fenton system. Conventional ozone or hydrogen peroxide oxidation of organic compounds does not completely oxidized organics to carbon dioxide ($CO_2$) and water ($H_2O$). In some reactions, certain oxidation products still remain in the solution. Completing the oxidation reaction, as well as oxidative destruction, can be achieved by supplementing the reaction with UV radiation, which is the "photochemical" path that can also generate the hydroxyl radical.

Table 2.5 Classification of some Advanced oxidation processes as photochemical and non-photochemical processes (Olalla, 2007).

| Non-photochemical processes | Photochemical processes |
|---|---|
| Ozonation in basic media ($O_3$/•OH) | $O_3$/UV |
| $O_3/H_2O_2$ | $H_2O_2$/UV |
| $O_3$/Ultrasound | $O_3/H_2O_2$/UV |
| $H_2O_2$/ Ultrasound | Photocatalytic ozonation |
| Electron Beam | Heterogeneous photocatalysis ($TiO_2$/UV) |
| Fenton ($Fe^{2+}/H_2O_2$) | Water photolysis in ultravacuum (UVV) |
| Electro-Fenton | Photo-Fenton ($Fe^{2+}/H_2O_2$/UV) |
|  | Photoelectro-Fenton |

There are many processes able to generate the highly reactive hydroxyl radical species (•OH) including heterogeneous photocatalytic, photo and non-photocatalytic homogeneous processes. In heterogeneous photolysis, •OH is generated at the surface of a semiconductor (usually $TiO_2$) in the presence of UVA. $O_3$/UV, $O_3/H_2O_2$/UV and $H_2O_2$/UV are common photocatalytic combinations which can also generate •OH (Rodger and Bunce, 2001). However, the most interest in this study is Fenton's reagent ($Fe^{2+}/H_2O_2$).

AOPs are being widely applied to treat contaminated groundwater, to purify and disinfect drinking waters and process waters, and to destroy refractory of organics in industrial water.

## 2.3 Fenton Process

Fenton's reaction is a homogenous catalytic oxidation process using a mixture of hydrogen peroxide ($H_2O_2$) and ferrous ions ($Fe^{2+}$) in an acidic medium, which was firstly discovered by its inventor Henry.J.Fenton in 1894 (Fenton, 1984), but it application as an oxidizing process for destroying toxic organics was not applied until the late 1960s (Huang et al., 1993). Fenton's reaction has been introduced into wastewater treatment processes, and it has been well proven that a variety of refractory organics could be effectively degraded through Fenton's reaction without producing any toxic substances in environment.

Fenton reaction is one kind of AOPs that uses hydrogen peroxide ($H_2O_2$) and ferrous ions ($Fe^{2+}$) to produce hydroxyl radical (•OH) that can oxidize many kinds of chemical quickly. While $Fe^{2+}$ is oxidized to ferric ($Fe^{3+}$) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. However, reaction rates with Fenton's reagent are generally limited by the rate of •OH generation (i.e., concentration of iron catalyst) and less so by the specific wastewater being treated. Typical Fe: $H_2O_2$ ratios are 1:5-10 wt/wt, though iron levels less than 25-50 mg/L can require excessive reaction times (10-24 hours). This is particularly true where the oxidation products (organic acids) sequester the iron and remove it from the catalytic cycle. Fenton's Reagent is most effective as a pretreatment tool where COD is greater than 500 mg/L. This is due to the loss in selectivity as pollutant levels decrease (US. Peroxide, 2008).

The main advantage of Fenton's reaction is the complete destruction of contaminants to harmless compounds, e.g. $CO_2$, water and inorganic salts, biodegradability improvement, BOD/COD removal, and odor and color removal. In addition, the Fenton reaction causes the separation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants (Neyens and Baeyens, 2003). However, the limited range of pH (3-5) in which the reaction takes place and the recovery of iron species are the major drawbacks of this homogeneous process.

### 2.3.1 Hydrogen Peroxide

#### 2.3.1.1 History

Hydrogen peroxide was first isolated in 1818 by Louis Jacques Thénard by reacting barium peroxide with nitric acid. An improved version of this process used hydrochloric acid, followed by sulfuric acid to precipitate the barium sulfate byproduct. Thénard' s process was used from the end of the 19th century until the middle of the 20th century. Modern production methods are discussed below. For a long time it was believed that pure hydrogen peroxide was unstable, because attempts to separate the hydrogen peroxide from the water, which is present during synthesis, failed. This was because traces of solids and heavy metal ions led to a catalytic decomposition explosions of the hydrogen peroxide. 100% pure hydrogen peroxide was first obtained through vacuum distillation by Richard Wolffenstein in 1894. At the end of 19th century, Petre Melikishvili and his pupil L. Pizarjevski showed that of the many proposed formulas of hydrogen peroxide, the correct one was H-O-O-H (US. Peroxide, 2008).

### 2.3.1.2 General Information

Hydrogen peroxide ($H_2O_2$) is a very pale blue liquid which appears colorless in a dilute solution, slightly more viscous than water. It is a weak acid. It has strong oxidizing properties and is therefore a powerful bleaching agent that is mostly used for bleaching paper, but has also found use as a disinfectant, as an oxidizer, as an antiseptic, and in rocketry (particularly in high concentrations as high-test peroxide or HTP) as a monopropellant, and in bipropellant systems. The oxidizing capacity of hydrogen peroxide is so strong that the chemical is considered a highly reactive oxygen species.

Hydrogen peroxide is naturally produced as a byproduct of oxygen metabolism, and virtually all organisms possess enzymes known as peroxidases, which harmlessly and catalytically decompose low concentrations of hydrogen peroxide to water and oxygen

Aqueous solution of hydrogen peroxide is mainly used for oxidation reactions, including bleaching process, chemical syntheses, and for water and wastewater treatment. In drinking water purification, hydrogen peroxide is used to pre-oxidize organic constituents and to eliminate iron and manganese ions.

### 2.3.1.3 Physical and Chemical properties

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

Hydrogen peroxide always decomposes (disproportionate) exothermically into water and oxygen gas spontaneously: $2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$

Table 2.6 Physical and Chemical properties of hydrogen peroxides (Wells, 1984; Greenwood, and Earnshaw, 1997)

| **General** | |
|---|---|
| IUPAC names | Hydrogen peroxide |
| Other names | Dioxidane |
| **Identifiers** | |
| CAS number | 7722-84-1 |
| EC number | 231-765-0 |
| **Identifiers** | |
| UN number | 2015 (>60% soln.)<br>2014 (20–60% soln.)<br>2984 (8–20% soln.) |
| **Properties** | |
| Molecular formula | $H_2O_2$ |
| Molar mass | 34.015 g/mol |
| Appearance | Very light blue color, colorless in solution |
| Density | 1.44 g/cm$^3$ , liquid ( approximate) |
| Melting point | -0.41 °C (272.74 K) |
| Boiling point | 150.2 °C (423.35 K) |
| Solubility in water | Miscible |
| Acidity (p$K_a$) | 11.65 |
| Viscosity | 1.245 cP (20 °C) |
| Dipole moment | 2.26 D |
| **Hazards** | |
| MSDS | ICSC 0164 (>60% soln.) |
| EU classification | Oxidant (O), Corrosive (C),<br>Harmful (Xn) |

| Hazards | |
|---|---|
| EU Index | 008-003-00-9 |
| Flash point | Non-flammable |
| **Related compound** | |
| Related compounds | Water , Ozone, Hydrazine |

### 2.3.1.4 Toxicology information

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

$H_2O_2$ vapors can form sensitive contact explosives with hydrocarbons such as greases. Hazardous reactions ranging from ignition to explosion have been reported with alcohols, ketones, carboxylic acids (particularly acetic acid), amines and phosphorus.

Spilling high concentrations of $H_2O_2$ on a flammable substance can cause an immediate fire, which is further fueled by the oxygen released by the decomposing hydrogen peroxide. High-strength peroxide (also called high-test peroxide, or HTP) must be stored in a suitable,vented container to prevent the buildup of oxygen gas, which would otherwise lead to the eventual rupture of the container. Concentrated hydrogen peroxide, if spilled on clothing (or other flammable materials), will preferentially evaporate water until the concentration reaches sufficient strength, at which point the material may spontaneously ignite. (NTSB - Hazardous Materials Incident Brief and Armadilloaerospace material tests with HTP)

Concentrated $H_2O_2$ (>50%) is corrosive, and even domestic-strength solutions can cause irritation to the eyes, mucous membranes and skin. Swallowing hydrogen peroxide solutions is particularly dangerous, as decomposition in the stomach releases large quantities of gas (10 times the volume of a 3% solution) leading to internal bleeding. Inhaling over 10% can cause severe pulmonary irritation.

Low concentrations of $H_2O_2$, on the order of 3% or less, will chemically bleach many types of clothing to a pinkish hue. Caution should be exercised when using common products that may contain hydrogen peroxide, such as facial cleaner or contact lens solution, which easily splatter upon other surfaces.

Large oral doses of $H_2O_2$ at a 3% concentration may cause irritation and blistering to the mouth, (which is known as Black Hairy Tongue) throat, and abdomen, as well as abdominal pain, vomiting, and diarrhea

#### 2.1.3.5 Environmental Application of $H_2O_2$ (US. Peroxide, 2008)

$H_2O_2$ application spans the range of possible media including air, water, wastewater, soils and sludge. Depending on the objective, $H_2O_2$ may be use either alone or in combination with other process to enhance their performance.

- Odor control: $H_2O_2$ is a strong oxidizer effective in controlling sulfide and organic related odors in wastewater collection and treatment systems. It is typically applied to a wastewater system where there is a retention time of 30 minutes to 5 hours before hydrogen sulfide is released. Hydrogen peroxide oxidizes the hydrogen sulfide and promotes bio-oxidation of organic odors. $H_2O_2$ may be applied directly to aqueous wastes containing these odorants, or to wet scrubbers used to remove them from airstreams. If the odors are the result of biological activity, $H_2O_2$ may instead be added as a preventative to eliminate the anoxic conditions which favor the generation of odors.
- Corrosion control: $H_2O_2$ destroys residual chlorine and reduced sulfur compounds thiosulfates, sulfites, and sulfides which form corrosive acids when condensed onto processing equipment and oxidized by air.
- BOD/COD removal: $H_2O_2$ oxidizes both organic and inorganic pollutants which contribute to BOD and COD. $H_2O_2$ may also affect BOD/COD removal by enhancing the performance of other processes (see enhancement combination applications).
- Inorganic oxidation: $H_2O_2$ oxidizes cyanides, $NO_x/SO_x$, nitrites, hydrazine, carbonyl sulfide, and other reduced sulfur compounds mentioned above (odor/corrosion control).

- Organic oxidation: $H_2O_2$ can hydrolyzes formaldehyde, carbon disulfide, carbohydrates, organophosphorus and nitrogen compounds, and various water-soluble polymers; and (with catalysis) destroys phenols, BTEX pesticides, solvents, plasticizers, chelants, and any other organic requiring treatment.
- Toxicity reduction/Biodegradability improvement: With catalysis, chemically digests complex organics into smaller, less toxic and more biodegradable fragments.

#### 2.1.3.6 $H_2O_2$ Processes (US. Peroxide, 2008)

Most $H_2O_2$ applications involve its simple injection into the water stream with no requirement for additional chemicals or equipment. These include the control of biogrowth (slime), the supply of supplemental oxygen, the removal of FOG and chlorine residuals, and the oxidation of sulfides/sulfites, metals, and other easy-to-oxidize components of BOD/COD. Activation of $H_2O_2$ in these applications may be affected by the adjustment/control of pH, temperature, and/or reaction time. The more difficult-to-oxidize pollutants may require the $H_2O_2$ to be activated with catalysts such as iron, copper, manganese, or other transition metal compounds. These catalysts may also be used to speed up $H_2O_2$ reactions that may otherwise take hours or days to complete. $H_2O_2$ catalysis may occur either in solution (using soluble catalysts) or in packed columns (using solid catalysts).

Solution catalysis: The most commonly used solution catalyst is iron, which when used with $H_2O_2$ is referred to as Fenton's Reagent. The reaction requires a slightly acidic pH and results in the formation of highly reactive hydroxyl radicals ($OH^{\bullet}$) which are capable of degrading most organic pollutants. Another solution catalyst is copper, which is often used to destroy cyanides. Other metals also show catalytic activity with $H_2O_2$ and may be used to selectively destroy specific pollutants

Packed column catalysis: Solid catalysts eliminate the need to add soluble metals to the waste stream, and may offer greater flexibility in terms of reaction rates, selectivity, and the need for pH adjustment. This is an active area of research and many new developments are underway for a variety of applications.

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

### 2.3.2 Hydroxyl Radical

The hydroxyl radical, •OH, is the neutral form of the hydroxide ion. Hydroxyl radicals are highly reactive and consequently short-lived. However, they form an important part of radical chemistry. Most notably hydroxyl radicals are produced from the decomposition of hydroperoxides (ROOH) or, in atmospheric chemistry, by the reaction of excited atomic oxygen with water. It is also an important radical formed in radiation chemistry, since it leads to the formation of hydrogen peroxide and oxygen, which can enhance corrosion and Stress Corrosion Cracking in coolant systems subjected to radioactive environments. Hydroxyl radicals are also produced during UV-light dissociation of $H_2O_2$ (suggested in 1879) and likely in Fenton chemistry, where trace amounts of reduced transition metals catalyze peroxide-mediated oxidations of organic compounds. In organic synthesis hydroxyl radicals are most commonly generated by photolysis of 1-Hydroxy-2(1H)-pyridinethione

The hydroxyl radical is an extremely reactive, short lived and non-selective transient species. This radical is one of the most reactive free radical and one of strongest oxidants. It has a very high oxidizing capacity equal to 2.8 V. (Prengle et al.,1978; Masten and Divies, 1994). It attacks the organic compounds relatively non-selective with rate constants ranging from $10^6$-$10^{10}$ $M^{-1}.s^{-1}$ (Buxton et al., 1998). The hydroxyl radical is the second strongest oxidant that is inferior to fluoride as shown in Table 2.7

Table 2.7 Oxidation-Reduction Potentials of Chemical Reagents for Water and Wastewater Treatment (Lide, 1992)

| Reaction | Potential in Volts ( $E^0$) at 25 °C |
|---|---|
| $F_2 + 2e^- = 2F^-$ | 2.87 |
| $OH^{\bullet} + H^+ + e^- = H_2O$ | 2.33 |
| $FeO_4^{2-} + 8H^+ + 3e^- = Fe^{3+} + 4H_2O$ | 2.20 |
| $O_3 + 2H^+ + 2e^- = O_2 + H_2O$ | 2.07 |
| $H_2O_2 + 2H^+ + 2e^- = 2H_2O_2$ (acid) | 1.76 |
| $MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$ | 1.68 |
| $HClO_2 + 3H^+ + 4e^- = Cl^- + 2H_2O$ | 1.57 |
| $MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$ | 1.49 |
| $HOCl + H^+ + 2e^- = Cl^- + H_2O$ | 1.49 |
| $Cl_2 + 2e^- = 2Cl^{-1}$ | 1.36 |
| $HBrO + H^+ + 2e^- = Cl^- + H_2O$ | 1.33 |
| $O_3 + H_2O + 2e^- = O_2 + 2OH^-$ | 1.24 |
| $O_2 + 4H^+ + 4e^- = 2H_2O$ | 1.23 |
| $ClO_2(g) + e = ClO_2^-$ | 1.15 |
| $Br_2 + 2e^- = 2Br^-$ | 1.07 |
| $HOI + H^+ + 2e^- = I^- + H_2O$ | 0.99 |
| $ClO_2(aq) + e^- = Cl$ | 0.95 |
| $ClO^- + 2H_20 + 2e^- = Cl + 2OH^-$ | 0.90 |
| $H_2O_2 + 2H^+ + 2e^- = 2H_2O$ | 0.87 |
| $ClO_2 + 2H_20 + 4e^- = Cl^- + 4OH^-$ | 0.78 |
| $BrO^- + H_20 + 2e^- = Br^- + 4OH^-$ | 0.70 |
| $I_2 + 2e^- = 2I$ | 0.54 |
| $I_3 + 3e^- = 3I$ | 0.53 |
| $IO^- + H_20 + 2e^- = I^- + 2OH^-$ | 0.49 |

There are four typical chemical reactions of the hydroxyl radical in water which are: (US. Peroxide, 2008).

1. **Addition.:**

$$\bullet OH + C_6H_6 \quad ---> \quad \bullet(OH)C_6H_6 \qquad (2\text{-}1)$$

The hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product such as cyclohexadienyl radical as shown above

2. **Hydrogen Abstraction :**

$$\bullet OH + CH_3OH \quad ---> \quad CH_2HO\bullet + H_2O \qquad (2\text{-}2)$$

An organic free radical and water are formed as shown above.

3. **Electron Transfer :**

$$\bullet OH + [Fe(CN)_6]^{4-} \quad ---> \quad [Fe(CN)_6]^{3-} + \bullet OH \qquad (2\text{-}3)$$

Ions of a higher valence state are formed, or an atom or free radical if a mononegative ion is oxidized as shown above.

4. **Radical Interaction :**

$$\bullet OH + \bullet OH \quad ---> \quad H_2O_2 \qquad (2\text{-}4)$$

The hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product as shown above.

In applying Fenton's Reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanisms (hydrogen abstraction and oxygen addition) predominate.

The key Fenton's reagents, $H_2O_2$ and iron salts are relatively inexpensive. Iron is highly abundant (and may be naturally occurring in the system being treated) and is non-toxic. $H_2O_2$ is relatively easy to transport and handle, as well as being environmentally being in diluted form.

Use of Fenton processes can lead to the complete mineralization of some organic compounds, converting them to $CO_2$, $H_2O$ and inorganic ions. However, this would usually involve a large excess of chemicals which the production of substantial amounts of sludge is the major drawback of Fenton reaction.

### 2.3.3 Fenton's Reaction

Fenton's reaction is mixture of hydrogen peroxide and ferrous ion, which generates hydroxyl radical with powerful oxidizing abilities to degrade toxic organic compounds as shown in the following equation (Kitis et al.,1999; Yoon et al.,2001; Lu et al.,2001).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \bullet OH + OH^- \qquad (2\text{-}5)$$

The ferrous ion ($Fe^{2+}$) initiates and catalyses the decomposition of $H_2O_2$, resulting in the generation of hydroxyl radicals. The generation of the radicals involves a complex reaction sequence in an aqueous solution. Under acidic condition and with an excess of ferrous ion, the hydroxyl radicals generated can further react with ferrous ions to produce ferric ions:

$$Fe^{2+} + \bullet OH \longrightarrow Fe^{3+} + OH^- \qquad (2\text{-}6)$$

Moreover, ferric ions can be regenerated back to ferrous ion in a subsequent reaction with hydrogen peroxide and this reaction is referred to as a Fenton-like reaction (equation (2-7) and (2-8)) (Walling and Goosen, 1973; DeLaat and Gallard, 1999).

$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}OOH^{2+} + H^+ \qquad (2\text{-}7)$$

$$Fe\text{-}OOH^{2+} \longrightarrow Fe^{2+} + HO_2\bullet + H^+ \qquad (2\text{-}8)$$

Ferrous ions and radicals are also produced during the reactions The reactions are as shown in equation (2-9) to (2-11) (Neyens and Baeyens, 2003).:

$$Fe^{2+} + \bullet HO_2 \longrightarrow Fe^{3+} + HO_2^- \qquad (2\text{-}9)$$

$$Fe^{3+} + \bullet HO_2 \longrightarrow Fe^{2+} + O_2 + H^+ \qquad (2\text{-}10)$$

$$\bullet OH + H_2O_2 \longrightarrow H_2O + HO_2\bullet \qquad (2\text{-}11)$$

Hydroxyl radicals can oxidize organics (RH) by abstraction of protons producing organic radicals ($R^\bullet$), which are highly reactive and can be further oxidized (Walling and Kato, 1971; Venkatadri and Peters, 1993; Lin and Lo, 1997)

$$RH + \bullet OH \longrightarrow H_2O + R^\bullet \longrightarrow \text{further oxidation} \qquad (2\text{-}12)$$

The reaction rate in equation (2-7) is much slower than that of equation (2-8). This is due to the fact that ferrous ions are consumed quickly, but reproduced more slowly (Pignatello, 1992). Consequently, the oxidation rate of organic compounds is fast when large amount of ferrous ions are present due to the high generation rate of hydroxyl radicals. However, the Fenton reaction may slow down because the rate of ferrous ions production is low.

The Fenton process consists of two phase: the $Fe^{2+}/H_2O_2$ and $Fe^{3+}/H_2O_2$ stages (Lu et al., 1999). At the initial stage, ferrous ions react very quickly with hydrogen peroxide to produce large amount of hydroxyl radicals (equation (2-5)). The produced hydroxyl radicals can react rapidly with organic matter, thus at first stage, organics are decomposed quickly; this is referred to as the $Fe^{2+}/H_2O_2$ stage. The ferric ions produced in the first stage can react with hydrogen peroxide to produce hydroperoxyl radicals ($HO_2\bullet$) and ferrous ions. The reactions are shown in equation (2-7) and (2-8). However, •OH are the main species causing the decomposition of organics. They are much higher in oxidation strength than hydroperoxyl radicals.

Therefore, the former reaction is far swifter than the latter, resulting in a higher rate of hydroxyl radical formation at the first stage of reaction than at the second stage of reaction. In the present, the two-stage reaction may have resulted from the lower generation of $Fe^{2+}$ from $Fe^{3+}$ in equation (2-7) to(2-10) and the complication of $Fe^{3+}$and degradation intermediates (Lu et al., 1999).

Table 2.8 Rate constant of Fenton’s reactions (Kang et al., 2002)

| **Reaction** | **k( $M^{-1}s^{-1}$)** |
|---|---|
| $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \bullet OH + OH^-$ | 63 |
| $Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2\bullet + H^+$ | 0.01 |
| $\bullet OH + H_2O_2 \longrightarrow HO_2\bullet + H_2O$ | $2.7 \times 10^7$ |
| $HO_2\bullet \longrightarrow O_2^{-\bullet} + H^+$ | $1.58 \times 10^5$ |
| $O_2^{-\bullet} + H^+ \longrightarrow HO_2\bullet$ | $1.0 \times 10^{10}$ |
| $\bullet OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^-$ | $3.2 \times 10^8$ |
| $HO_2\bullet + Fe^{2+} (+ H^+) \longrightarrow Fe^{3+} + H_2O_2$ | $1.2 \times 10^6$ |
| $HO_2\bullet + Fe^{3+} \longrightarrow Fe^{2+} + O_2 + H^+$ | $3.1 \times 10^5$ |
| $O_2^{-\bullet} + Fe^{2+} (+ 2H^+) \longrightarrow Fe^{3+} + H_2O_2$ | $1.0 \times 10^7$ |
| $O_2^{-\bullet} + Fe^{3+} \longrightarrow Fe^{2+} + O_2$ | $5 \times 10^7$ |
| $\bullet OH + \bullet OH \longrightarrow H_2O_2$ | $4.2 \times 10^9$ |
| $HO_2\bullet + HO_2\bullet \longrightarrow H_2O_2 + O_2$ | $8.3 \times 10^5$ |
| $\bullet OH + HO_2\bullet \longrightarrow H_2O + O_2$ | $1.0 \times 10^{10}$ |
| $\bullet OH + O_2^{-\bullet} \longrightarrow OH^- + O_2$ | $1.0 \times 10^{10}$ |
| $HO_2\bullet + O_2^{-\bullet} (+ H^+) \longrightarrow H_2O_2 + O_2$ | $9.7 \times 10^7$ |

Huang et al. (1993) summarized the major advantages of using Fenton’s process over other oxidation processes to treat hazardous wastes:

1) There are no chlorinated organic compounds formed during the oxidation process as in chlorination.
2) Both iron and hydrogen peroxide are inexpensive and non-toxic.
3) There are no mass transfer limitations because the reaction is homogeneous.
4) No light is required as a catalyst and, therefore, the design is much simpler than ultraviolet light systems.
5) Hydrogen peroxide can be electrochemically generated in situ, which may further increase the economic feasibility and effectiveness of this process for treating contaminated sites.

The factor affect the efficiency of Fenton's reaction are wastewater characteristics such as phosphates, EDTA, formaldehyde and citric/oxalic acids. Because of the sensitivity of Fenton system to different wastewaters, it is recommended that the reaction should always be characterized through laboratory treat ability tests before proceeding to a plant scale.

### 2.3.4 Type of Fenton Processes (Parsons, 2004)

#### 2.3.4.1 Homogeneous processes

When all the reactants are presents in the dissolved phase, the process is said to be homogeneous. These processes may still, however, lead to the precipitation of some insoluble species, such as metal hydroxides, but this is not part of the main process. The example of homogenous Fenton processes are : Fenton processes (Fe(II) /$H_2O_2$ /dark), Photo-Fenton processes (Fe(II) /$H_2O_2$ /light), Fenton-like reagent (Cu(I), Co(II), Ti(III)).

#### 2.3.4.2 Heterogeneous processes

The source of iron used as a catalyst for the Fenton process can be a solid surface, including iron-containing minerals or iron-coated silica particles (sand), as well as iron adsorbed onto zeolites.

A major disadvantage of wastewater treatment by homogenous Fenton process is that the iron must usually be removed from the water after treatment is complete. This can usually be achieved the pH of the solution, however this can lead to the production of large volumes of iron-containing sludge. Heterogeneous Fenton processes are of particular interest, since most of the iron remains in the solid phase. The solid phase is usually granular (iron oxides, sand or zeolites), hence the treated water is easily separated from the iron. The example of heterogeneous Fenton processes are: Iron oxide catalyst, goethite, iepidocrocite, hematite, limonite and magnetite.

### 2.3.5 Effect of Substances and Conditions in the Fenton Process

#### 2.3.5.1 Effect of Iron Concentration

In the absence of iron, there is no evidence of hydroxyl radical formation, for example, $H_2O_2$ is added to a phenolic wastewater (i.e., no reduction in the level of phenol occurs). As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes inefficient. This feature (an optimal dose range for iron catalyst) is characteristic of Fenton's Reagent, although the definition of the range varies between wastewaters.

Three factors typically influence its definition (Walling, 1975):

1. A minimal threshold concentration of 3-15 mg/L Fe which allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material.
2. A constant ratio of Fe: substrate above the minimal threshold, typically 1 part Fe per 10-50 parts substrate, which produces the desired end products. (the ratio of Fe: substrate may affect the distribution of reaction products)
3. A supplemental aliquot of Fe which saturates the chelating properties in the wastewater, thereby availing unsequestered iron to catalyze the formation of hydroxyl radicals.

However, the ferrous ion and hydrogen peroxide not only react to form hydroxyl radicals, but also scavengers of hydroxyl radicals. The ratio of $H_2O_2$ to $Fe^{2+}$ should affect the rate of hydroxyl radical production and scavenging. Therefore it is important to use the optimum $H_2O_2$ to $Fe^{2+}$ concentration (Parson, 2004) Generally, iron dose is expressed as a ratio to hydrogen peroxide dose. Typical ranges are 1 part Fe per 5-25 parts $H_2O_2$ (wt/wt) ($Fe^{2+}$: $H_2O_2$ = 1:5-1:25).

#### 2.3.5.2 Effect of Iron Type (Ferrous or Ferric)

For most applications, it does not matter whether $Fe^{2+}$ or $Fe^{3+}$ salts are used to catalyze the reaction. The catalytic cycle begins quickly if $H_2O_2$ and organic material are in abundance. However, if low doses of Fenton's Reagent are being used (e.g., < 10-25 mg/L $H_2O_2$), Bishop (1968) suggests that ferrous iron may be preferred (Bishop et al.,1968). Neither does it matter whether a chloride or sulfate salt of the iron is used, although with the former, chlorine may be generated at high rates of application. It is also possible to recycle the iron following the reaction. This can be done by raising the pH, separating the iron sludge, and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

#### 2.5.3.3 Effect of $H_2O_2$ Concentration

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory for each waste to be treated. For example, in a typical application the following series of reactions will occur (US. Peroxide,2008):

**Substrate ⇨ Oxidized ⇨ Oxidized ⇨ Oxidized ⇨ Oxidized ⇨ $CO_2$**
**Intermediate Intermediate Intermediate Intermediate**
**“A” “B” “C” “D”**

Each transformation in this series has its own reaction rate and is frequently seen when pretreating a complex organic wastewater for toxicity reduction. As the $H_2O_2$ dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, where upon further addition of $H_2O_2$ results in a rapid decrease in wastewater toxicity.

#### 2.3.5.4 Effect of Temperature

Temperature is one of the important parameters in Fenton’s reaction. The rate of reaction with Fenton’s Reagent increases with increasing temperature, with the effect more pronounced at temperatures < 20 $^{O}$C. However, as temperatures increase above 40-50 $^{O}$C, the efficiency of $H_2O_2$ utilization declines due to the accelerated decomposition of $H_2O_2$ into oxygen and water. As a practical, most commercial applications of Fenton’s reagent occur at temperatures between 20-40 $^{O}$C. Applications of Fenton’s Reagent for retreating high strength wastes may require controlled or sequential addition of $H_2O_2$ to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when $H_2O_2$ doses exceed 10-20 g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well (US. Peroxide, 2008).

### 2.3.5.5 Effect of pH

The effect of pH on reaction efficiency is illustrated below:

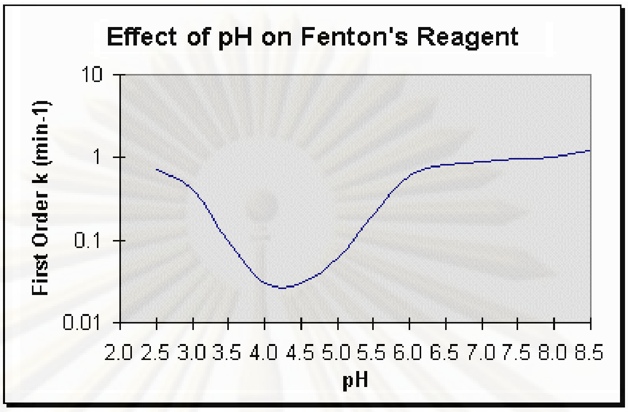


Figure 2.2 Effect of pH on Fenton’s Reagent (US. Peroxide, 2008)

The optimal pH occurs between pH 3 and pH 6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the $H_2O_2$ into oxygen and water, without forming hydroxyl radicals. There have been some recent developments using non-radical scavenging sequestering agents (e.g., NTA and gallic acid) to extend the useful pH range to pH 8-9, but no commercial applications are known. The drop in efficiency on the acid side is less dramatic given the logarithmic function of pH, and is generally a concern only with high application rates.

A second aspect of pH deals with its shift as the reaction progresses. Provided an initial wastewater pH of 6.0, the following profile is typical of Fenton reactions. The first inflection is caused by the addition of $FeSO_4$ catalyst which typically contains residual $H_2SO_4$. A second, more pronounced drop in pH occurs as the $H_2O_2$ is added, and continues gradually at a rate which is largely dependent on catalyst concentration. This drop in pH is attributed to the fragmenting of organic material into organic acids. This pH change is often monitored to ensure that the reaction is progressing as planned -- the absence of such a pH decrease may mean that the reaction is inhibited and that a potentially hazardous build-up of $H_2O_2$ is occurring within the reaction mixture.

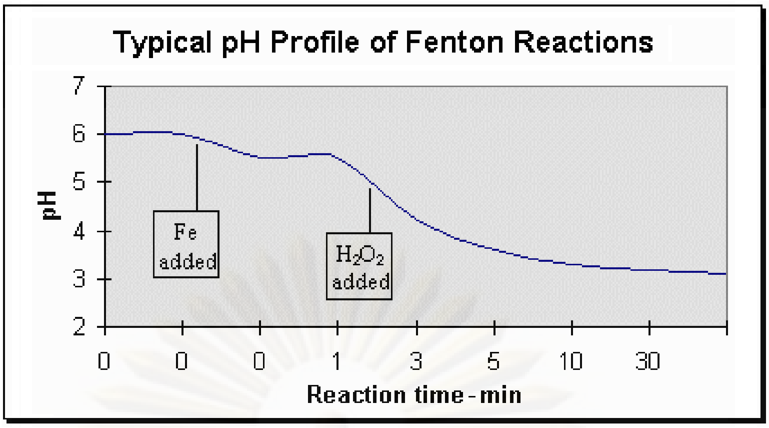


Figure 2.3 Typical pH profile of Fenton reactions(US. Peroxide , 2008)

In highly concentrated waste streams (>10 g/L COD), it may be necessary to perform the oxidation in steps, readjusting the pH upwards to pH 4-5 after each step so as to prevent low pH from inhibiting the reaction.

### 2.3.5.6 Effect of Reaction time

The time needed to complete a Fenton reaction will depend on the many variables discussed above, most notably catalyst dose and wastewater strength. For simple phenol oxidation (less than 250 mg/L), typical reaction times are 30 - 60 minutes. For more complex or more concentrated wastes, the reaction may take several hours.

Determining the completion of the reaction may prove troublesome. The presence of residual $H_2O_2$ will interfere with many wastewater analyses. Residual $H_2O_2$ may be removed by raising the pH to e.g., pH 7-10, or by neutralizing with bisulphate solution. Often, observing color changes can used to assess the reaction progression. Wastewaters will typically darken upon $H_2O_2$ addition and clear up as the reaction reaches completion.

#### 2.3.5.7 Effect of Post Treatment

As a result of degrading complex organic materials into organic acid fragments, the pre-oxidized effluent is generally more amenable to conventional treatment, e.g., flocculation and biotreatment. The presence of iron in the reaction mixture makes it particularly suited to subsequent lime flocculation. In many cases, it may be possible to remove up to 80% of the wastewater COD through a combination of Fenton's Reagent and lime flocculation. Significantly, this may be achieved with an $H_2O_2$ dose of 50-75% of the stoichiometry.

#### 2.3.5.8 Effect of inorganic anion concentration

Fenton oxidation of organic compounds is inhibited in varying degrees by phosphate, sulfate, fluoride, bromide and chloride ions, depending on their concentrations. Such anions may be present initially in the wastewater or formed as end products from the compounds undergoing degradation. Inhibition by these species may be due to precipitation of iron, scavenging of •OH , or coordination to dissolved $Fe^{3+}$ to form a less reactive complex which led decreasing in the degradation rates by a Fenton process.

Lu et al., 1997 cited in Parsons 2004 found that anions suppresses the degradation of dichlorvos by $Fe^{2+}/H_2O_2$ in order $H_2PO_4^- >> Cl^- > NO_3^- \approx ClO_4^-$ . The inhibition by $H_2PO_4^-$ was attributed to the information of unreactive $Fe^{3+}$ complexes. It can be seen that the Fenton reaction is extremely sensitive to anions. Phosphate ions in particular will seriously suppress the Fenton system's ability to oxidize dichlorvos.

In a study of the degradation of 2,4-dichorophenoxyacetic acid (2,4-D) by $Fe^{3+}/H_2O_2$, Pignatello, 1992 cited in Parsons 2004 found that the inhibition of 2,4-D degradation followed the order $SO_4^{2-} \approx Cl^- >> NO_3^- \approx ClO_4^-$ , whereas the inhibition of $Fe^{3+}$ – catalyzed decomposition of $H_2O_2$ followed the order $SO_4^{2-} >> Cl^- > NO_3^- \approx ClO_4^-$. It was concluded that sulphate ligands reduced the reactivity of $Fe^{3+}$, while chloride was responsible for hydroxyl radical scavenging.

### 2.3.6 Fluidized-bed Fenton Process

Fenton reaction has been widely used in degradation of various organic contaminants in industrial wastewater. Although Fenton's reaction has provide a highly reactive oxidants, •OH , but the major problem in Fenton process is the production of a significant amount of iron hydroxide sludge that requires further separation and disposal.

The fluidized-bed Fenton process is one of alternatives to ease the production of a substantial amount of ferric precipitation, the major disadvantage of Fenton's reagent. The carriers in fluidized-bed Fenton reactor can reduce iron precipitate via crystallization process to from iron oxide species onto their surface (Chou et al., 2004).

Fluidized-bed is used to transform $Fe^{3+}$ generated in Fenton reaction into an iron oxide such as FeOOH. Iron oxide is generated on the carrier surface by crystallization or sedimentation (Hsueh et al., 2006). Moreover, the FeOOH synthesized in the reaction can act as a heterogeneous catalyst of the decomposition of $H_2O_2$ (Chou et al., 2001). The factors that effect on the adsorption of iron oxide at the surfaces of fluidized-bed carrier are pH, specific iron loading, $Fe^{2+}$/ $H_2O_2$ ratio, and superficial velocity (Chou et al., 2004). Many studies using iron oxide catalyst to treat organic contaminants were performed in batch reactors. Although the batch reactors are quite simple, there are some disadvantages about the operation time of each batch and the amount of wastewater.

In fluidized-bed Fenton reactor (FBR), several processes occur simultaneously including:

(a) Homogeneous chemical oxidation ($H_2O_2$ /$Fe^{2+}$)
(b) Heterogeneous chemical oxidation ($H_2O_2$/iron oxide)
(c) Fluidized-bed crystallization
(d) Reductive dissolution of iron oxides

The factors that effect on the adsorption of iron oxide at the surfaces of fluidized-bed carrier are pH, specific iron loading, $H_2O_2/Fe^{2+}$, and superficial velocity (Chou et al., 2004). As figure 3.2 illustrates several processes simultaneously occur in fluidized-bed Fenton reaction. The Fenton's reagents produce the non-selective oxidant, •OH, via homogeneous reaction (a). Then, this strongly oxidant attacks the aromatic hydrocarbon to initiate ring opening in oxidation reaction (b). After that, the intermediate products from previous reaction appears, these lead into further oxidation (c). $Fe^{3+}$ can be converted from the reducing one electron of $Fe^{2+}$ in Fenton's reaction (d). Some $Fe^{3+}$ can also convert back to $Fe^{2+}$ by reacting with $H_2O_2$ or $HO_2$• and initiate Fenton reaction further as reaction (h). However, in the presence of solid carrier, the ferric hydrolysis product from Fenton's reaction can also crystallize and adsorb on the surface of the carriers via reaction (e); therefore, a substantial amount of ferric hydroxide from was decreased (Chou et al., 1999a). At the same time, the synthesized ferric oxide can also serve as a catalyst for hydrogen peroxide decomposition in heterogeneous reaction (i) (Chou et al., 2003). By this step, the •OH generated can go further in organic compound degradation. When, considering iron oxide on the surface carriers, can re-dissolve via reductive dissolution (g) or heterogeneous reaction (f) also to become $Fe^{2+}$ form. In acidic environment, iron species can reform by the way ferric can alter to ferrous form also (d).

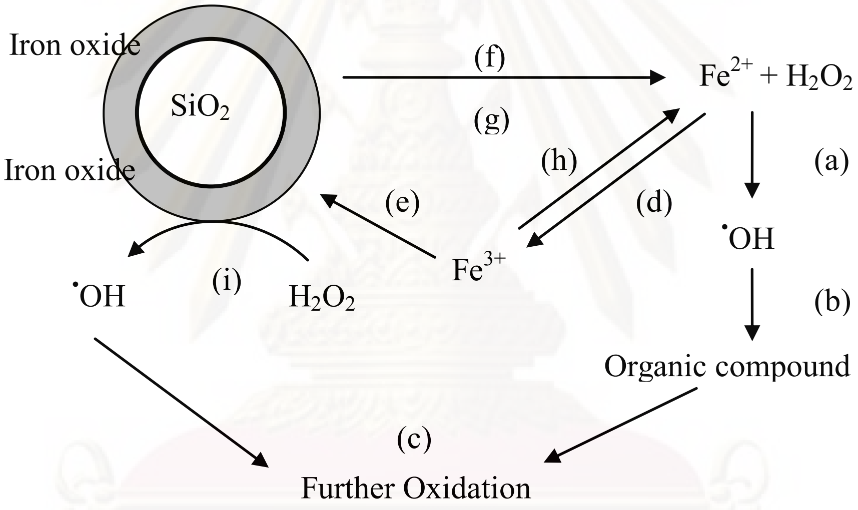


Figure 2.4 Fluidized-bed Fenton reactions (Chou et al., 2004)

Fluidized-bed Fenton process lets ferric ion ($Fe^{3+}$), produced in the Fenton reaction, be transformed into iron oxide (FeOOH) and accumulated on the carrier surface via the crystallization or sedimentation. This process combines the functions of homogeneous chemical oxidation ($H_2O_2/Fe^{2+}$), heterogeneous chemical oxidation ($H_2O_2$/iron oxide), Fluidized-bed crystallization, and reductive dissolution of iron oxide. This process not only attains high COD removal efficiency but also reduces the large amount of iron sludge. Furthermore, iron oxide synthesized from the reaction of hydrogen peroxide and ferrous ion can also be used as the heterogeneous catalyst of hydrogen peroxide (Chou et al., 2003).

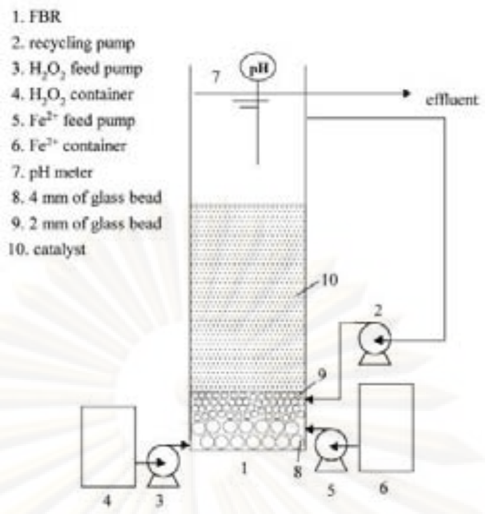


Figure 2.5 Fluidized-bed Reactor (Chou et al., 2003)

Key factors in the design of fluidized-bed Fenton process are (Chintitanun, 2007):

- Selection of the carrier, including the material, gravity and particle size.
- Design of distributors.
- Superficial velocity
- Feed mode and dosage of Fenton's reagent (hydrogen peroxide and ferrous ion).
- Size, configuration and recycle ratio of reactor.

## 2.4 **Silica dioxide** (CERAM Research, 2001)

Silicon Dioxide or Silica, is one of the most common chemical compounds. $SiO_2$ crystals are found in nature in three polymorphic forms, the most common of which is quartz, sand, agate, onyx, opal, amethyst and flint are silicon dioxide with traces of impurities. It is insoluble in water, slightly soluble in alkaline, and soluble in dilute hydrofluoric acid. Pure silica is colorless to white. Silica occurs commonly in nature as sandstone, silica sand or quartzite. Silica is one of the most abundant oxide materials in the earth's crust. It can exist in an amorphous form (vitreous silica) or in a variety of crystalline forms. Often it will occur as a non-crystalline oxidation product on the surface of silicon or silicon compounds.

Silica has many important uses. It is used as a filler for paint and rubber; in making ordinary glass; in ceramics; in construction; and in the preparation of other substances, e.g., silicon carbide. Furthermore, it is the starting material for the production of silicate glasses and ceramics. Fused quartz is pure amorphous silica; it is used in special chemical and optical apparatus. Unlike ordinary glass, it does not absorb infrared and ultraviolet light.

Silica sand has been proved to be good media for mineral coating, especially iron oxides (Scheidegger et al., 1993); therefore, silica sand is suitable to be used for removing $Fe^{3+}$ form Fenton process. The properties of $SiO_2$ are shown in Table 2.9

Table 2.9 Physical and Chemical Properties of Silica dioxide (Wells, 1984; Greenwood and Earnshaw, 1997).

| **General** | |
|---|---|
| Other names | Silica quartz |
| **Identifiers** | |
| CAS number | 7631-86-9 |
| Chemical spider ID | 22683 |
| **Properties** | |
| Molecular formula | $SiO_2$ |
| Molecular weight | 60.08 g/mol |
| Appearance | White or colorless crystal |
| **Properties** | |
| Density | 2.2 g/$cm^3$ |
| Melting point | 1650 (± 75)°C |
| Boiling point | 2230 °C |
| Solubility in water | 0.012 g/100 ml |
| **Properties** | |
| Structure | Crystal structure |
| Molecular shape | Linear ( gas-phase) |
| **Hazards** | |
| EU index | Not listed |
| Main hazard | Inhalation of fine powders can damage the respiratory tract |
| Flash point | Non-flammable |

| Related compounds | |
|---|---|
| Other ions | Silicon sulfide |
| Other cations | Carbon dioxide, Germanium dioxide<br>Tin dioxide , Lead dioxide |
| Related silicon oxides | Silicon monoxide |
| Related compounds | Silica acid “ Silica gel” |

## 2.5 Statistical Experimental Design Methodology

The traditional approach has only focus on the basic single--factor-at-a-time approach. By this process, studying the effect of each experimental parameter on the process performance while keeping all other conditions constant. However, this approach does not take into account cross-effects from the factors considered and leads to a poor optimization result. To deal with this problem, the use of statistically based strategies has proven to be quite advantageous, allowing the use of the minimum number of experiments while simultaneously changing several variables. Statistical design of experiments reduces the number of experiments to be performed, considers interactions among the variables and can be used for optimization of the operating parameters in multivariable systems (Ay et al., 2009). The design of experiments (DOE) methodology is a modern approach, which has been widely used in several applications including process modeling. Instead of the process optimization, the design of experiments (DOE) is used to identify or screen the important factors affecting a process or product and to develop statistically significant empirical models (Ramirez et al., 2005).

Response surface methodology (RSM) is used when only several significant factors are involved in optimization. The main idea of RSM which is an efficient statistical technique for optimization of multiple variables with the minimum number of experiment is to use a set of designed experiments to obtain an optimal response (Krishna et al., 2000, Vohra and Satyanarayana, 2002 and Francis et al., 2003). Different types of RSM designs include three-level factorial design, central composite design (CCD), Box-Behnken and D-optimal designs.

The Box-Behnken design is an independent, rotatable quadratic design with no embedded factorial or fractional factorial points where the variables combinations are at the midpoints of the edges of the variable space and at the center. Among all RSM designs, Box-Benhken design require fewer runs than the others. The number of experiments required for Box-Behnken design is defined as:

$$N = 2k(k-1) + C_0 \qquad (2\text{-}13)$$

where N is the number of experiments

k is the number of factors

$C_0$ is the number of central points (which usually is 5)

For three factors with three levels (high, center, and low), the graphical representation of Box-Behnken design can be seen in a cube form, as shown in Figure 2.6. From this figure, the cube consists of the central point and the middle points of the edge. The $X_1$, $X_2$, and $X_3$ represent the value for each of three factors. The sum of all point in Figure 2.6 is the number of experimental runs, which is equal to the calculation from equation 2-13.

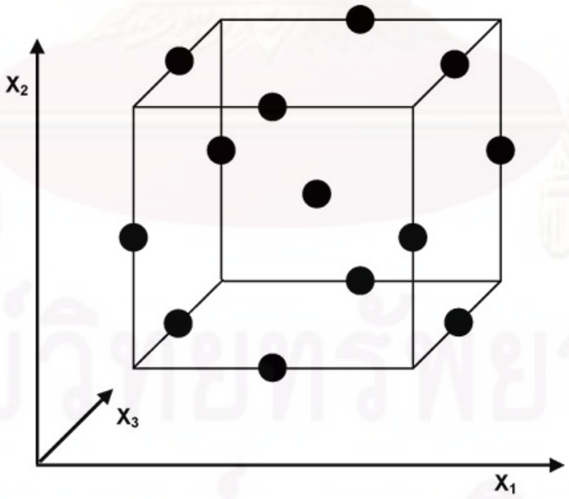


Figure 2.6 A cube for Box-Behnken design with three factors (Ferreira et al., 2007)

For four factors with three levels (high, center, and low), the coded values of factor levels for Box-Behnken design can be described in table 2.10. From this table, the cube consists of the central point and the middle points of the edge. The $X_1$, $X_2$, $X_3$ and $X_4$ represent the four factors while -1,0 and +1 represent coded in the minimum, center and maximum of three levels. The sum of all coded in table 2.10 is the number of experimental runs, which is equal to the calculation from equation 2-13. Another advantage of the Box-Behnken is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. So these designs are useful in avoiding experiments performed under extreme conditions, for which unsatisfactory results might occur.

Table 2.10 Coded factor levels for Box-Behnken designs for optimization involving four factors.

| Four-factors | | | |
|---|---|---|---|
| X1 | X2 | X3 | X4 |
| ±1 | ±1 | 0 | 0 |
| 0 | 0 | ±1 | ±1 |
| 0 | 0 | ±1 | ±1 |
| ±1 | 0 | 0 | ±1 |
| 0 | ±1 | ±1 | 0 |
| 0 | 0 | 0 | 0 |
| ±1 | 0 | ±1 | 0 |
| 0 | ±1 | 0 | ±1 |
| 0 | 0 | 0 | 0 |

## 2.6 Literature Reviews

### 2.6.1 Degradation of 2,4-dichlorophenol by Advanced Oxidation Processes.

Doocey et al. (2004) studied zeolite-mediated advanced oxidation of model chlorinated phenolic aqueous waste. In the experimental, the adsorption of 2,4-dichlorophenol (2,4-DCP) in aqueous solution onto zeolites Beta and Y at 20°C. The Fenton oxidation of 2,4-DCP without zeolite was investigated at pH 3.5. The effect of model inorganic and organic "scavenger" on the adsorption process was investigated using 0.1 M sodium sulphate and 1 and 10% acetone as the "scavenger". They found that Fenton's reagent was shown to be an effective advanced oxidation process for treatment of a 2,4-DCP aqueous water stream. Zeolites Bata and Y were found to be effective selective adsorbents for these pollutions in order to improve the efficiency of an advanced oxidation process by eliminating "scavenger" effects. The former zeolite, although having a lower adsorption capacity than Y, exhibited the preferred adsorption behaviour. Furthermore, an adsorption column packed with zeolite Beta was a successful adsorbent for 2,4-DCP in an aqueous waste stream and could be successfully regenerated using Fenton's reagent.

Momani et al. (2004) studied on the degradation of 2,4-dichlorophenol by Advanced Oxidation Processes through UV, UV/$H_2O_2$, Fenton and photo-Fenton processes. The effects on degradation of difference reactant concentrations, irradiation time, temperature and pH were assessed. The experimental result showed that UV photolysis was less efficient for total DCP degradation than other AOPs. The photo-Fenton and Fenton reactions can be used successfully for the total DCP degradation. The degradation rate was influenced by many factors, such as initial hydrogen peroxide concentration, initial iron concentration , pH , temperature and initial DCP concentration. From all the processes studied, The photo-Fenton reaction showed the best efficiency in DCP elimination, chlorine ion release and in the change of oxidation state. Sixty minutes of treatment were sufficient for 100% DCP removal with 75 $mgl^{-1}$ $H_2O_2$ and 10 $mgl^{-1}$ Fe(II) initial concentrations. In these conditions, a first-order degradation constant for DCP of 0.057 $min^{-1}$ was obtained.

Li et al. (2007) investigated on degradation of 2,4-Dichlorophenol in aqueous solution by hybrid oxidation process which consists of three functional electrodes : a $TiO_2$/Ti sheet as the anode, a steel (Fe) sheet as another anode in parallel and a piece of graphite felt (GF) as the cathode. While an electrical current is applied between the Fe anode and GF cathode and UV light is irradiated on the surface of $TiO_2$/Ti anode, both of E-Fenton reaction and photoelectrocatalytic (PEC) reaction are involved simultaneously. Experimental results confirmed that 2,4-DCP in aqueous solution was successfully degraded by 93% and mineralized by 78% within 60 min in such a hybrid oxidation process. When a current intensity of 3.2 mA was applied on the GF cathode, the current efficiency for $H_2O_2$ generation was determined to be 61%. Furthermore, the experimental demonstrated that combination of E-Fenton reaction with photocatalytic reaction let the process be less pH sensitive and can be applied under a more neutralized pH condition, which would be favorable to water and wastewater treatment in practice.

Zhao at el. (2007) applied a novel $TiO_2$/Ti-Fe-graphite felt photoelectrocatalytic (PEC) oxidation process to treat 2,4-Dichlorophenol. $H_2O_2$ was produced nearby cathode and $Fe^{2+}$ continuously generated form Fe anode in solution when current and $O_2$ were applied. In this integrative process, $H_2O_2$ conducting $H_2O_2$-assisted $TiO_2$ PEC and ferrous conducting E-Fenton reaction were produced by process itself. The factors influencing the degradation rate such as applied current, flow speed of $O_2$ , pH, adscititious voltage and initial 2,4-DCP concentration were investigated and optimized. The degradation ratio of 2,4-DCP was 93% in this integrative process, while it was only 31% in E-Fenton process and 46% in $H_2O_2$- assisted $TiO_2$ PEC process. By the investigation of pH, it showed that this integrative process could work well in a wide pH range from pH 3 to pH 9. In addition, the whole integrative reaction abided by first-order kinetics. A clear conclusion was gotten that the combination of E-Fenton and $H_2O_2$- assisted $TiO_2$ PEC oxidation could boots the degradation of 2,4-DCP.

Zhou et al. (2008) investigated the effect of ultrasound (US) enhancement on the degradation of 2,4-Dichlorophenol in a new Fenton like system (Fe/EDTA). An obviously synergistic effect was observed after introduction of US into the Fe/EDTA system. From the same operating conditions of pH, US input power, iron and EDTA dosage showed the decomposition of DCP was followed the sequence of US/Fe/EDTA > Fe/EDTA > US/Fe > Us alone. It was demonstrated that the degradation of DCP in US/Fe/EDTA , Fe/EDTA and US system all followed pseudo-first-order kinetic with the $k_{obs}$ being 0.0725, 0.0094 and 0.0022 $min^{-1}$, respectively. At 60 minute reaction time, removals of 81% TOC , complete DCP and 89% EDTA were achieved. Low molecular weight organic acids are identified as the main products , which contribute to the solution self-buffer at about pH 6.5 along with the reaction. In addition, the effect of initials condition ,i.e., iron addition, EDTA dosage, DCP concentration and US input power as well as reaction temperature were studied and reaction activation energy (Ea) was also calculated.

### 2.6.2 The degradation of various chemical by Fenton Processes.

Chamarro et al. (2001) used Fenton reagent to improve organic chemical biodegradability. They has been used Fenton reagent to test the degradation of different organic compounds (formic acid, phenol, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene) in aqueous solution. A stoichiometric coefficient for the Fenton reaction was found to be 0.5 mol of organic compound/mol of hydrogen peroxide, except for the formic acid where a value of approximately one was obtained (due to the direct formation of carbon dioxide). The treatment eliminates the toxic substances and increases the biodegradability of the treated water (measured as the ratio $BOD_5$/COD). Biodegradability is attained when the initial compound is removed. Moreover , it is found that there are two important factors affecting the rate of Fenton's reaction: peroxide dose and iron concentration. The peroxide dose is important in order to obtain a better degradation efficiency, while the iron concentration is important for the reaction kinetics.

Kang et al. (2002) evaluates the Fenton process, involving oxidation and coagulation, for the removal of color and chemical oxygen demand (COD) from synthetic textile wastewater containing polyvinyl alcohol and a reactive dyestuff, R94H. This study reported that the removal of color by Fenton process requires relatively lower dosages of $H_2O_2$ and $Fe^{2+}$ ,whereas, much higher dosages of both $H_2O_2$ and $Fe^{2+}$ are necessary to obtain the same level of COD removal. The four reaction modes at same iron dosage, the color removal follow the decreasing order :

Fenton oxidation > Fenton-like oxidation > ferric coagulation > ferrous coagulation. The color removal is more sensitive to deteriorate at relatively low and high levels of COD, but not at medium COD level. It is concluded that Fenton process for the treatment of textile wastewater favors the removal of color rather than COD.

Lu et al. (1999) investigated on the decomposition of dichlorovos insecticide by Fenton process. The results told that dichlorovos decomposed through 2-stage reaction . The first stage is a $Fe^{2+}$/ $H_2O_2$ reaction in which dichlorovos decomposed swiftly. In the second stage, dichlorovos decomposed less rapidly than first stage. The detection of ferrous ions also supports the theory of 2-stage reaction for the oxidation of dichlorovos by Fenton's reagent. The dissolved oxygen of the solution decreased rapidly than first stage reaction, but it slowly increases in the second stage with a zero-order kinetics. The increasing of concentration of hydrogen peroxide or ferrous ion can enhance the decomposition of dichlorovos.

Sun et al. (2007) examined a kinetic study on the degradation of *p*-nitroaniline by Fenton oxidation process. Batch experiments were carried out to investigate the role of pH, hydrogen peroxide and $Fe^{2+}$ levels, PNA concentration and the temperature. The result show that the decomposition of PNA proceeded rapidly only at pH value of 3.0. Increasing the dosage of $H_2O_2$ and $Fe^{2+}$ enhance the $k_{ap}$ of PNA degradation. However, higher levels of $H_2O_2$ also inhibited the reaction kinetics. The $k_{ap}$ of PNA degradation decreased with the increase of initial PNA concentration, but increased with the increase of temperature. Based on the rate constants obtained at different temperatures, the empirical Arrhenius expression of PNA degradation was derived. The derived activation energy for PNA degradation by Fenton oxidation is 53.96 $kJmol^{-1}$.

Wang et al. (2008) applied a full-scale combined treatment plant for jean-wash wastewater (JWW). This combined process consisted of coagulation, hydrolysis/acidification and Fenton oxidation. Chemical coagulation treatment with polymeric ferric sulfate (PFS)/ lime alone proved to be effective in removing the COD (> 70%) and part of the color (> 50%) from the JWW. Fenton oxidation combined with hydrolysis/acidification as pretreatment offered a noticeable BOD removal efficiency. The average removal efficiencies for COD, BOD, SS , color and aromatic compounds of the combined process were about 95%, 94%, 97%. 95% and 90%, respectively, with the average effluent quality of COD 58 mg/l , BOD 19 mg/L , SS 4 mg/L and color 15 (multiple), consistent with the national discharge limits for textile wastewater. The result indicated that the combined procedure could offer an attractive solution for JWW treatment with considerable synergistic advantages.

Wang et al. (2008) investigate the treatment of a surfactant wastewater containing abundant sulfate by Fenton oxidation and aerobic biological processes. The optimum operating conditions for the Fenton oxidation process were working at initial pH value of 8 , a Fe $^{2+}$ dosage of 600 mgL$^{-1}$ and a $H_2O_2$ dosage of 120 mgL$^{-1}$ .The chemical oxygen demand (COD) and linear alkylbenzene sulfonate (LAS) were decreased from 1500 and 490 mgL$^{-1}$ to 230 mgL$^{-1}$ and 23 mgL$^{-1}$ after 40 min for Fenton oxidation respectively. Moreover, Fenton oxidation pretreatment was also highly effective at enhancing the biodegradability of wastewater . It was found that the COD and LAS of the final effluent were less than 100 and 5 mgL$^{-1}$ after aerobic biological process based on an immobilized biomass reactor with a HRT of 20 h.

### 2.6.3 The application of Fluidized-bed Fenton reactor (FBR)

Chen at el. (2007) applied a moving-bed biofilm reactor combine with Fenton-coagulation as a pretreatment to treat of pesticide wastewater. It was found that Fenton process can not only reduce COD to a desired degree but also improve the biodegradability for the subsequent biological treatment. The experimental results indicated that the optimum value of $H_2O_2$ dosage was 97 mmol/L and Fe $^{2+}$ dosage was 40 mmol/L at initial pH 3. The interaction mechanism of organophosphorous pesticide and hydroxyl radicals was suggested to be the breakage of the P=S double bond and formation of sulfate ions and various organic intermediates. With the improvement of biodegradability by using Fenton pretreatment, also due to the high concentration of biomass and high biofilm activity using fluidizing bio-carriers, high removal efficiency and stable operation could be achieved in the biological process even at a high COD loading of 37.5 gCOD/(m$^2$ carrier day)

Chou and Huang (1999a) investigated the effect of Fe$^{2+}$ on catalytic oxidation in the Fluidized-bed reactor applying supported $\gamma$ -FeOOH as the carrier. Processes without Fe$^{2+}$ addition and with Fe$^{2+}$ addition (FBR-Fenton method) were performed on the oxidation of benzoic acid (BA) by $H_2O_2$. When Fe$^{2+}$ was not added in the FBR, the dissolve Fe and the removal efficiency of COD at low pH are higher than those at medium pH which caused by homogeneous catalysis of $Fe^{2+}$ formed via reductive dissolution of $\gamma$-FeOOH. In the FBR-Fenton process, they found that both mineralization of organics and crystallization of Fe(III) were simultaneously well performed under adequate condition. Moreover, the reductive dissolution and crystallization of $\gamma$-FeOOH as well as the oxidation of BA was proposed based on the experimental results.

Chou and Huang (1998) studied the application of a supported iron oxyhydroxide catalyst in oxidation of benzoic acid by hydrogen peroxide. They found that $\gamma$-FeOOH absorbed up to 11% of the input benzoic acid in the absence of hydrogen peroxide. The treatment efficiency of benzoic acid at an initial pH of 3.2 was higher than at initial pHs of 6.0 and 10.0 which could partly explained by reductive dissolution of $\gamma$-FeOOH . Beside, the majority of mineralization of benzoic acid take placed on the catalyst surface through heterogeneous catalysis, with some occurred in the aqueous phase through homogeneous catalysis. Without benzoic acid, hydrogen peroxide is decomposed primarily on the catalyst surface. The decomposition rate followed a first-order kinetics and appears to increase as pH increase in the heterogeneous catalysis system.

Chou et al. (2004) investigated factors influencing the preparation of supported iron oxide in fluidized-bed crystallization reactor. In terms of the crystallization conditions of FeOOH, some parameters including the operational pH, specific iron loading , $H_2O_2/Fe^{2+}$ ratio, and superficial velocity, have been demonstrated to affect the crystallization efficiency. Two types of FeOOH catalysts were synthesized : FeOOH I was prepared at pH 3.5, and FeOOH II was formed by aging FeOOH I at pH 13. The percentages of surface amorphous FeOOH reduced from 70% to 30 % after aging. The FeOOH II catalyst presented a higher reactivity toward $H_2O_2$ but lower stoichiometric efficiency in oxidizing benzoic acid than FeOOH I, similar to the result of the commercial goethite. Therefore, it is conclude that the crystalline property significantly affects the performance of catalytic oxidation.

Chintitanun (2007) investigated the chloride ions affecting nitrobenzene oxidation by Fenton's reagent. Fluidized-bed experiments were carried out to investigated the effects of pH, $Fe^{2+}$, $H_2O_2$ and chloride concentration on the oxidation reaction. Result showed that the best efficiency for nitrobenzene oxidation by Fluidized-bed Fenton process was used $Al_2O_3$ as the carrier which has the $pH_{pzc}$ of 9.16 and size of 2.50 mm. Optimum pH for nitrobenzene was 2.8. The removal efficiency oxidation of nitrobenzene by fluidized-bed Fenton process was better than Fenton process. However, the inhibition effect by chloride ions can be overcome by extending the reaction time if the concentration of chloride ions is at low level. If the ratio of $[Cl^-]/[Fe^{2+}]$ was ≤ 200, the inhabitation effect was very significant. In other words, adding more ferrous ions rather than hydrogen peroxide can break the inhibition originating from the chloride ions at the initial stage of pH 2.8. Moreover, The extent of inhibition decreased with increasing the initial pH as long as the pH was less than 6.

Hsueh et al. (2006) applied a novel catalyst of the photoassisted Fenton degradation of azo-dye (Reactive Black 5). The catalyst greatly promotes not only the decolorization but also the mineralization of RB5 at neutral pH. Furthermore, this catalyst is much cheaper than Nafion-based catalysts and can markedly accelerate the degradation of RB5 under irradiation by UVA ($\lambda$ = 365 nm). The effects of the molar concentration of $H_2O_2$, the pH of the solution and the catalyst loading on the degradation of RB5 are elucidated. A simplified mechanism of RB5 decomposition that is consistent with the experimental findings for a solution with a pH of up to 7.0 is proposed. About 70% decolorization was measured and 45% of the total organic carbon was eliminated on the surface of the iron oxide at pH 7.0 after 480 min in the presence of 0.055mM RB5, 5.0 g iron oxide/L, 29.4mM $H_2O_2$, under 15W UVA. This technique can be employed as the basis of a cost – effective method for Fenton-type degradation of a pollutant, without the end-of pipe discharge of iron sludge into the environment.

Khunikakorn (2005) investigated oxidation of aniline (AN) and nitrobenzene (NB) by fluidized-bed Fenton process using $Al_2O_3$ and $SiO_2$ as the carriers which have the pzc of 8.44 and 6.54, respectively. Optimum pH for AN and NB oxidation were 3.2 and 2.8, respectively. $Al_2O_3$ was better than $SiO_2$ possible due to higher positive-charged surface at pH 2.8. In spite of comparable performance in organic oxidation, the fluidized-bed Fenton process was able to remove iron whereas the ordinary Fenton process could not. Empirical kinetic equations for the oxidation of individual AN and NB oxidation as well as the combination by fluidized-bed Fenton process were determined and found to be inconsistency with those derived by stoichiometric equations. AN was found to be more vulnerable to hydroxyl radical oxidation than NB, i.e., when presenting at the same concentration, 72% of the generated hydroxyl radical reacted with AN whereas the rest of 28% were captured by NB. From the EDX analysis, iron oxide was crystallized onto the surface of the carriers and these iron-coated carriers could be reused successfully.

Kitimongkonsak (2006) investigated degradation of reactive dyes by fluidized- bed Fenton process for the removal of color and chemical oxygen demand (COD) from synthetic textile wastewater. This investigation reveals that fluidized-bed Fenton method can remove the color and COD of these dyes. The pH of all experiments was fixed at 3.0. Increasing the dose of ferrous enhanced the dye decolorization and COD removal. The optimum levels of $H_2O_2$ required for the process were also examined. High levels of $H_2O_2$ appeared to reduce color and COD removal .However, when the $H_2O_2$ concentration was higher than a specific level, the degradation rate of reactive dyes slightly slows down. This can be explained by the so-called scavenging effect. Then, the COD and color removal by fluidized-bed Fenton process was applied to remove the COD and color of wastewater from textile factory in Taiwan. Target remaining COD and color for treating the wastewater from textile factory in this study was less than the discharge standard of Taiwan. From the results, the condition for treating the textile wastewater was $[COD]:[Fe^{2+}]:[H_2O_2] = 1 : 0.95 : 7.94$, carrier = 74.07 g/l, initial pH = 3.

### 2.6.4 The optimization process by statistical experimental design

Ay et al. (2009) studied the advanced oxidation of an azo-dye, Direct Red 28 by photo-Fenton treatment in batch experiments using Box-Behnken statistical experiment design and response surface analysis. The results showed the prediction of dyestuffs oxidation obtained from the response functions were in good agreement with the experimental results indicating the reliability of the method used. The response surface analysis also provided a better understanding for the roles of Fe(II) and $H_2O_2$ doses on degradation of the dyestuff for the large range of concentration. The result also show that color removal increased with increasing $H_2O_2$ and Fe(II) concentrations up to a certain level. High concentrations of $H_2O_2$ and Fe(II) adversely affected the color and TOC removals due to hydroxyl radical scavenging effects of high oxidant and catalyst concentrations. The optimal reagent doses varied depending on the initial dyestuff dose. For the highest dyestuff concentration tested, the optimal $H_2O_2$/Fe(II)/dyestuff ratio resulting in the maximum color removal (100%) was predicted to be 715/71/250 ($mgL^{-1}$), while this ratio was 1550/96.5/250 for maximum mineralization (97.5%).

Arslan-Alaton et al. (2009) investigated treatment of azo dye production wastewaters via Photo-Fenton-like advanced oxidation processes. For this purpose, synthetic Acid Blue 193 and Reactive Black 39 production wastewaters from the synthesis reactor rinsing stage as well as real Reactive Black 39 production wastewater from the reverse osmosis purification stage of the azo dye manufacturing process were select as model effluents. Response surface methodology was employed to assess individual and interactive effects of critical process parameters ($Fe^{3+}$, $H_2O_2$ concentration; initial chemical oxygen demand(COD) and reaction time) on treatment performance in terms of color, COD and total organic carbon(TOC) removal efficiencies. Optimized reaction conditions for synthetic AB193 production wastewater were established as $Fe^{3+}$ = 1.5 mM ; $H_2O_2$ = 35 mM for CODs ≤ 200 mg/L and a reaction time of 45 min. Under these condition, 98% of color, 78% of COD and 59% of TOC removals were experimentally obtained and fitted the model predictions well. Experimental findings have revealed that Photo-Fenton-like advanced oxidation is an effective treatment method for complete decolorization accompanied with appreciable COD and TOC removals from azo dye production wastewater.

Korbahti and Rauf (2009) determined the optimum condition of carmine decoloration by UV/$H_2O_2$ using response surface methodology. According to analysis of variance (ANOVA) results, the proposed model can be used to navigate the design space. It was found that the response of carmine degradation is very sensitive to the independent factors of carmine concentration, $H_2O_2$ concentration, pH and reaction time. The proposed model for D-optimal design fitted very well with the experimental data with $R^2$ and $R^2$ adj correlation coefficients of 0.998 and 0.997, respectively.

Oliveira et al. (2006) applied an experiment design methodology for 2,4-dichlorophenol oxidation by Fenton's reaction. The use of design of experiment technique allowed us to investigate the effects of process variables (temperature, ferrous ion and hydrogen peroxide concentrations) in the process performance. Response factors consider were 2,4-dichlorophenol degradation after 5,10 and 20 min of the reaction time, for an initial 2,4-dichlorophenol concentration of 100 mg/L. The result show that, within the range studied, the ferrous ion concentration has a positive effect on the oxidation performance. However, for the peroxide load, an optimum value exists that must be taken into account in order to obtain the best results. Data obtained point to a positive effect of reaction temperature in the range studied (20-40°C) when responses considered are chlorophenol conversions for short reaction times. The result also show that, oxidation with Fenton's reagent has proven to be an efficient and fast process for 2,4-dichlorophenol degradation, where efficiencies above 99% can be obtained in just 10 min of reaction time.

Paterlini et al. (2005) studied the degradation of the herbicides in aqueous solution by the photo-Fenton process using ferrioxalate complex (FeOx) as source of $Fe^{2+}$ under the blacklight irradiation. The response surface methodology was applied to evaluate the role of FeOx and hydrogen concentration as variables in the degradation process, The degradation process was evaluated by the determination of the remaining total organic carbon content (TOC), by monitoring the decrease of the concentrations of the original compounds using HPLC and by the chloride ion release in the case of diuron and 2,4-D. Under optimized conditions, 20 min were sufficient to mineralize 93% of TOC from 2,4-D and 90% of diuron , including oxalate. Complete dechlorination of these compounds was achieved after 10 min reaction. Furthermore, the experimental results obtained under optimized concentrations were very close to the expected theoretical results, evidencing the reliability of the design within the range of the concentrations investigated.

# CHAPTER III

# METHODOLOGY

## 3.1 Experimental Instruments and Chemicals

### 3.1.1 Chemicals

All chemical substances used in this study were reagent grade and obtained from Merck Company. All of solutions were prepared by de-ionized water from a Millipore system with a resistivity of 18.2 M$\Omega$/cm.

1. Target organic compounds

| | |
|---|---|
| 2,4-dicholorophenol (98%) | $C_6H_4Cl_2O$ |

2. Fenton's reagent

| | |
|---|---|
| Ferrous Sulfate Hepta- hydrated | $FeSO_4 \cdot 7H_2O$ |
| Hydrogen peroxide (35%) | $H_2O_2$ |

3. The carriers

| | |
|---|---|
| Silica dioxide | $SiO_2$ |

Silica dioxide has a grain-shape with 0.84-2.00 mm. of particle diameter

4. Chemical for stop the reaction

| | |
|---|---|
| Sodium hydroxide (0.1 Normality of NaOH) | NaOH |

5. Chemical for pH adjustment

| | |
|---|---|
| Sodium hydroxide (1 Normality of NaOH) | NaOH |
| Sulfuric acid (1:4 $H_2SO_4$) | $H_2SO_4$ |

6. Ferrous ion measurement

| | |
|---|---|
| Hydrochloric acid (0.64%) | HCl |
| Ammonium acetate | $NH_4C_2H_3O_2$ |
| 1,10- phenanthroline | $C_{12}H_8N_2 \cdot H_2O$ |

7. Hydrogen peroxide measurement

| | |
|---|---|
| Potassium titatium (IV) oxalate | $K_2TiO$ |

8. HPLC measurement

| | |
|---|---|
| Acetonitrile | $CH_3CN$ |

9. COD measurement

| | |
|---|---|
| Silver sulfate | $AgSO_4$ |
| Mercury Sulfate | $HgSO_4$ |
| Sulfuric acid | $H_2SO_4$ |
| Ammonium iron(III) sulfatehexahydrate | $FeH_8N_2O_8S_2 \cdot 6\ H_2O$ |
| Potassium dichromate | $Cr_2K_2O_7$ |
| Ferroin indicator solution | - |

10. Total ion measurement

| | |
|---|---|
| Nitric acid (conc.) | $HNO_3$ |

### 3.1.2 Experimental Instruments and Equipment

1. pH meter: SUNTEX TS-1 Digital pH/MV meter
2. UV-VIS Spectrophotometer: Thermo Spectronic™ GENESYS™ 20
3. Thermometer
4. Auto Pipette: 1,000 μl and 5,000 μl
5. Weighing Machine (4-Digits Balance)
6. Magnetic Stirrers
7. Magnetic Bars
8. Fluidized-bed reactor 1.35-liter cylinder with recycle pump
9. Glasswares
10. Glass Bead Ø 4 mm
11. Clock Timer
12. Membrane Filter :0.20 μm and 0.45 μm
13. Syringe
14. High Performance liquid chromatography (HPLC): The pump was SpectraSYSTEM model SN4000 with the operating flow rate were 1 ml/min through Asahipak ODP-506D column (150mm × 6mm × 5μm).
15. PerkinElmer Atomic Absorption Spectrometer (AAS) model AAnalyst 200

16. COD Closed Reflux Heater Block

17. Total Organic Carbon (TOC) performed in an elementar liquid TOC analyzer with high temperature catalytic oxidation mode coupled with non-dispersive infrared (NDIR) detector.

18. Ion Chromatograph (IC): (Dionex DX-120) equipped with RFC-30 EGCII (KOH),IonPac®AG11 guard column(4x50mm), IonPac®AS11 analytical column (4x250mm), ASRS®-ULTRA II (4mm) suppressor and conductivity detector.

## 3.2 Fluidized- bed Reactor

A 1.35-litre fluidized-bed reactor (FBR) was operated in all experiments. A fluidized – bed reactor is a cylinder vessel which consists of the outlet, the inlet and a recirculating sections as shown in the figure 3.1. The carriers were fluidized at the optimum bed expansion by adjusting the internal circulation rate.

## 3.3 Experimental Procedures

### 3.3.1 Fluidized-bed Fenton Experiment

At the beginning, the synthetic wastewater was prepared by using the reagent grade 2,4-dichlorophenol diluted with de-ionized water from a Millipore system with a resistivity of 18.2 $M\Omega\ cm^{-1}$, to the desired 2,4-dichlorophenol concentration of 1 mM. Then the pH of solution was adjusted to 3-3.5 by using 1:4 $H_2SO_4$ in order to prevent the precipitation of ferric oxide ($Fe(OH)_3$). The calculated amount of Ferrous Sulfate Hepta- hydrated ($FeSO_4 \cdot 7H_2O$) was added in to the volumetric flask prepared the synthetic wastewater as the source of ferrous. The silica dioxide was added initially into the reactor followed by the above synthetic wastewater. After that, the re-circulated pump was turned on to suspend the carriers to a desired bed expansion level and to mix the solution. Next, the pH of the solution was adjusted to the desired value by adding of 1:4 $H_2SO_4$. When hydrogen peroxide was added in to the reactor and the reaction was simultaneously started. Solution pH was monitored and controlled within ± 0.2 unit through out the experiment by adding either 1:4 $H_2SO_4$ or 1N NaOH. At selected time intervals of 0, 2, 5, 10, 20, 30, 60, 90 and 120 minutes, 5 ml of solution samples were taken fromthe reactor and were analyzed for residual hydrogen peroxide, ferrous ion , total iron, 2,4-dichlorophenol, and COD. The schematic diagram of this experiment is shown in Figure 3.2

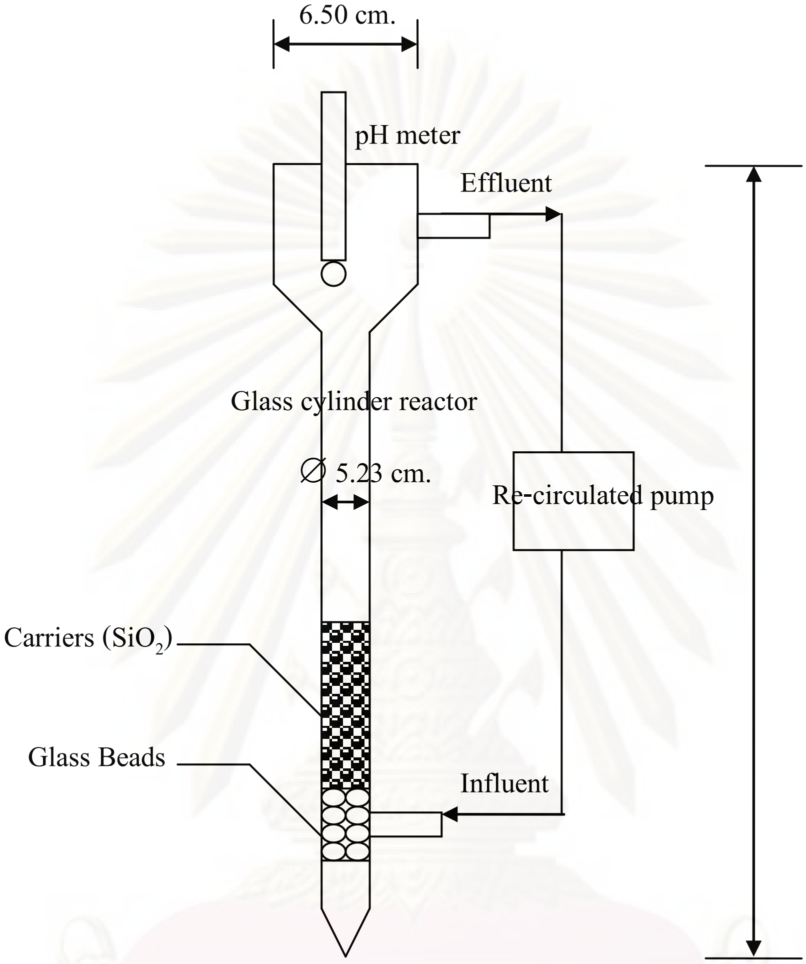


Figure 3.1 Fluidized-bed reactor (FBR) compartments

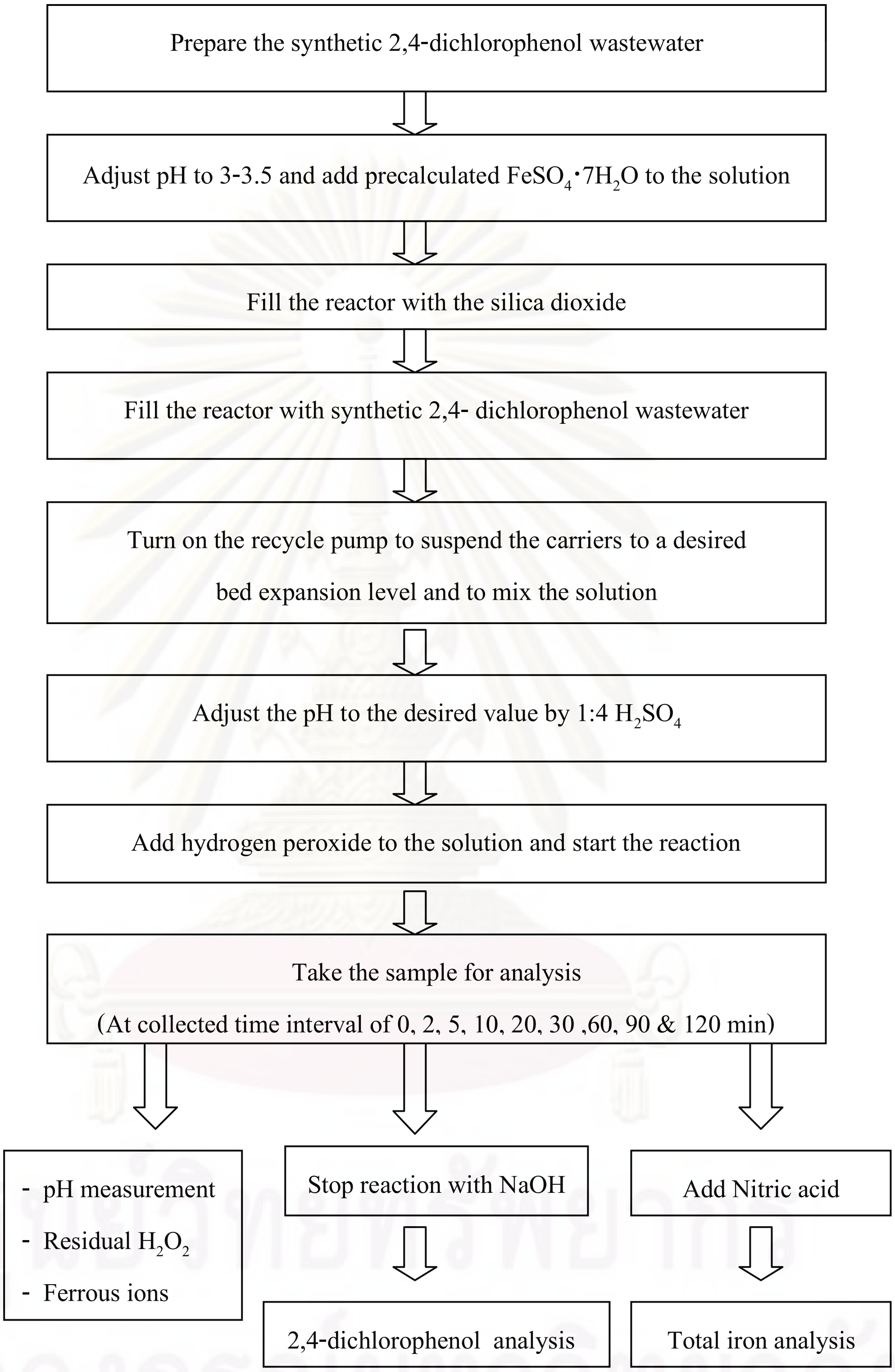


Figure 3.2 The experimental schemes for Fluidized-bed Fenton process.

### 3.3.2 Statistical Design of Experiments

The Design-Expert software version 7.0. (Stat-Ease, Inc., Minneapolis, USA) was used to design the number of experiments to be performed, calculate the experimental data and evaluate the experimental results. In order to investigate the effects of significant factors and to obtain the optimum condition, in this study, were determined by Box-Behnken statistical design.

First, consider the major factors that possibly affecting the performance in fluidized-bed Fenton process. These variables; namely, pH, initial $Fe^{2+}$, $H_2O_2$ concentration and the amount of carriers were chosen as factors in the Box-Behnken statistical design. Then, the appropriate studied ranges of each variable were also selected into the software. Another kind of inputs needed for the software is the response. In this study, 2,4-dichlorophenol, COD and total iron removal efficiencies were selected as the response function which represent all of the result in experiments. After all parameters were input into the software, then the experiments were designed. The number of experiments for the Box-Behnken statistical design of four variables and three-level were 29 experimental runs including five replications at the center point (0,0,0,0,0). The data then were analyzed and evaluated after the design matrix was completed. The optimum condition was obtained from this design. The optimization procedure involves studying the response of statistically designed combination, estimating the coefficients by fitting experimental data to the response functions and predicting the response of fit model (Ay et al., 2009).

### 3.4 Framework of overall experiment

The framework of overall experiment for the degradation of 2,4-dichlorophenol by fluidized-bed Fenton process was followed by figure 3.3.

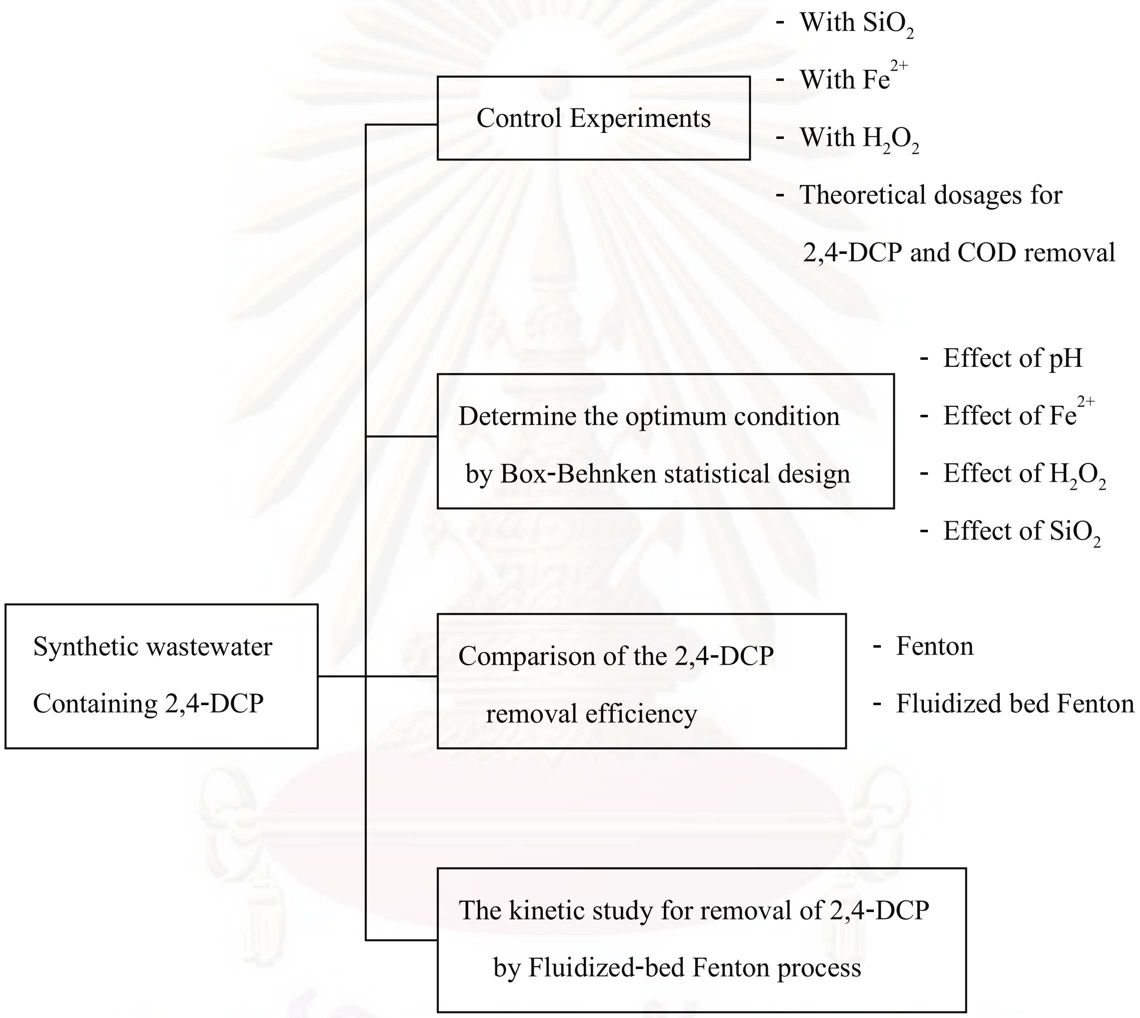


Figure 3.3 The Schematic diagram of the research

## 3.5 Experimental Scenarios

### 3.5.1 Control Experiment

The control experiment is the basic experiment which aim to investigate the effect of individual component of Fenton process in the degradation of 2,4-dichlorophenol. There are three possibly parts that effect to the degradation of 2,4-dichlorophenol. The first experiment investigated the effect of adsorption in the degradation of 2,4-dichlorophenol by using the carriers. The second investigated the effects of initial concentration of ferrous ion and the last experiment investigated the effect of initial concentration of hydrogen peroxide in the oxidation of 2,4-dichlorophenol. These experiments were conducted under the same conditions using 1 mM of 2,4-dichlorophenol concentration and control pH about 3.0.

Table 3.1 Effects of individual component by Fluidized-bed Fenton process .

| 2,4-Dichlorophenol (mM) | pH | Control parameter |
|---|---|---|
| 1 | 3.0 ± 0.2 | Adsorption ( with carriers) |
| | | With $Fe^{2+}$ |
| | | With $H_2O_2$ |

The control experiment in terms of theoretical dosage for chemical and COD removal were also examined. For the theoretical dosage of Fenton's reagent on the 2,4-dichlorophenol removal was calculated as 1 :1 :1 (2,4-dichlorophenol : $Fe^{2+}$ : $H_2O_2$). In order to remove 1 mM of 2,4-dichlorophenol, 1 mM of both $Fe^{2+}$ and $H_2O_2$ were needed. Moreover, the theoretical dosage for COD removal was 1:1:12 (2,4-dichlorophenol : $Fe^{2+}$ : $H_2O_2$). Normally, 0.47 mg/l of COD is needed to remove 1 mg/l of $H_2O_2$. Since 1 mM of 2,4-dichlorophenol has 192 mg/l of COD, then $H_2O_2$ required in this study was 408 mg/l or 12 mM (when 1 mM of $H_2O_2$ equal 34 mg/l).

Table 3.2 Theoretical dosages for 2,4-DCP and COD removal by Fluidized-bed Fenton process .

| 2,4-Dichlorophenol (mM) | pH | $Fe^{2+}$ (mM) | $H_2O_2$ (mM) | Metal oxide in FBR (grams) |
|---|---|---|---|---|
| 1 | 3 | 1 | 1 | 100 |
| 1 | 3 | 1 | 12 | 100 |

### 3.5.2 Optimization Experiment

This part aims to identify the optimum condition for the 2,4-dichlorophenol oxidation by fluidized-bed Fenton process. The four important factors affecting on the performance of fluidized-bed Fenton process including pH (A), initial $Fe^{2+}$ (B) and initial $H_2O_2$ (C) concentrations as well as the amount of carriers were selected as factors in Box-Behnken statistical design. The appropriate ranges consisting of the low, center and high levels of each variable were also included as input in the software as shown Table 3.3. The low, center and high levels for each variable were designated as -1, 0 and +1, respectively. The concentration of 2,4-dichlorophenol was fixed as 1 mM for all experimental run in the Box-Behnken statistical design. From the Box-Behnken statistical design of four variables and three-levels were 29 experimental runs as shown in Table 3.4. The responses or dependent variables of the Box-Behnken statistical design were 2,4-dichlorophenol, COD and total iron removal.

Table 3.3 The levels of variables in Box-Behnken statistical experiment design.

| Variables | Symbol | Variable level | | |
|---|---|---|---|---|
| | | Low | Center | High |
| | | -1 | 0 | +1 |
| pH | A | 2 | 3 | 4 |
| $Fe^{2+}$ (mM) | B | 0.1 | 0.55 | 1 |
| $H_2O_2$ (mM) | C | 1 | 5.5 | 10 |
| Amount of carriers (g) | D | 50 | 150 | 250 |

Table 3.4 Design of experimental runs for the Box-Behnken statistical design of fluidized-bed Fenton process.

| Run number | Actual and coded level of variables | | | |
|---|---|---|---|---|
| | pH | $Fe^{2+}$ (mM) | $H_2O_2$ (mM) | Carriers (g) |
| 1 | 2(-1) | 0.1(-1) | 5.5(0) | 150(0) |
| 2 | 4(+1) | 0.1(-1) | 5.5(0) | 150(0) |
| 3 | 2(-1) | 1(+1) | 5.5(0) | 150(0) |
| 4 | 4(+1) | 1(+1) | 5.5(0) | 150(0) |
| 5 | 3(0) | 0.55(0) | 1(-1) | 50(-1) |
| 6 | 3(0) | 0.55(0) | 10(+1) | 50(-1) |
| 7 | 3(0) | 0.55(0) | 1(-1) | 250(+1) |
| 8 | 3(0) | 0.55(0) | 10(+1) | 250(+1) |
| 9 | 2(-1) | 0.55(0) | 5.5(0) | 50(-1) |
| 10 | 4(+1) | 0.55(0) | 5.5(0) | 50(-1) |
| 11 | 2(-1) | 0.55(0) | 5.5(0) | 250(+1) |
| 12 | 4(+1) | 0.55(0) | 5.5(0) | 250(+1) |
| 13 | 3(0) | 0.1(-1) | 1(-1) | 150(0) |
| 14 | 3(0) | 1(+1) | 1(-1) | 150(0) |
| 15 | 3(0) | 0.1(-1) | 10(+1) | 150(0) |
| 16 | 3(0) | 1(+1) | 10(+1) | 150(0) |
| 17 | 2(-1) | 0.55(0) | 1(-1) | 150(0) |
| 18 | 4(+1) | 0.55(0) | 1(-1) | 150(0) |
| 19 | 2(-1) | 0.55(0) | 10(+1) | 150(0) |
| 20 | 4(+1) | 0.55(0) | 10(+1) | 150(0) |
| 21 | 3(0) | 0.1(-1) | 5.5(0) | 50(-1) |
| 22 | 3(0) | 1(+1) | 5.5(0) | 50(-1) |
| 23 | 3(0) | 0.1(-1) | 5.5(0) | 250(+1) |
| 24 | 3(0) | 1(+1) | 5.5(0) | 250(+1) |
| 25 | 3(0) | 0.55(0) | 5.5(0) | 150(0) |
| 26 | 3(0) | 0.55(0) | 5.5(0) | 150(0) |
| 27 | 3(0) | 0.55(0) | 5.5(0) | 150(0) |
| 28 | 3(0) | 0.55(0) | 5.5(0) | 150(0) |
| 29 | 3(0) | 0.55(0) | 5.5(0) | 150(0) |

### 3.5.3 Comparison of 2,4-dichlorophenol removal efficiency by Fenton and Fluidized- bed Fenton processes.

This part want to compare the degradation of 2,4-dichlorophenol between Fenton process and fluidized-bed Fenton process by using the optimum condition that got from Box-Behnken statistical design.

The first experiment was operated by Fenton process without using carriers while the other was operated by Fluidized- bed Fenton process with same optimum condition, which obtained from the software in the previous part.

Table 3.5 Comparison of 2,4-DCP removal efficiency by Fenton and Fluidized- bed Fenton process.

| 2,4-Dichlorophenol (mM) | pH | $Fe^{2+}$ (mM) | $H_2O_2$ (mM) | Metal oxide in FBR (grams) |
|---|---|---|---|---|
| 1 | Optimum value | Optimum value | Optimum value | 0 |
| | | | | Optimum value |

### 3.5.4 The kinetic study for removal of 2,4-dichlorophenol by Fluidized-bed Fenton process

In this part, the kinetics of 2,4-dichlorophenol degradation by hydroxyl radicals in the fluidized-bed Fenton process was investigated. Three independent variables were studied including 2,4-dichlorophenol, $Fe^{2+}$, and $H_2O_2$ concentrations. The studied ranges for each variable were shown in Tables 3.5 to 3.7.

#### 3.5.4.1 Effects of initial $Fe^{2+}$ concentration

To determine the effects of initial $Fe^{2+}$ concentration on 2,4-dichlorophenol removal. The amounts of $Fe^{2+}$ was varied at 0.1 mM, 0.25 mM, 0.5 mM and 1 mM while initial concentration of $H_2O_2$ and pH was obtained from optimum condition in the previous part .

Table 3.6 Effects of initial $Fe^{2+}$ concentration on degradation of 2,4-dichlorophenol.

| 2,4-Dichlorophenol (mM) | $H_2O_2$ (mM) | pH | Carriers (grams) | $Fe^{2+}$ (mM) |
|---|---|---|---|---|
| 1 | 10 | 3.0 ± 0.2 | 100 | 0.1 |
| | | | | 0.25 |
| | | | | 0.50 |
| | | | | 1 |

#### 3.5.4.2 Effects of initial $H_2O_2$ concentration

To determine the effects of hydrogen peroxide dosage on 2,4-dichlorophenol removal. $H_2O_2$ concentration was varied at 1 mM, 5 mM, 10 mM and 20 mM for 1 mM of 2,4-dichlorophenol concentration. The optimum pH value and $Fe^{2+}$ concentration was obtained from the Box-Benhken statistic design part.

Table 3.7 Effects of initial $H_2O_2$ concentration on degradation of 2,4-dichlorophenol.

| 2,4-Dichlorophenol (mM) | $Fe^{2+}$ (mM) | pH | Carriers (grams) | $H_2O_2$ (mM) |
|---|---|---|---|---|
| 1 | 0.25 | 3.0 ± 0.2 | 100 | 1 |
| | | | | 5 |
| | | | | 10 |
| | | | | 20 |

### 3.5.4.3 Effects of initial 2,4-dichlorophenol concentration

To determine the effects of different amounts of 2,4-dichlorophenol concentration 0.5 mM, 1 mM, 2 mM and 5 mM was varied. The optimum value of $Fe^{2+}$ and $H_2O_2$ from the previous experiment, was use as initial concentration. From these studies, the kinetic information for treating 2,4-dichlorophenol by fluidized-bed Fenton process was obtained.

Table 3.8 Effects of initial 2,4-dichlorophenol concentration on degradation of 2,4-dichlorophenol.

| $Fe^{2+}$ (mM) | $H_2O_2$ (mM) | pH | Carriers (grams) | 2,4-dichlorophenol (mM) |
|---|---|---|---|---|
| 0.25 | 10 | 3.0 ± 0.2 | 100 | 0.5 |
| | | | | 1 |
| | | | | 2 |
| | | | | 5 |

Additionally, The intermediated product from the optimum condition of 2,4-dichlorophenol degradation were also identified.

## 3.6 Analytical Methods

### 3.6.1 Measurement of 2,4-dichlorophenol

In the beginning, the samples were filtered with 0.20 μm syringe micro-filters to separate precipitated iron from the solutions. The residual of 2,4-dichlrophenol was analyzed by high performance liquid chromatography (HPLC) with mobile phase of 60% Acetonitrile with DI water 40%. The column was operated between 18 and 22 °C. The pump was Spectra SYSTEM model SN4000 with the operating flow rate of 1 ml/min through Asahipak ODP-506D column (150mm × 6mm × 5μm). The 285 nm outputs from UV1000 detector were measured 20 μL of sample was injected.

### 3.6.2 Analysis of ferrous concentration

The samples will be analyzed by phenanthroline method describe by Standard Methods (American Public Health Association [APHA], 1992) in Appendix A-1. DI water was added to adjust the volume to 50 ml. DI water mixed with the sample but no phenanthroline was used as a blank for every sample.

### 3.6.3 Analysis for hydrogen peroxide concentration

The concentration of hydrogen peroxide was determined by a spectrophotometric method using potassium titanium (IV) oxalate as described in Appendix A-2. The absorbance of samples was measured by the the Spectronic™ GENESYS™ 20 spectrophotometer.

### 3.6.4 Analysis of total iron concentration

Sample was digested by nitric acid and diluted 10 times by DI water (dilution). The total iron concentration was analyzed by using PerkinElmer Atomic Absorption Spectrometer (AAS) model AAnalyst 200 with hollow cathode lamps Fe at 248.33 nm with Slit of 1.8/1.35 and used acetylene gas as the carrier.

### 3.6.5 Analysis of chemical oxygen demand

COD was measured by closed reflux titrimetric method based on the Standard methods, APHA, 1992.

### 3.6.6 Analysis of anions

Anions concentration were determined by Ion Chromatography (IC) Dionex DX-120 Ion Chromatograph with the operating flow rate were 1.0 ml/min, Reagent-Free$^{TM}$ Controller with RFIC$^{TM}$ EGC II KOH (RFC-30), Autosampler Thermo Finnigan SpectraSYSTEM model AS1000 with 20 μl injection volume, Guard column IonPac® AG-11 (4x50 mm), analytical column IonPac® AS-11 (4x250 mm), column temperature stabilizer model CTS-10 control at 30 °C, suppressor ASRS®-ULTRA II 4-mm with conductivity detector. The intermediate (oxalic acid, citric acid, formic acid, acetic acid, lactic acid, maleic acid, nitrate, nitrite, ammonium, sulphate, chloride, perchloric acid) were determined.

### 3.6.7 Other measurements

The pH measurement is carried out by a SUNTEX TS-1 Digital pH/MV meter.

# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Control Experiment

Control experiment is the basic part that aims to determine the degradation of target compounds in fluidized-bed Fenton process deriving from each individual constituent via non-Fenton reaction. The initial conditions used in these experiments were as follows: 1 mM of 2,4-dichlorophenol, 0.25 mM of initial $Fe^{2+}$ concentration, 10 mM of initial $H_2O_2$ concentration, pH 3 and 100 g of carriers. Figure 4.1 shows the plot of 2,4-dichlorophenol remaining versus time obtained from control experiments. The portion of 2,4-dichlorophenol being removed in 120 minutes by adsorption (on to the surface of carriers and apparatus) and volatilization in the absence of $Fe^{2+}$ and $H_2O_2$ was 9.47%, in the presence of $Fe^{2+}$ was 20.48% and in the presence of $H_2O_2$ was 22.53%. This means that using $Fe^{2+}$ or $H_2O_2$ alone have no significant effect on 2,4-dichlorophenol removal.

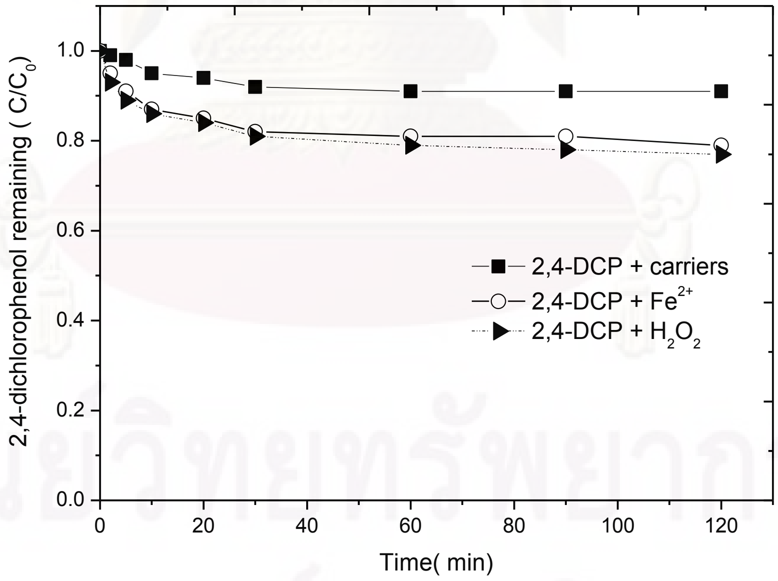


Figure 4.1 Effect of control experiments on 2,4-dichlorophenol removal efficiency. [2,4-dichlorophenol] = 1 mM, $[Fe^{2+}]$ = 0.25 mM, $[H_2O_2]$ = 10 mM, $SiO_2$ = 100 g and pH = 3.0

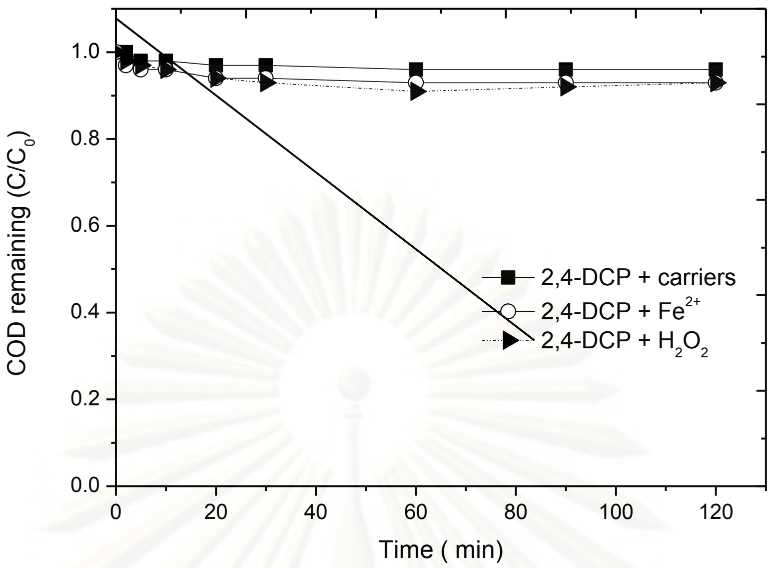


Figure 4.2 Effect of control experiments on COD removal efficiency.
[2,4-dichlorophenol] = 1 mM, [$Fe^{2+}$] = 0.25 mM, [$H_2O_2$] = 10 mM, $SiO_2$ = 100 g and pH = 3.0

Figure 4.2 shows the plot of COD remaining of 2,4-dichlorophenol 1 mM versus time obtained from control experiments. It was found that COD hardly removed when $Fe^{2+}$ or $H_2O_2$ was applied alone in the solution. The COD removal in the absence of $Fe^{2+}$ and $H_2O_2$ was only 3.91%, in the presence of $Fe^{2+}$ was 6.05 % and in the presence of $H_2O_2$ was 6.80 %. Therefore, the removal of 2,4-dichlorophenol and COD could not be effectively degraded without an involvement of •OH from Fenton's reaction.

Table 4.1 Summarizes the results from all control experiments.

| Control Experiment | % 2,4-dichlorophenol removal | % COD removal |
|---|---|---|
| 2,4-DCP + Carriers | 9.47 | 3.91 |
| 2,4-DCP + $H_2O_2$ | 22.52 | 6.80 |
| 2,4-DCP + $Fe^{2+}$ | 20.50 | 6.05 |

## 4.2 Box-Behnken design

The Box-Behnken statistical experiment design was used to investigate the effects of the four independent variables on the response function and to determine the optimal conditions (Catalkaya and Kargi, 2007), which maximizing the percent removal of 2,4-dichlorophenol, COD and total iron. The levels of the four factors namely; pH (A), initial $Fe^{2+}$ concentration (B), initial $H_2O_2$ concentration (C) and the amount of carriers (D) were used in this study as shown in Table 3.2. The low, center and high levels for each variable were designated as -1, 0 and +1, respectively. The response functions were represented by 2,4-dichlorophenol, COD, and total iron removal efficiencies. The total number of experiment with four variables and three-levels in Box-Behnken statistical design were 29 experimental runs, including five replications at the center point (0,0,0,0,0). The complete 29 numbers of experimental design matrix and responses based on experimental runs are given in Table 4.2.

Results from the experiment revealed that the maximum removal of 2,4-dichlorophenol was 99.9%, while the minimum removal was 65.4%. The removal of COD and total iron were between 36.6% to 62.0% and 1.65% to 43.0%, respectively. The results show that increasing $H_2O_2$ concentration would increase 2,4-dichlorophenol removal efficiency. The 2,4-dichlorophenol removal was only 65.4%. When 1 mM of $Fe^{2+}$ and 1 mM of $H_2O_2$ were applied (run number 14). However, when $H_2O_2$ concentration was increased from 1 to 10 mM with 1 mM of $Fe^{2+}$ concentration the 2,4-dichlorophenol removal increased to 98.4% (run number 16). This means that $H_2O_2$ played an important role on the degradation of 2,4-dichlorophenol. On the other hand, increasing $Fe^{2+}$concentration would slightly decrease 2,4-dichlorophenol removal efficiency. When $Fe^{2+}$ concentration was increased from 0.1 to 1 mM, the removal efficiency was decreased from 98.7% to 91.0% (run number 23 and 24). This was due to the scavenging effect of •OH on $Fe^{2+}$ (Sun et al., 2007). The amount of carriers was considers as less significant factor affected the removal efficiency. Increasing the amount of carriers would slightly increase 2,4-dichlorophenol removal (run number 9 and 11). In addition, it was derived that initial pH did not substantially affect the degradation efficiency.

Table 4.2 Design of experimental runs for the Box-Behnken statistical design of fluidized-bed Fenton process with 1 mM of 2,4-dichlorophenol.

| **Run** | **Actual and coded level of variables** | | | | **Experimental percent removal** | | |
|---|---|---|---|---|---|---|---|
| **number** | **pH, A** | **$Fe^{2+}$, B (mM)** | **$H_2O_2$, C (mM)** | **Carriers ,D (g)** | **2,4-DCP** | **COD** | **Total iron** |
| 1 | 2(-1) | 0.1(-1) | 5.5(0) | 150(0) | 93.0 | 36.7 | 11.6 |
| 2 | 4(+1) | 0.1(-1) | 5.5(0) | 150(0) | 93.1 | 36.9 | 17.1 |
| 3 | 2(-1) | 1(+1) | 5.5(0) | 150(0) | 92.8 | 52.4 | 1.65 |
| 4 | 4(+1) | 1(+1) | 5.5(0) | 150(0) | 92.5 | 48.3 | 14.9 |
| 5 | 3(0) | 0.55(0) | 1(-1) | 50(-1) | 69.1 | 48.1 | 5.08 |
| 6 | 3(0) | 0.55(0) | 10(+1) | 50(-1) | 99.8 | 56.5 | 6.37 |
| 7 | 3(0) | 0.55(0) | 1(-1) | 250(+1) | 79.0 | 45.9 | 5.34 |
| 8 | 3(0) | 0.55(0) | 10(+1) | 250(+1) | 99.8 | 47.7 | 13.7 |
| 9 | 2(-1) | 0.55(0) | 5.5(0) | 50(-1) | 95.9 | 43.1 | 4.35 |
| 10 | 4(+1) | 0.55(0) | 5.5(0) | 50(-1) | 97.6 | 58.9 | 21.7 |
| 11 | 2(-1) | 0.55(0) | 5.5(0) | 250(+1) | 96.5 | 53.4 | 7.00 |
| 12 | 4(+1) | 0.55(0) | 5.5(0) | 250(+1) | 96.8 | 40.4 | 23.6 |
| 13 | 3(0) | 0.1(-1) | 1(-1) | 150(0) | 70.7 | 36.6 | 10.3 |
| 14 | 3(0) | 1(+1) | 1(-1) | 150(0) | 65.4 | 49.3 | 9.63 |
| 15 | 3(0) | 0.1(-1) | 10(+1) | 150(0) | 98.3 | 55.6 | 16.8 |
| 16 | 3(0) | 1(+1) | 10(+1) | 150(0) | 98.4 | 61.3 | 12.3 |
| 17 | 2(-1) | 0.55(0) | 1(-1) | 150(0) | 84.8 | 52.2 | 4.00 |
| 18 | 4(+1) | 0.55(0) | 1(-1) | 150(0) | 67.7 | 54.7 | 11.8 |
| 19 | 2(-1) | 0.55(0) | 10(+1) | 150(0) | 99.5 | 62.1 | 5.79 |
| 20 | 4(+1) | 0.55(0) | 10(+1) | 150(0) | 99.9 | 53.1 | 15.1 |
| 21 | 3(0) | 0.1(-1) | 5.5(0) | 50(-1) | 97.9 | 47.2 | 9.56 |
| 22 | 3(0) | 1(+1) | 5.5(0) | 50(-1) | 93.1 | 38.3 | 5.95 |
| 23 | 3(0) | 0.1(-1) | 5.5(0) | 250(+1) | 98.7 | 41.4 | 43.0 |
| 24 | 3(0) | 1(+1) | 5.5(0) | 250(+1) | 91.0 | 46.3 | 9.71 |
| 25 | 3(0) | 0.55(0) | 5.5(0) | 150(0) | 97.6 | 52.1 | 10.1 |
| 26 | 3(0) | 0.55(0) | 5.5(0) | 150(0) | 97.9 | 46.2 | 10.7 |
| 27 | 3(0) | 0.55(0) | 5.5(0) | 150(0) | 99.2 | 55.2 | 8.43 |
| 28 | 3(0) | 0.55(0) | 5.5(0) | 150(0) | 96.6 | 46.6 | 8.28 |
| 29 | 3(0) | 0.55(0) | 5.5(0) | 150(0) | 97.2 | 47.7 | 9.21 |

COD removal was improved as the concentration of $Fe^{2+}$ and $H_2O_2$ increased as shown in run number 13, 14 and 16. However, further increase in $Fe^{2+}$ concentrations resulted in the decrease in COD removal (run number 21 and 22) probably due to scavenging effects of high $Fe^{2+}$ concentrations on •OH. Increasing pH from 2 to 4 would increase total iron removal from 1.65 % to 14.9 % (run number 3 and 4) because $Fe(OH)_3$ usually precipitated in a higher pH. Hence, the amount of iron in the solution would be decreased. Additionally, total iron removal was increased from 5.95 % to 9.71 % (run number 22 and 24) as increasing in the amount of carriers from 50 to 250 g.

### 4.2.1 Regression model coefficients

The application of Box-Behnken design offers an empirical relationship between the response function and the variables. For 2,4-dichlorophenol and COD removals, the mathematical relationships between response function and four significant variables can be approximated by a quadratic polynomial equation whereas the empirical relationships between total iron and the independent variables can be estimated by linear model. The equation for the removal of 2,4-dichlorophenol, COD and total iron by fluidized-bed Fenton process in terms of actual factors are shown below:

$$\begin{aligned}\text{2,4-dichlorophenol removal} \;=\;& 70.77 - 2.61\text{pH} + 15.92[Fe^{2+}] + 6.07[H_2O_2] + 0.05\text{cariers} \\ & - 0.18\text{pH}[Fe^{2+}] + 0.97\text{pH}[H_2O_2] - 3.25\times10^{-3}(\text{pH})(\text{carriers}) \\ & + 0.67[Fe^{2+}][H_2O_2] - 0.02[Fe^{2+}]\text{carriers} - 5.52\times10^{-3}[H_2O_2]\text{carriers} \\ & - 0.57\text{pH}^2 - 18.40[Fe^{2+}]^2 - 0.51[H_2O_2]^2 + 8.84\times10^{-3}\text{carriers}^2 \qquad (4\text{-}1)\end{aligned}$$

$$\begin{aligned}\text{COD removal} \;=\;& 34.33 + 3.39\text{pH} - 36.87[Fe^{2+}] + 1.48[H_2O_2] - 0.29\text{cariers} \\ & + 17.31\,\text{pH}[Fe^{2+}] - 0.64\text{pH}[H_2O_2] - 0.07(\text{pH})(\text{carriers}) \\ & - 1.68[Fe^{2+}][H_2O_2] + 0.07[Fe^{2+}]\text{carriers} - 3.76\times10^{-3}[H_2O_2]\text{carriers} \\ & + 0.072\text{pH}^2 - 22.53[Fe^{2+}]^2 + 0.19[H_2O_2]^2 - 3.53\times10^{-4}\text{carriers}^2 \qquad (4\text{-}2)\end{aligned}$$

$$\text{Total iron removal} = -9.17 + 5.84\text{pH} - 9.96[Fe^{2+}] + 0.44[H_2O_2] + 0.44\text{carriers} \qquad (4\text{-}3)$$

The equations (4-1) to (4-3) used to determine the 2,4-dichlorophenol, COD and total iron removal at each actual value of pH, $Fe^{2+}$ and $H_2O_2$ concentration and the amount of carriers. The result of analysis of variance (ANOVA) test were also conducted for 2,4-dichlorophenol, COD and total iron removal presented in Tables 4.3, 4.4 and 4.5, respectively. It indicates that the predictability of the model is at 95% confidence interval. The mean squares were obtained by dividing the sum of squares of each of two sources of variation, the model and the error (residual) variance, by the respective degrees of freedom(df). The model F-value was calculated by dividing the model mean square by residual mean square (Arsian-Alaton et al., 2009).

Values of "Prob > F" less than 0.0500 imply that the model is significant, whereas the values greater than 0.1000 are usually consider as insignificant. Prob > F values of 0.0133, 0.0013 and less than 0.0001 indicate that the employed models are significant for percentages of COD, removal, total iron removal and 2,4-dichlorophenol removal, respectively.

The coefficients of determination "$R^2$" value of the response variables were determined. The highest $R^2$ obtained for 2,4-dichlorophenol removal efficiency ($R^2_{2,4\text{-DCP}}$= 0.9589 ) shows that 95.89% of the total variation data could be explained by the established model expressing a satisfactory quadratic fit. However, in terms of COD and total iron removal, 77.60% and only around 55% of the total variation could be explained by the model, respectively. ($R^2_{COD}$= 0.7760, $R^2_{\text{Total iron}}$ = 0.5507).

The ANOVA results from the Table 4.3, 4.4 and 4.5 show that the Model F-values of 23.31, 3.46 and 6.26 implies the models are significant in terms of 2,4-dichlorophenol, COD and total iron removal efficiencies, respectively. There is only a 0.01% chance for 2,4-dichlorophenol removal, 1.33% chance for COD removal and 0.13% chance for total iron removal that a "Model F-Value" could large due to noise. Furthermore, the model also revealed statistically significant with the "Lack of Fit F-value" of 13.07. and 39.84 in terms of 2,4-dichlorophenol and total iron removal. There is only a 1.22% chance for 2,4-dichlorophenol removal and 0.13% chance for total iron removal that a "Lack of Fit F-value" could large due to noise. For the COD removal, the model shows that "Lack of Fit F-value" of 0.58 is not significant relative to the pure error. There is a 78.00% chance that a "Lack of Fit F-value" could large due to noise.

Table 4.3 ANOVA test for response surface quadratic model of 2,4-dichlorophenol removal by Box-Behnken design.

| Source | Sum of Squares | df | Mean Square | F value | P-value Prob > F | |
|---|---|---|---|---|---|---|
| Model | 3033.71 | 14 | 216.69 | 23.31 | $< 0.0001$ | Significant |
| A (pH) | 18.55 | 1 | 18.55 | 2.00 | 0.1796 | |
| B ($Fe^{2+}$) | 29.20 | 1 | 29.20 | 3.14 | 0.0981 | |
| C ( $H_2O_2$) | 2112.85 | 1 | 2112.85 | 227.25 | $< 0.0001$ | |
| D ( mass of carrier) | 5.75 | 1 | 5.75 | 0.62 | 0.4446 | |
| AB | 0.027 | 1 | 0.027 | 2.928E-003 | 0.9576 | |
| AC | 76.48 | 1 | 76.48 | 8.23 | 0.0124 | |
| AD | 0.42 | 1 | 0.42 | 0.045 | 0.8343 | |
| BC | 7.43 | 1 | 7.43 | 0.80 | 0.3866 | |
| BD | 1.90 | 1 | 1.90 | 0.20 | 0.6578 | |
| CD | 24.56 | 1 | 24.56 | 2.65 | 0.1257 | |
| $A^2$ | 2.07 | 1 | 2.07 | 0.22 | 0.6441 | |
| $B^2$ | 90.02 | 1 | 90.02 | 9.68 | 0.0077 | |
| $C^2$ | 685.36 | 1 | 685.36 | 73.71 | $< 0.0001$ | |
| $D^2$ | 0.051 | 1 | 0.051 | 5.454E-003 | 0.9422 | |
| Residual | 130.17 | 14 | 9.30 | | | |
| Lack of fit | 126.30 | 10 | 12.63 | 13.07 | 0.0122 | Significant |
| Pure error | 3.86 | 4 | 0.97 | | | |
| Total Cor | 3163.87 | 28 | | | | |
| $R^2 = 0.9589$ | | | | | | |

Table 4.4 ANOVA test for response surface quadratic model of COD removal by Box-Behnken design.

| Source | Sum of Squares | df | Mean Square | F value | p-value Prob > F | |
|---|---|---|---|---|---|---|
| Model | 1156.31 | 14 | 82.59 | 3.46 | 0.0133 | Significant |
| A (pH) | 10.93 | 1 | 10.93 | 0.46 | 0.5095 | |
| B (Fe $^{2+}$) | 134.34 | 1 | 134.34 | 5.63 | 0.0325 | |
| C ( $H_2O_2$) | 17.79 | 1 | 17.79 | 0.75 | 0.4023 | |
| D ( mass of carrier) | 24.00 | 1 | 24.00 | 1.01 | 0.3328 | |
| AB | 242.58 | 1 | 242.58 | 10.17 | 0.0066 | |
| AC | 33.29 | 1 | 33.29 | 1.40 | 0.2570 | |
| AD | 206.21 | 1 | 206.21 | 8.65 | 0.0107 | |
| BC | 46.51 | 1 | 46.51 | 1.95 | 0.1843 | |
| BD | 48.16 | 1 | 48.16 | 2.02 | 0.1771 | |
| CD | 11.19 | 1 | 11.19 | 0.47 | 0.5045 | |
| $A^2$ | 0.034 | 1 | 0.034 | 1.407E-003 | 0.9706 | |
| $B^2$ | 135.06 | 1 | 135.06 | 5.66 | 0.0321 | |
| $C^2$ | 105.84 | 1 | 105.84 | 4.44 | 0.0537 | |
| $D^2$ | 80.63 | 1 | 80.63 | 3.38 | 0.0872 | |
| Residual | 333.83 | 14 | 23.84 | | | |
| Lack of Fit | 197.38 | 10 | 19.74 | 0.58 | 0.7800 | Not Significant |
| Pure error | 136.44 | 4 | 34.11 | | | |
| Cor total | 1490.14 | 28 | | | | |
| $R^2 = 0.7760$ | | | | | | |

Table 4.5 ANOVA test for response surface linear model of total iron removal by Box-Behnken design.

| Source | Sum of Squares | df | Mean Square | F value | p-value Prob > F | |
|---|---|---|---|---|---|---|
| Model | 900.96 | 4 | 225.24 | 6.26 | 0.0013 | Significant |
| A (pH) | 409.73 | 1 | 409.73 | 11.39 | 0.0025 | |
| B ($Fe^{2+}$) | 241.11 | 1 | 241.11 | 6.70 | 0.0161 | |
| C ( $H_2O_2$) | 47.24 | 1 | 47.24 | 1.31 | 0.2631 | |
| D ( mass of carrier) | 202.87 | 1 | 202.87 | 5.64 | 0.0259 | |
| Residual | 863.27 | 24 | 35.97 | | | |
| Lack of Fit | 858.96 | 20 | 42.95 | 39.84 | 0.0013 | Significant |
| Pure error | 4.31 | 4 | 1.08 | | | |
| Cor total | 1764.23 | 28 | | | | |
| $R^2$ = 0.5507 | | | | | | |

The p-values are used as a tool to check significance of each variables, which also indicate the interaction strength between each independent variable (Liu et al., 2003). The smaller P-values, the bigger the significance of the corresponding varible (Muralidhar et al., 2001). P-values in this study less than 0.0500 indicate model terms are significant, whereas P-values greater than 0.1000 indicate the model terms are not significant. The ANOVA analysis for 2,4-dichlorophenol removal in Table 4.3 indicated that $H_2O_2$ concentration(C) and the interactions (AC, $B^2$, $C^2$) were significant model terms (factors) and played important role in 2,4-dichlorophenol degradation by fluidized-bed Fenton process. Other model terms were relatively less significant influencing 2,4-dichlorophenol removal due to their confidence level were less than 95% (P > 0.0500).

The results of ANOVA for COD and total iron removal, Tables 4.4 and 4.5 illustrated that $Fe^{2+}$ concentration (B) and the interactions (AB, AD, $B^2$) were significant model terms in COD removal, whereas pH (A), $Fe^{2+}$ concentration (B) and masss of carriers (D) were significant parameters in terms of total iron removal.

### 4.2.2 2,4-dichlorophenol removal

The degradation of 2,4-dichlorophenol increased with increasing $H_2O_2$ and $Fe^{2+}$ concentration because a large amount of •OH was produced at higher $Fe^{2+}$ and $H_2O_2$ concentrations; consequently, the removal efficiency was improved. However, $H_2O_2$ seemed to be more significant than $Fe^{2+}$.

The results also show that the degradation of 2,4-dichlorophenol would slightly increase as the amount of carriers increased. The pH value of solutions is an important parameter for Fenton's reactions, which controls the production rate of •OH and the concentration of ferrous ion (Sun et al., 2008). In this study, it can be derived that initial pH does not have an obvious effect on the degradation of 2,4-dichlorophenol. This finding agrees with Oliveira et al. (2006) in that the 2,4-dichlorophenol oxidation by Fenton's reaction appeared to be no different at initial pH 3-5. Moreover, Khan et al. (2009) also suggest that within the studied range of pH 2-4, the pH did not substantially affect the degradation efficiency of 2,4-dichlorophenol by Fenton's reaction. However, the effect of pH values on the degradation of 2,4-dichlorophenol was investigated and the results were shown in Figure 4.3. It can be seen that the removal efficiency of 2,4-dichloropheonl was almost the same at 120 minutes when pH 2, 3 and 4 were applied. While considering the reaction time, it was found that 2,4-dichlorophenol was rapidly oxidized at pH 3 more than pH 2 and 4.

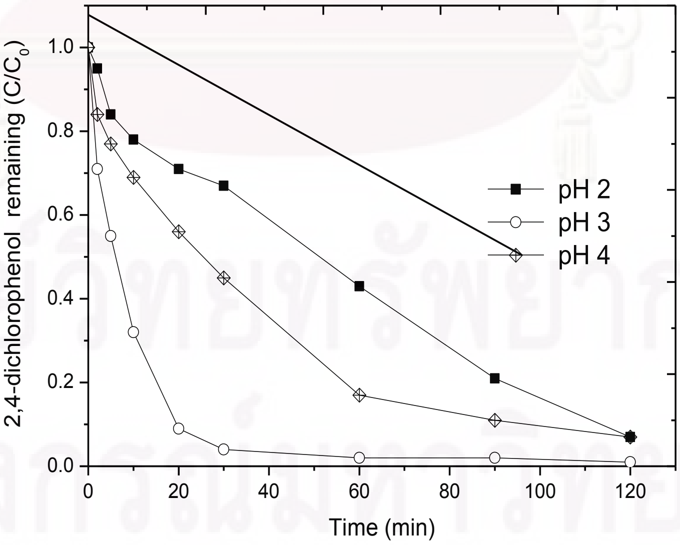


Figure 4.3 The effect of pH value on 2,4-dichlorophenol removal efficiency. [2,4-dichlorophenol] = 1 mM, $[Fe^{2+}]$ = 0.1 mM, $[H_2O_2]$ = 5.5 mM and $SiO_2$ = 150 g.

For pH value below 3, the reaction of $H_2O_2$ with $Fe^{2+}$ is seriously affected, causing the reduction in •OH production. So, the degradation of 2,4-dichloropheonl slowly decreased in the beginning of reaction at pH 2. Inhibition of •OH formation at pH below 3 was due to the decrease of the soluble amount of $Fe^{3+}$ that is in equilibrium with other iron species ($Fe(OH)^{2+}$ and $Fe(OH)_2^+$) under such conditions (Rodrigues et al., 2009). Both of $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ forming at low pH can react slowly with $H_2O_2$ and produce less amount of •OH (Gallard et al., 1998). On the other hand, at higher pH, the deactivation of $Fe^{2+}$caused the reduction of •OH due to the formation of ferric hydroxide complexes ($Fe(OH)_3$) (Sun et al., 2008). Besides, in such conditions $H_2O_2$ is less stable, being decomposed into water and oxygen (Ramirez et al., 2008). So, the degradation of 2,4-dichloropheonl gradually decreased at pH 4. However, the initial pH and final pH were not different, because pH was controlled during the reaction time. From this results, the initial pH 3 have an obvious effect on the removal efficiency of 2,4-dichlorophenol while consider the reaction time. Therefore, the optimum initial pH for this experiment should be pH 3.

The response surface plot of two effect on 2,4-dichlorophenol removal efficiency while the other parameters being fixed were shown in the Figure 4.4 (a)-(f) at the condition of pH 3, $[Fe^{2+}] = 0.55$ mM, $[H_2O_2] = 5.5$ mM and 150 grams of carriers. Each point on the surface represents the 2,4-dichlorophenol removal at each value of factors.

As it is clear from the Figure 4.4 (a), (c) and (d) that the removal efficiency of 2,4-dichlorophenol increased with increasing $H_2O_2$ concentration from 1 to 10 mM. The increase of 2,4-dichlorophenol removal was also observed when $Fe^{2+}$ concentration increased from 0.1 to 0.55 mM as shown in Figure 4.4 (a), (b) and (e) the amount of carriers increased from 50 to 250 grams as shown in Figure 4.4 (d), (e) and (f). The amount of carriers seem to have a positive effect on the total iron removal more than the degradation of 2,4-dichlorophenol because the surface of carriers in fluidized-bed reactor is the primary part where iron crystallization occurred (Chou et al., 2004). From Figure 4.4 (b), (c) and (f), it was found that the removal efficiency slightly decreased with increasing pH from 2 to 4.

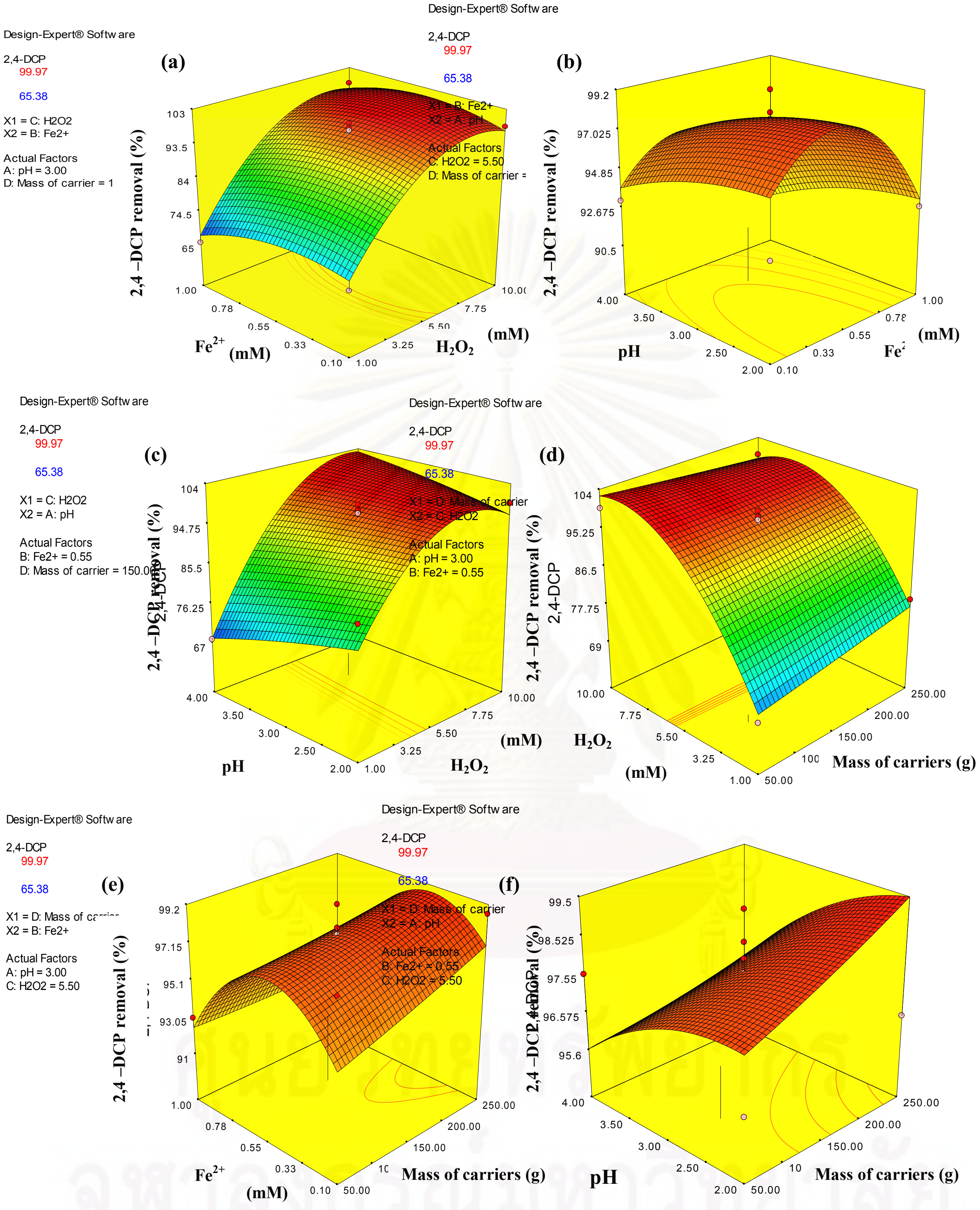


Figure 4.4 Response surface plots of the various effects on 2,4-DCP removal efficiency. At pH 3, [Fe$^{2+}$] = 0.55 mM, [$H_2O_2$] = 5.5 mM and 150 grams of carrier.

### 4.2.3 COD removal

The COD removal efficiency relied on the initial concentrations of $Fe^{2+}$and $H_2O_2$. The effects of $Fe^{2+}$ and $H_2O_2$ on COD removal are shown in Figure 4.5. Increasing $H_2O_2$ concentrations improved the COD removal. On the other hand, Increasing $Fe^{2+}$ concentration more than 0.55 mM could decrease the COD removal.

The interactions between two variables with the other variables being fixed on COD removal efficiency were shown in the Figure 4.5 at the condition of pH 3, $[Fe^{2+}] = 0.55$ mM, $[H_2O_2] = 5.5$ mM and 150 grams of carriers. Each point on the surface represents the COD removal at each value of factors.

It is obviously seen from Figure 4.5 (a) that the maximum COD removal (62%) occurred when the highest $H_2O_2$ concentration and the lowest concentration of $Fe^{2+}$ were applied. The Figure 4.5(c) and (e) also present that COD removal increased with increasing the $H_2O_2$ concentration. This was due to the increase in •OH concentration as a result of the addition of $H_2O_2$ (Sun et al., 2007). The increase in COD removal was also observed when $Fe^{2+}$ concentration increased. However, high $Fe^{2+}$ concentration would adversely affect to COD removal as illustrate in Figure4.5 (a), (b) and (d). The use of high catalyst dosages inhibited the COD removal due to the formation of radical scavengers as illustrate in equations (2-6) and (2-9).

Figure 4.5(b) explains that, at pH 2, COD removal decreased with increasing $Fe^{2+}$ concentration from 0.1 to 1 mM. However, at pH 4, COD removal increased when increased $Fe^{2+}$ concentration from 0.1 to 1 mM. The decrease in COD removal at pH 2 can be explained by a scavenging effect of $Fe^{2+}$. On the other hand, the increase in COD removal at pH 4 was because the amount of $Fe^{2+}$adding in to the solution was more than the amount of $Fe^{3+}$ being precipitated. Therefore, $Fe^{2+}$ was enough to stimulate the decomposition of $H_2O_2$ to generate •OH. Figure 4.5(f) explains that, at pH 4, COD removal was decreased when increased more carriers into the reactor. This was because ferrous ion can change to ferric ion at high pH, and then attach onto the carriers. Therefore, $Fe^{2+}$ was not enough to react with $H_2O_2$ to produce hydroxyl radicals, thus, reduced the COD removal efficiency. However, at pH 2, COD increased with increasing amounts of carriers. This was because, at low pH, ferrous ions can regenerate from iron oxide that coated on the surface of carriers. Therefore, adding more carriers in reactor could increase ferrous ion concentrations in the solution.

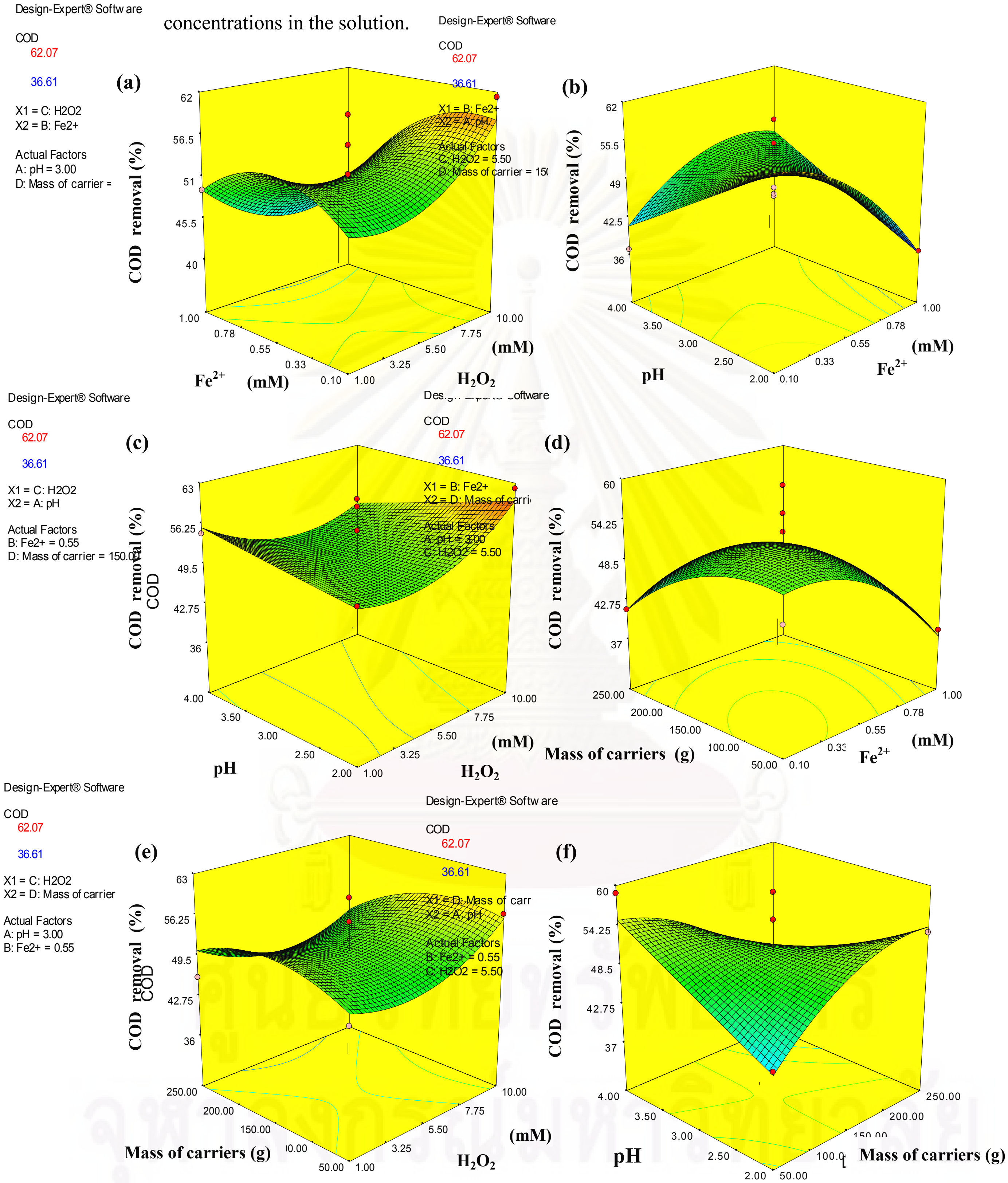


Figure 4.5 Response surface plots of the various effects on COD removal efficiency. At pH 3, $[Fe^{2+}]$ = 0.55 mM, $[H_2O_2]$ = 5.5 mM and 150 grams of carrier.

### 4.2.4 Total iron removal

pH, $H_2O_2$ concentration and the amount of carriers gave a positive effect on total iron removal. This means that total iron removal increased when pH, $H_2O_2$ concentration and the amount of carriers increased. On the other hand, increasing $Fe^{2+}$ concentration could decrease the total iron removal. The analysis of ANOVA shows that pH, $Fe^{2+}$ concentration and amount of carriers were significant parameters in terms of total iron removal because of their values of "Prob > F" less than 0.05.

The response surface plots of two effects on total iron removal efficiency with the other effects being fixed were shown in Figure 4.6 at the condition of pH 3, $[Fe^{2+}] = 0.55$ mM, $[H_2O_2] = 5.5$ mM and 150 grams of carriers. Each point on the surface represents the total iron removal at each value of factors.

As can be understood from Figure 4.6 (a), (e) and (f), increasing pH values enhance the total iron removal efficiency. This was due to the precipitation of iron hydroxide at higher pH resulted in the decreased of dissolve iron. Besides, $Fe^{2+}$ concentration also played an important role in total iron removal. Increasing $Fe^{2+}$ concentration would slightly decreased total iron removal as observed in Figure 4.6 (a), (b) and (c). The decrease in the total iron removal was because the amount of $Fe^{3+}$ generated from Fenton reaction more than the mass of carrier, so, a few amount of $Fe^{3+}$ could crystallize on the surface of carrier. By this way, total iron removal decreased when increased more ferrous ion concentration.

The results in Figure 4.6 (c), (d) and (f) show that the more amounts of carriers were applied in the experiment, the more total irons were removed. Because the large amount of carriers provided more surface area for iron crystallization. Additionally, increasing $H_2O_2$ concentration would slightly increase the total iron removal as shown in Figures 4.6 (b), (d) and (e). However, $H_2O_2$ was considered as less significant factor affecting total iron removal.

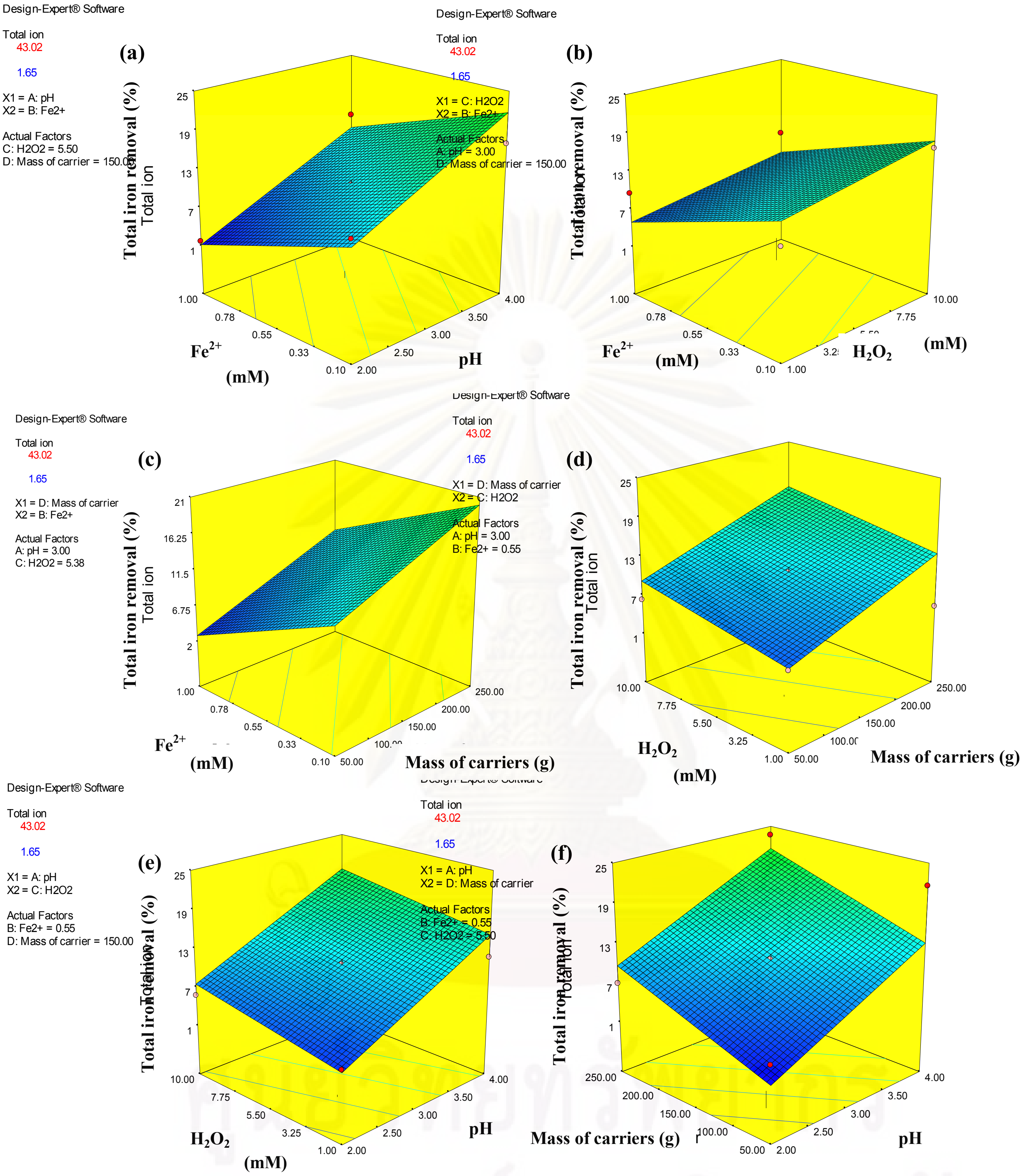


Figure 4.6 Response surface plots of the various effects on total iron removal efficiency. At pH 3, $[Fe^{2+}]$ = 0.55 mM, $[H_2O_2]$ = 5.5 mM and 150 grams of carrier.

## 4.3 Optimization process

The main objective of this optimization process was to determine the optimum conditions for removal of 2,4-dichlorophenol, COD and total iron in fluidized-bed Fenton process by predicting from the experimental data. The optimization module in Design-Expert searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses (Arslan-Alaton et al., 2009). For optimization process, the desired goals for each variable and response should be established first. In present study, the maximum level obtained in the experimental result was selected in terms of 2,4-dichlorophenol and COD removal while the total iron removal was selected to be in the range of experimental result. For the process of variable, pH was selected to equal 3 according to the optimum pH mentioned above, the amount of carriers were fixed at 100 grams, the initial concentration of Fe $^{2+}$ and $H_2O_2$ were selected to be in the range used in this study. After that, these individual goals were combined into an overall desirability function by the software for optimization process. The software provided the several runs of experiments which evaluated for a maximum removal. Then, the suitable run was selected to be repeated and check for the prediction from the model. Finally, the optimum condition for the removal of 2,4-dichlorophenol by fluidized-bed Fenton process was shown in Table 4.6.

Under this optimum condition of pH 3, 100 grams of carriers, 0.25 mM of Fe $^{2+}$ concentration and 10 mM of $H_2O_2$ concentrations, the removal efficiencies of 2,4-dichlorophenol, COD and total iron were predicted to be 99.86 %, 60.49% and 14.38 %, respectively. Furthermore, the actual removal efficiencies of 2,4-dichlorophenol, COD and total iron when followed these predicted optimum condition were 99.38%, 54.35% and 16.33%, respectively. It was found that the observed value between the predicted value was slightly different in terms of 2,4-dichlorophenol and total iron removal. But the predicted value was quite different with the observed value in terms of COD removal.

Table 4.6 Predicted optimum condition for removal of 2,4-dichlorophenol, COD and total iron by fluidized-bed Fenton process.

| **Experimental variables** | | | | **Response Function** | | |
|---|---|---|---|---|---|---|
| pH | $Fe^{2+}$ (mM) | $H_2O_2$ (mM) | Carrier (grams) | 2,4-dichlorophenol removal (%) | COD removal (%) | Total iron removal (%) |
| 3 | 0.25 | 10 | 100 | 99.86 | 60.49 | 14.38 |

Figure 4.7 shows the results from predicted optimum condition. The result show that more than 50 % of 2,4-dichlorophenol was rapidly degraded within 2 minutes and reaching 99% degradation in only 10 minutes. The data reveal that 2,4-dichlorophenol could be highly removed to 99.38 % in the end of reaction time. It can be seen from Figure 4.9 (a) that COD remaining was gradually decreased with time. The final COD removal in 120 minutes was less than that in the final 2,4-dichlorophenol. This was due to many intermediates produced from the reaction can hardly be degraded completely. Both of $Fe^{2+}$ and $H_2O_2$ concentration also decreased during the reaction because they were used for the production of •OH (equation 2-5).

In the beginning of reaction, high doses of Fenton's reagent were being used to produce a large amount of hydroxyl radicals. Then, the reaction occurred very fast as shown in the degradation of 2,4-dichlorophenol. As a result of the effective removal of 2,4-dichlorophenol in 10 minutes, 40% of $Fe^{2+}$ concentration and 30 % of $H_2O_2$ concentration still presented at the end of reactions as shown in Figure 4.7 (b). For the advantage of fluidized-bed Fenton process, the carriers serve for reducing ferric ions via crystallization process (Chou et al., 2004) as shown in Figure 2.4 reaction (e). The total iron removal at the optimum condition was shown in Figure 4.7(b). There was 16.33% of total iron removed within 120 minutes. The small amount of total iron was removed probably due to the initial pH applied in the optimum condition. High level of pH was more suitable for removing iron than pH 3 because ferric ions usually precipitated in the high pH solution (Rodrigues et al., 2009). Therefore, the suitable pH for iron removal should be 3.5-4 (Diz and Novak, 1998).

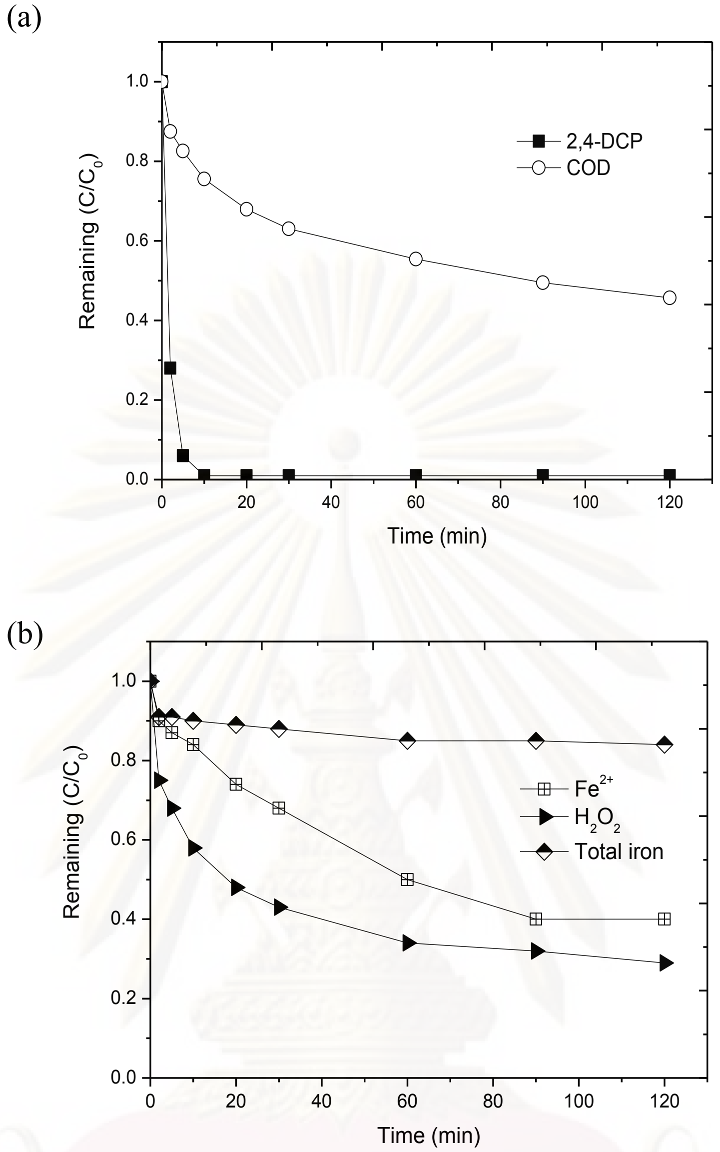


Figure 4.7 (a) 2,4-dichlorophenol and COD removal at the optimum condition ,
(b) $Fe^{2+}$, $H_2O_2$ and total iron removal at the optimum condition.
[2,4-DCP] = 1 mM, [$Fe^{2+}$] = 0.25 mM, [$H_2O_2$] = 10 mM, 100 grams of carrier at pH 3.

From Table 4.7, it can be summarized that the experimental results obtained under optimized concentration were very close to the predicted results in terms of 2,4-dichlorophenol and total iron removal, evidencing the reliability of the methodology used within the range of concentration investigated. While the observation value of COD removal obtained from the experimental results was quite different from the prediction value. This was due to the variance of COD removal in the experimental which observe from the error of COD removal in 5 repeated runs (run number 25 to

29 in Table 4.2). So, the observation value was slightly different from the prediction values in terms of COD removal.

Table 4.7 Summary of the prediction and the observation values from the optimum condition for percent removal of 2,4-dichlorophenol, COD and total iron by fluidized-bed Fenton process.

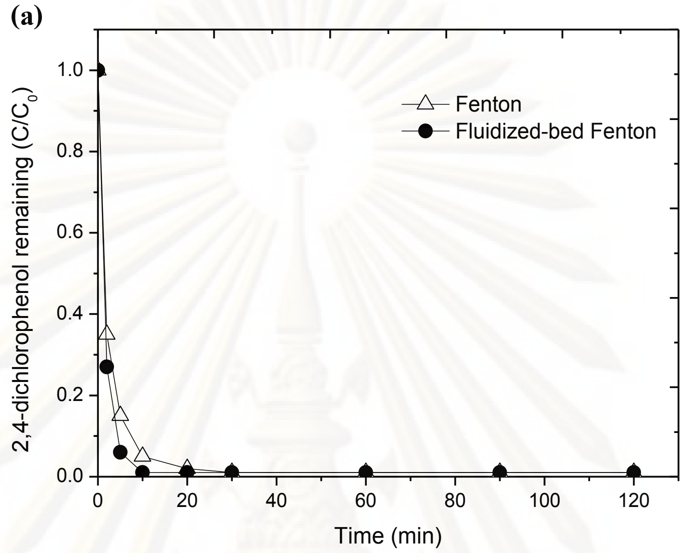
| **Percent removal** (%) | **Prediction** | **Observation** |
|---|---|---|
| 2,4-dichlorophenol | 99.86 | 99.38 |
| COD | 60.49 | 54.35 |
| Total iron | 14.38 | 16.33 |

### 4.4 Comparison between the fluidized-bed Fenton and Fenton process at the optimum condition.

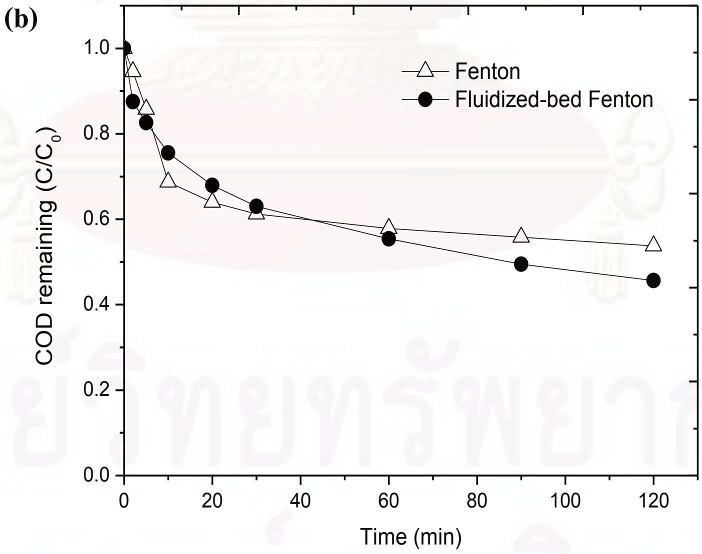
The optimum condition obtained from the Box-Benhnken experiment, in the previous parts was pH 3, initial concentration of 2,4-dichlorophenol 1 mM, 0.25 mM of $Fe^{2+}$ concentration, 10 mM of $H_2O_2$ concentration and 100 grams of $SiO_2$.

It can be seen from Figure 4.8 (a) that the removal of 2,4-dichlorophenol from Fenton process and fluidized-bed Fenton process were almost the same. The oxidation of 2,4-dichlorophenol was rapidly proceeded within 2 minutes and almost completed within 10 minutes for Fenton and fluidized-bed Fenton process. The removal efficiencies of 2,4-dichlorophenol in fluidized-bed Fenton and Fenton process were 99.38% and 99.42%, respectively.

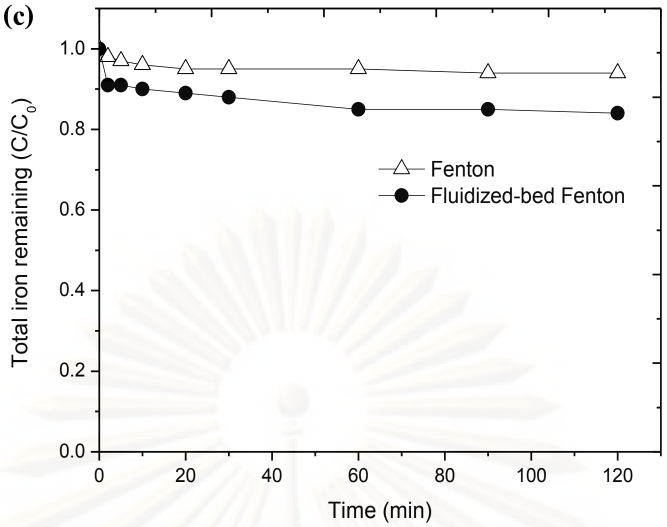
For COD removal as shown in Figure 4.8 (b), the COD removal efficiencies from Fenton and fluidized-bed Fenton process were 46.26 % and 54.35 %, respectively. The total iron remaining in the solution from fluidized-bed Fenton and Fenton process was illustrated in Figure 4.8 (c). There was 6.22% of total iron being removed from Fenton process while 16.33% of total iron could be removed in fluidized-bed Fenton process. It can be explained that total iron being removed was crystallized on surface of carrier 16.33% and left on the dead end of fluidized-bed reactor 6.22% while the soluble iron and settle iron ($Fe(OH)_3$) were 77.45%. Therefore, total iron being removed in fluidized-bed Fenton process can reduce 16.33% of the amount of sludge which can occur after adjust the pH before treatment. Moreover, decreasing in the amount of sludge was considered as an advantage of fluidized-bed Fenton process which also reduces the separation and disposal costs as well.



(a) 2,4-dichlorophenol remaining



(b) COD remaining



(c) Total iron remaining

Figure 4.8 Comparison of 2,4-dichlorophenol, COD and total iron remaining between Fenton and Fluidized-bed Fenton Process with the condition of [2,4-DCP] = 1 mM, $[Fe^{2+}]$ = 0.25 mM, $[H_2O_2]$ = 10 mM, pH = 3 and 100 grams of $SiO_2$.

## 4.5 Kinetics Study

The kinetics of 2,4-dichlorophenol degradation by fluidized-bed Fenton Process was investigated in order to understand the degradation behavior of this chemical. In this study, the initial rate technique was performed in order to eliminate any interference from intermediate that might occur during the reaction. Therefore, the oxidation rates of 2,4-dichlorophenol was discussed only the initial state at 5 minutes.

The basic single-factor at a time approach was performed in this method. The studied range of each parameter was chosen according to the optimum condition in order to obtain the trend of degradation and the kinetics study. The effects of initial concentration of $Fe^{2+}$, initial concentration of $H_2O_2$ and initial 2,4-dichlorophenol concentration on the kinetics study were investigated and separately discussed in the following parts.

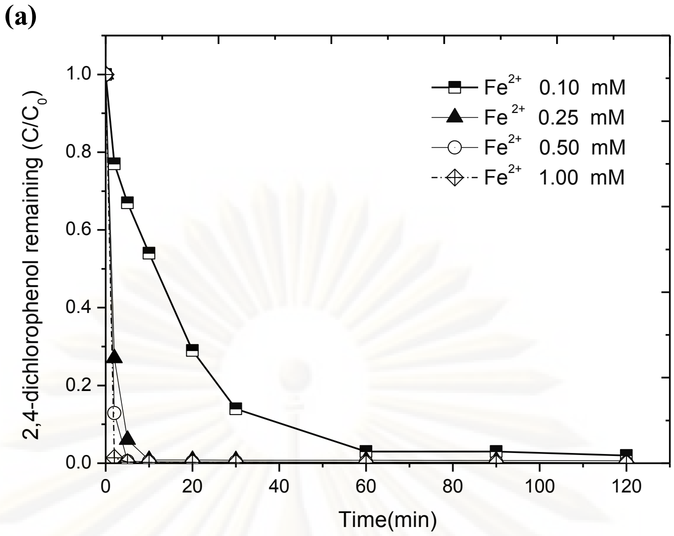
### 4.5.1 Effect of ferrous iron concentration

Ferrous ion acts as a catalyst in Fenton process which decomposes $H_2O_2$ to produce •OH and leads to the degradation of organic matter. Generally, the rate of degradation increases with an increase in the concentration of ferrous ion (Gogate and Pandit, 2004). The effect of initial $Fe^{2+}$ on the 2,4-dichlorophenol degradation was studied by varying the $Fe^{2+}$ concentration to 0.1 ,0.25 , 0.5 and 1 mM with the experimental condition of initial 2,4-dichlorophenol concentration 1 mM , 10 mM of $H_2O_2$ , 100 grams of $SiO_2$ and pH 3. The results show that the 2,4-dichlorophenol was removed completely when the concentration of $Fe^{2+}$ greater than 0.1 mM. It can be seen from Figure 4.9 (a) that the more $Fe^{2+}$ concentration applied in the experiment, the faster completely oxidized 2,4-dichlorophenol would be obtained. The 2,4-dichlorophenol could remove more than 99% within 10, 5 and 2 minute when 0.25, 0.50 and 1 mM of $Fe^{2+}$ was applied, respectively. This indicated that initial oxidation rate of 2,4-dichlorophenol was significantly enhanced as the $Fe^{2+}$ concentration increased from 0.1 to 1 mM.

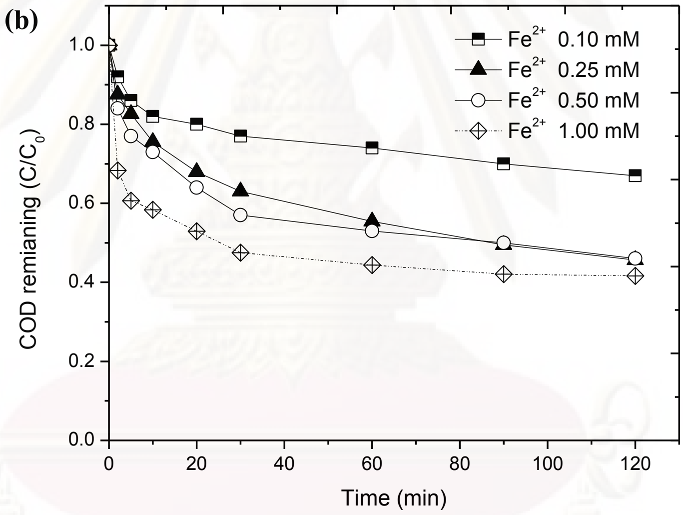
From Figure 4.9 (b), it is clear that COD removal efficiency increased with increasing $Fe^{2+}$ concentration. This increasing trend is due to the higher dosage of $Fe^{2+}$ available for more generation of •OH, leading to a higher of COD removal efficiency. The COD removal efficiencies were 32.18%, 54.35%, 54.89% and 58.57% with the $Fe^{2+}$ concentration of 0.1, 0.25, 0.5 and 1 mM, respectively.

The total iron removal efficiency in Figure 4.10 (a) was corresponding with the result obtained in the previous part. That is increasing $Fe^{2+}$ concentration would decrease total iron removal efficiency. However, the mass of iron being removed was increased with increasing $Fe^{2+}$ concentration. As a result of the experimental was applied at the same reactor, so the volume of the reactor was constant. The mass of iron being removed can be calculated as the following equation:

$$\text{The mass of iron being removed} = \text{the percentage of total iron removal} \times \text{initial } Fe^{2+} \text{ concentration} \times \text{the molecular weight of } Fe^{2+} \quad (4\text{-}4)$$

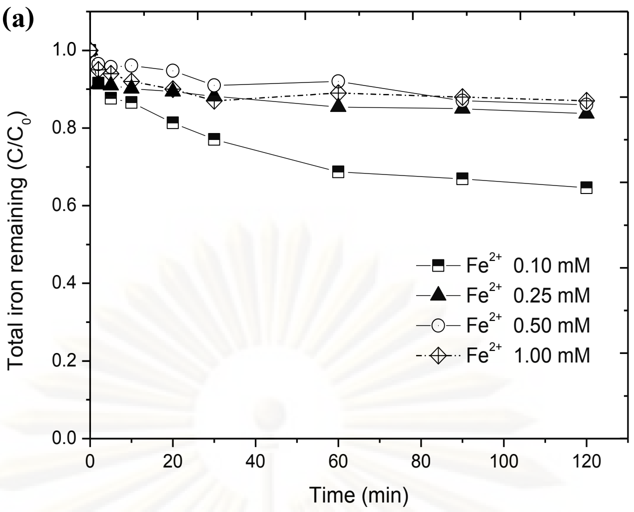


(a) 2,4-dichlorophenol remaining

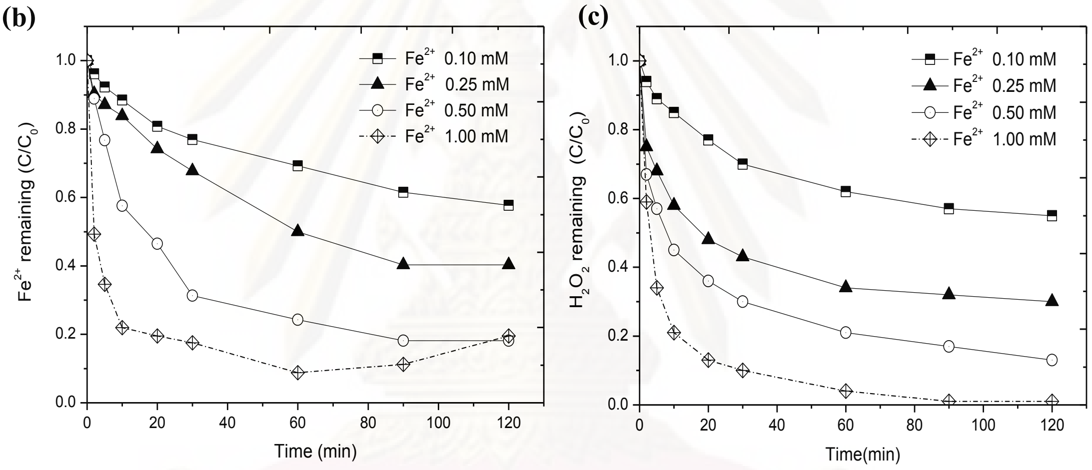


(b) COD remaining

Figure 4.9 Effect of initial ferrous ion concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process (a) 2,4-dichlorophenol remaining , (b) COD remaining ;with the condition of [2,4-DCP] = 1mM , [$H_2O_2$] = 10 mM , pH =3 and 100 grams of $SiO_2$



(a) Total iron remaining



(b) Ferrous ion remaining

(c) $H_2O_2$ remaining

Figure 4.10 Effect of initial ferrous ion concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process (a) total iron remaining , (b) $Fe^{2+}$ remaining and (c) $H_2O_2$ remaining; With the condition of [2,4-DCP] = 1mM , [$H_2O_2$] = 10 mM , pH =3 and 100 grams of $SiO_2$

Increasing $Fe^{2+}$ concentration would increase in the mass of iron being removed in the solution. Increasing the mass of iron being removed implied that crystallized iron coated onto the surface of carriers. From the results, the total iron removal efficiency and the mass of ion being removed under the different $Fe^{2+}$ concentration of 0.1 mM, 0.25 mM, 0.50 mM and 1 mM was shown in Table 4.8

Table 4.8 the removal efficiency of total iron and the mass of iron being removed under the different ferrous ion concentration with the condition of [2,4-DCP] = 1 mM , $[H_2O_2]$ = 10 mM , pH =3 and 100 grams of $SiO_2$.

| $Fe^{2+}$ concentration (mM) | Total iron removal efficiency (%) | Mass of iron being removed (mg/l) |
|---|---|---|
| 0.10 | 35.39 | 1.95 |
| 0.25 | 16.33 | 2.28 |
| 0.5 | 14.57 | 4.06 |
| 1.0 | 13.76 | 7.68 |

It can be clearly seen from Figure 4.10 (b) and (c) that $Fe^{2+}$ and $H_2O_2$ decreased with time of reaction. From the Figure 4.10(b), it can be seen that low concentration of $Fe^{2+}$ (0.1 and 0.25 mM), was not enough to react with $H_2O_2$. So, there were some amount of $H_2O_2$ remained in the solution. On the other hand, increasing $Fe^{2+}$ concentration up to 1 mM, $H_2O_2$ was used very fast and not enough in the end of reaction. In this study, the initial degradation rate of 2,4-dichlorophenol was obtained from the slope of plot between 2,4-dichlorophenol remaining ($C/C_0$) and time within 5 minutes. Therefore, the initial rate and 2,4-dichlorophenol removal efficiency were listed in Table 4.9.

Table 4.9 Initial rate of 2,4-dichlorophenol degradation and the removal efficiency of 2,4-dichlorophenol under the different ferrous ion concentration with the condition of [2,4-DCP] = 1 mM , $[H_2O_2]$ = 10 mM , pH =3 and 100 grams of $SiO_2$.

| $Fe^{2+}$ concentration (mM) | Initial rate * (x $10^{-1}$ mM/min) | 2,4-dichlorophenol ** removal efficiency (%) |
|---|---|---|
| 0.10 | 0.553 | 98.28% |
| 0.25 | 1.782 | 99.38% |
| 0.50 | 1.866 | 99.89% |
| 1.00 | 1.840 | 99.98% |

* After 5 minutes of reaction, ** After 120 minutes of reaction

Further analysis on initial 2,4-dichlorophenol degradation rate indicated that the oxidation rate of 2,4-dichlorophenol increased from 0.0553 mM/min to 0.1782 mM/min as increasing $Fe^{2+}$ concentration from 0.10 to 0.25 mM. Because the added amount of $Fe^{2+}$ directly influenced the generation rate of •OH via equation(2-5), However, initial 2,4-dichlorophenol degradation rate were rather steady above 0.25 mM. It implies that in the solution with initial $Fe^{2+}$of 0.5 and 1.0 mM, $Fe^{2+}$ was present in excess, so the degradation rate became independent from $Fe^{2+}$concentration or zero order with respect to $Fe^{2+}$. The relationship between initial rate and ferrous ion concentration on a plot of log-log scale obtained a straight line with the slope of 0.51. Therefore, the reaction rate can be written as following equation:

$$\frac{d[2,4\text{-DCP}]}{dt} = -k_{Fe\,2+}\,[Fe^{2+}]^{0.51} \qquad (4\text{-}5)$$

Where 2,4-DCP is 2,4-dichlorophenol , d[2,4-DCP]/dt is mM/min , and $k_{Fe\,2+}$ is the apparent rate constants with respect to $Fe^{2+}$ concentration.

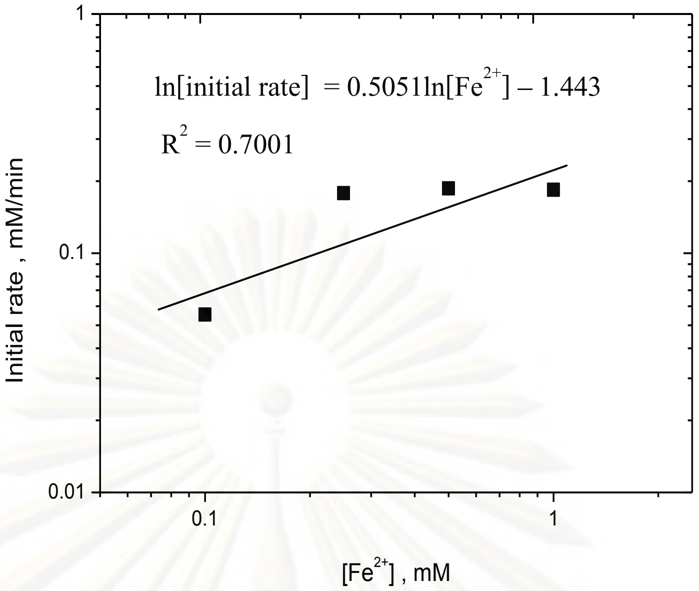
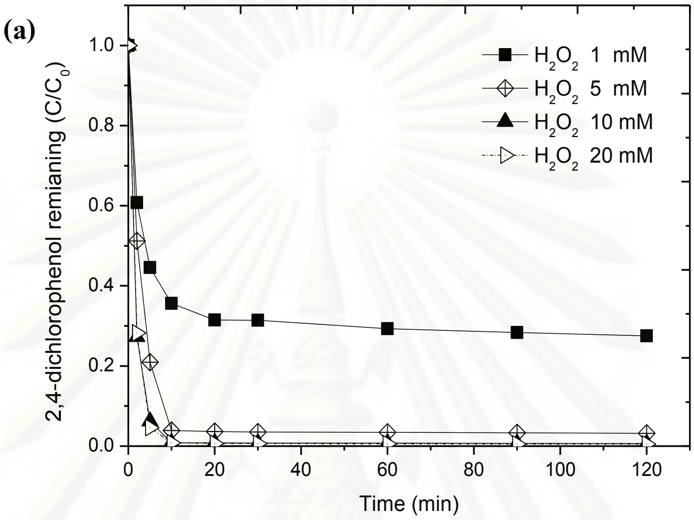


Figure 4.11 Relationship between initial $Fe^{2+}$ concentration and initial rate of 2,4-dichlorophenol degradation on a log-log scale; with the condition of [2,4-DCP] = 1 mM, $[H_2O_2]$ = 10 mM, pH =3 and 100 grams of $SiO_2$

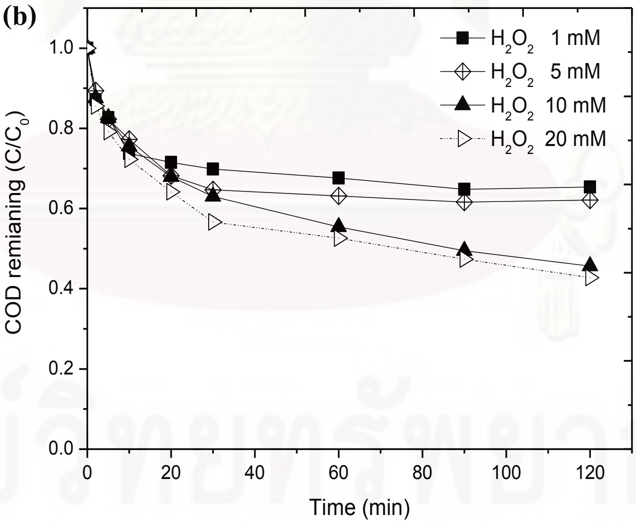
### 4.5.2 Effect of hydrogen peroxide concentration

Hydrogen peroxide plays an important role as a source of •OH that generated from Fenton's reaction (Sun et al., 2009). The effect of $H_2O_2$ on the 2,4-dichlorophenol degradation was examined by varying initial $H_2O_2$ concentration to 1, 5, 10 and 20 mM under the initial condition of 1 mM 2,4-dichlorophenol concentration, 0.25 mM of $Fe^{2+}$, 100 grams of $SiO_2$ and pH 3. The results are shown in figure 4.12(a). The removal efficiency of 2,4-dichlorophenol increased from 72.49% to 99.48% when $H_2O_2$ concentration increased from 1 to 20 mM. Additionally, it can be seen that the effect of $H_2O_2$ concentration on 2,4-dichlorophenol degradation followed the same trend of the effect of $Fe^{2+}$ concentration. It should be noted that the removal efficiency will be improved as the concentration of Fenton's reagents ($Fe^{2+}$ and $H_2O_2$) increases because the generation of •OH directly increase.

The COD removal efficiency increased with increasing $H_2O_2$ concentration from 1 to 10 mM as presented in Figure 4.12(b). The COD removal efficiencies were 34.64%, 37.88%, 54.35% and 58.23% for $H_2O_2$ concentration 1, 5, 10 and 20 mM, respectively. The result from control experiment shows that 6.80% of COD removal efficiency could oxidize by 10 mM of $H_2O_2$. This means that the oxidation by $H_2O_2$ was not the major effect contributed to COD removal efficiency. Therefore, the increase in COD removal efficiency was due to the increase in •OH concentration as a result of the addition of $H_2O_2$ concentration.



(a) 2,4-dichlorophenol remaining



(b) COD remaining

Figure 4.12 Effect of initial hydrogen peroxide concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process (a) 2,4-dichlorophenol remaining, (b) COD remaining; with the condition of [2,4-DCP] = 1mM, [$Fe^{2+}$] = 0.25 mM, pH = 3 and 100 grams of $SiO_2$.

The change of total iron remaining during the reaction was shown in Figure 4.13 (a). The maximum total iron removal was obtained from the condition of $H_2O_2$ 10 mM while the minimum was from the condition of $H_2O_2$ 1 mM. However, the total iron removal was not increased further when increasing $H_2O_2$ concentration up to 20 mM. This might be from the excessive amount of $H_2O_2$ can react with the iron oxide coated on surface of carrier or react with $Fe^{3+}$ via the following equation (Pinatello, 1992). Therefore, a few amount of ferric ion could be removed by crystallization process.

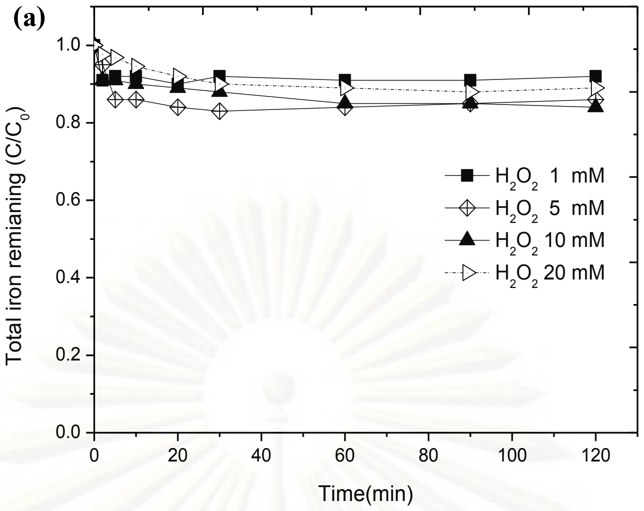
$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}OOH^{2+} + H^+ \qquad (4\text{-}6)$$

$$Fe\text{-}OOH^{2+} \longrightarrow Fe^{2+} + HO_2\bullet + H^+ \qquad (4\text{-}7)$$

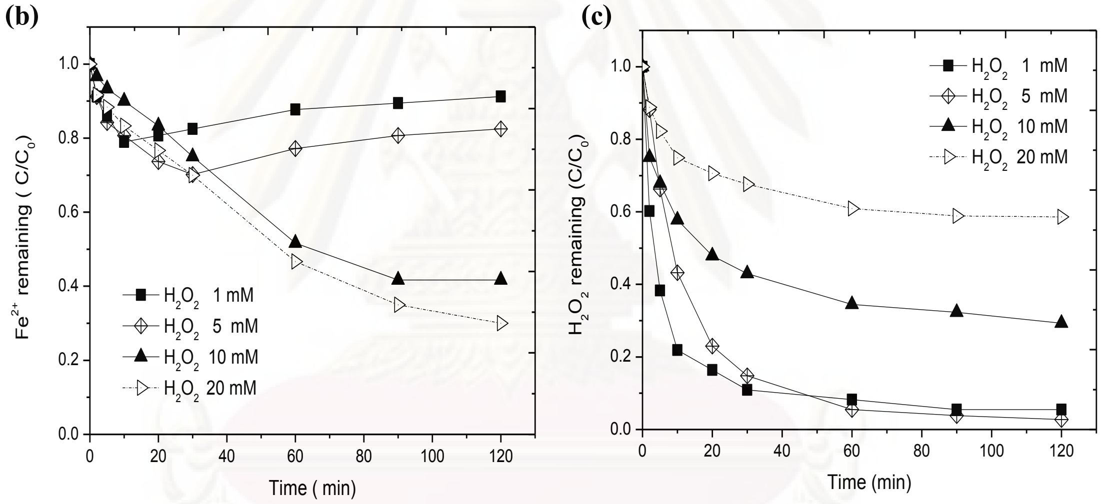
The profile of $Fe^{2+}$ and $H_2O_2$ were presented in Figure 4.13 (b) and (c). Figure 4.13(b) shows the regeneration of $Fe^{2+}$ when applied 1 and 5 mM of $H_2O_2$. The $Fe^{2+}$ regeneration occurred continuously even though $H_2O_2$ depletes. This finding agrees with Kang et al. (2002) in that the $Fe^{2+}$ is regenerated by some intermediates of ring structure for the decomposition of phenol and monochlorophenol by Fenton oxidation. In addition, benzenediol was suggested as a main $Fe^{3+}$ reducing intermediate in phenol decomposition as shown in the following equation (Chen and Pignatello, 1997; Mentasti et al., 1973).

$$\text{(Cl)benzendiols} + Fe^{3+} \longrightarrow Fe^{2+} + \text{(Cl)semiquinones}\bullet \qquad (4\text{-}8)$$

However, $Fe^{3+}$ reacting with $H_2O_2$ via equation (4-6 to 4-7) with the rate constant of 0.01 $M^{-1}s^{-1}$ could not overcome $Fe^{2+}$ reacting with $H_2O_2$ with the rate constant of 53-76 $M^{-1}s^{-1}$ (Walling, 1975 and Kang et al., 2002). So, the regeneration of $Fe^{2+}$ could not be seen for 10 and 20 mM of $H_2O_2$ concentration.



(a) Total iron remaining



(b) Ferrous ion remaining (c) $H_2O_2$ remaining

Figure 4.13 Effect of initial hydrogen peroxide concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process (a) total iron remaining, (b) $Fe^{2+}$ remaining and (c) $H_2O_2$ remaining; with the condition of [2,4-DCP] = 1 mM, $[Fe^{2+}]$ = 0.25 mM, pH = 3 and 100 grams of $SiO_2$ .

The slope obtained from the plot of 2,4-dichlorophenol remaining ($C/C_0$) versus time within 5 minutes represents the initial degradation rate of 2,4-dichlorophenol, whereas 2,4-dichlorophenol removal efficiency was considered in 120 minutes of reaction as shown in Table 4.10.

Table 4.10 Initial rate of 2,4-dichlorophenol degradation and the removal efficiency of 2,4-dichlorophenol under the different hydrogen peroxide concentration with the condition of [2,4-DCP] = 1 mM, [$Fe^{2+}$] = 0.25 mM, pH =3 and 100 grams of $SiO_2$.

| $H_2O_2$ concentration (mM) | Initial rate * (x $10^{-1}$ mM/ min) | 2,4-dichlorophenol ** removal efficiency (%) |
|---|---|---|
| 1 | 1.064 | 72.49% |
| 5 | 1.536 | 96.80% |
| 10 | 1.784 | 99.38% |
| 20 | 1.819 | 99.48% |

* After 5 minutes of reaction, ** After 120 minutes of reaction

As $H_2O_2$ increased from 1 mM to 5, 10, and 20 mM while other factors remained constant, the removal efficiency significantly improved from 72.49% to 96.80%, 99.38% and 99.48%, respectively. The variation of $Fe^{2+}$ from 0.1 mM to 1 mM did not show such an obvious enhancement as in the $H_2O_2$ scenario. This implied that $H_2O_2$ concentration was a more important factor influencing on 2,4-dichlorophenol degradation efficiency than $Fe^{2+}$ under this studied conditions. However, the faster oxidation of 2,4-dichlorophenol increase were observed as increase $Fe^{2+}$ concentration.

For the degradation rate listed in Table 4.10, it can be observed that the degradation rate of 2,4-dichlorophenol increased with increasing $H_2O_2$ concentration from 1 to 20 mM. This increase in initial degradation rate was due to the presence of excessive amount of $H_2O_2$ available for the more production of •OH. However, when the $H_2O_2$ concentration was increased from 10 to 20 mM, the degradation rate of 2,4-dichlorophenol was found slightly increase. This might be from a scavenging effect of the •OH by $H_2O_2$ including the consequent formation of less reactive radical $HO_2$• and the recombination of •OH are presented in the following equations (Walling, 1975 and Zhao et. al, 2004).

$$H_2O_2 + \bullet OH \longrightarrow H_2O + HO_2\bullet \qquad (4\text{-}9)$$

$$HO_2\bullet + \bullet OH \longrightarrow H_2O + O_2 \qquad (4\text{-}10)$$

$$\bullet OH + \bullet OH \longrightarrow H_2O_2 \qquad (4\text{-}11)$$

Present a large quantity of $H_2O_2$ will act as a scavenger for the generate of •OH and might favor reacted with •OH to from hydroperoxyl radicals ($HO_2\bullet$) via equation (4-9) with the rate constant $2.7 \times 10^7\ M^{-1}s^{-1}$ (Kang et al., 2002) and the recombination of •OH via equation (4-10) and (4-11) with the rate constant of $1.0 \times 10^{10}$ and $4.2 \times 10^9\ M^{-1}s^{-1}$, respectively (Kang et al., 2002). Therefore, the high concentration of $H_2O_2$ could affect the removal efficiency and initial degradation rate by favor the side reactions that scavenged the •OH (Masomboon, 2008).

The relationship between initial rate and $H_2O_2$ concentration is a linear on a log-log scale graph with the slope of 0.19 as presented in Figure 4.14. Therefore, the kinetic for 2,4-dichlorophenol degradation can be described by the following equation:

$$\frac{d[2,4\text{-DCP}]}{dt} = -k_{H2O2}\,[H_2O_2]^{0.19} \qquad (4\text{-}12)$$

Where $-k_{H2O2}$ is the apparent rate constants for 2,4-dichlorophenol degradation in fluidized-bed Fenton process with respect to hydrogen peroxide concentration.

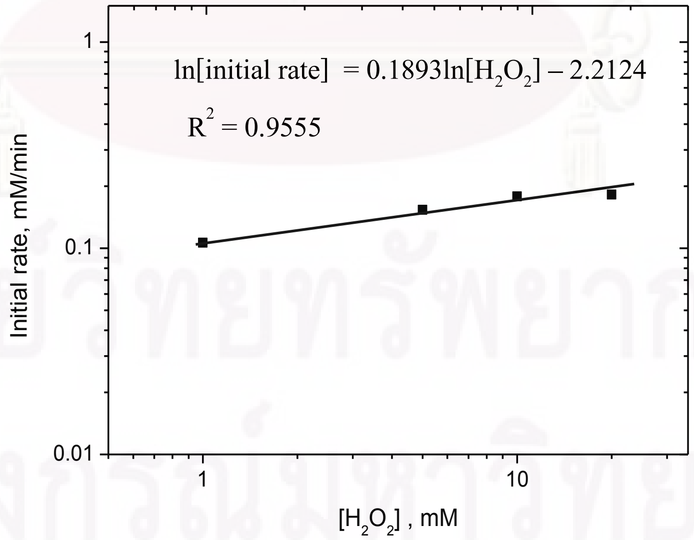


Figure 4.14 Relationship between initial hydrogen peroxide concentration and initial rate of 2,4-dichlorophenol degradation on a log-log scale graph; with the condition of $[2,4\text{-DCP}] = 1$ mM, $[Fe^{2+}] = 0.25$ mM, pH = 3 and 100 grams of $SiO_2$

### 4.5.3 Effect of 2,4-dichlorophenol concentration

The effect of 2,4-dichlorophenol concentration on the degradation rate was investigated by varying initial 2,4-dichlorophenol concentration to 0.5, 1 ,2 and 5 mM with the experimental condition of 10 mM of $H_2O_2$, 0.25 mM of $Fe^{2+}$, 100 grams of $SiO_2$ and pH 3. The results show that 0.5, 1 and 2 mM of 2,4-dichlorophenol could be oxidized more than 99% within 120 minutes as shown in Figure 4.15. However, 82.28% of the removal efficiency was obtained when increasing 2,4-dichlorophenol concentration to 5 mM. This was because the initial concentration of 2,4-dichlorophenol increased but the generation of •OH was not increases correspondingly, so a lower •OH concentration resulted in the decreased of degradation efficiency of 2,4-dichlorophenol.

Increasing 2,4-dichlorophenol concentration also affected COD removal efficiency. As observe in Figure 4.16, the COD removal was decreased as increase in the 2,4-dichlorophenol concentration. Decreasing in COD removal was because the amount of •OH was not enough to degrade a high concentration of 2,4-dichlorophenol and some intermediates generated during the reaction. The result showed that percent COD removal for 0.5, 1, 2 and 5 mM of 2,4-dichlorophenol were 56.67%, 54.35%, 40.10 % and 30.16 %, respectively.

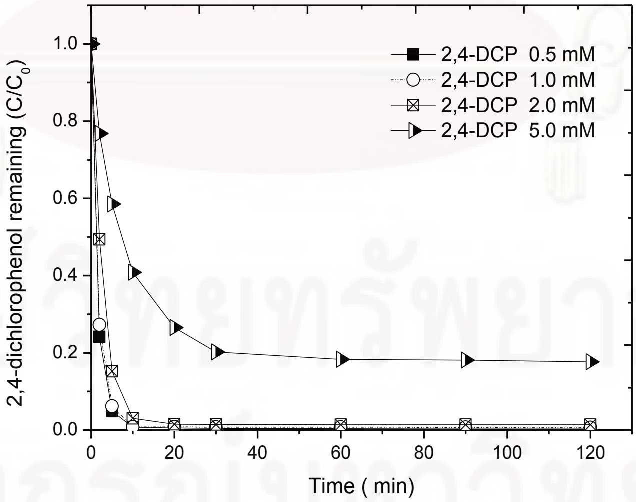


Figure 4.15 Effect of initial 2,4-dichlorophenol concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process; with the condition of $[Fe^{2+}]$ = 0.25 mM, $[H_2O_2]$ = 10mM, pH = 3 and 100 grams of $SiO_2$.

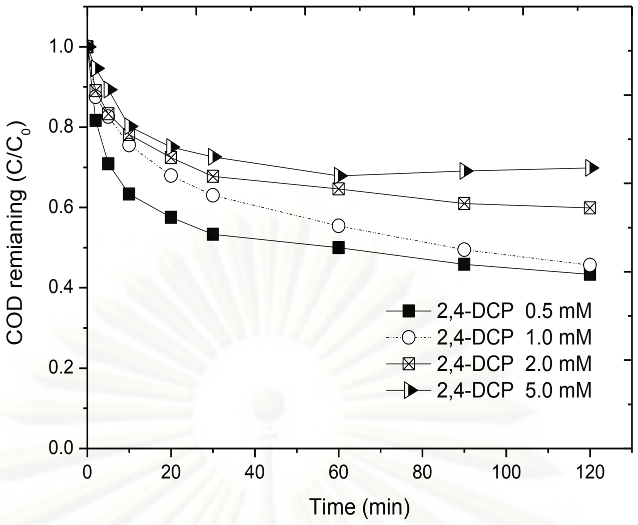
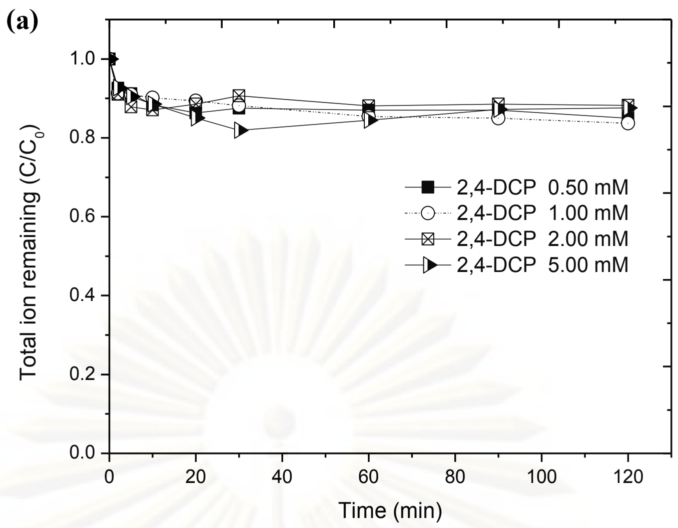


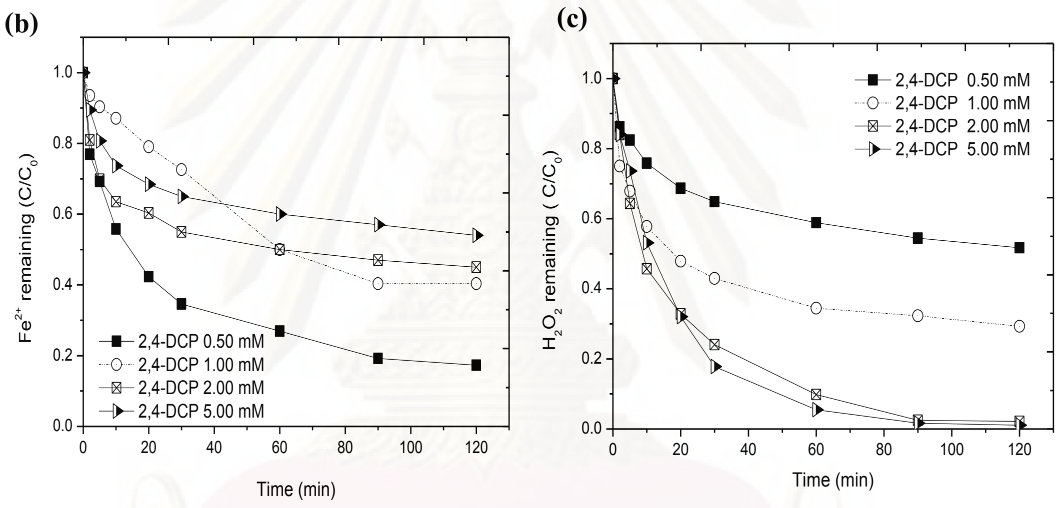
Figure 4.16 Effect of initial 2,4-dichlorophenol concentration on COD removal in fluidized-bed Fenton process; with the condition of $[Fe^{2+}]$ = 0.25 mM, $[H_2O_2]$ = 10 mM, pH = 3 and 100 grams of $SiO_2$.

The different of 2,4-dichlorophenol concentration did not affect the total iron removal. As clearly seen from the Figure 4.17 (a), the total iron removal efficiencies were almost the same. The total iron removal in the condition of 0.5, 1, 2 and 5 mM of 2,4-dichlorophenol were 14.54%, 16.33%, 11.29 % and 12.44 %, respectively.

The profile of $Fe^{2+}$ and $H_2O_2$ were shown in Figure 4.17 (b) and (c). $Fe^{2+}$ and $H_2O_2$concentration decreased as the reaction increase because they were used for the production of •OH.



(a) Total iron remaining



(b) Ferrous ion remaining

(c) $H_2O_2$ remaining

Figure 4.17 Effect of initial 2,4-dichlorophenol concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process(a) total iron remaining, (b) $Fe^{2+}$ remaining and (c) $H_2O_2$ remaining; with the condition of $[Fe^{2+}] = 0.25$ mM, $[H_2O_2] = 10$mM, pH = 3 and 100 grams of $SiO_2$.

The initial rate of 2,4-dichlorophenol degradation and the removal efficiency of 2,4-dichlorophenol were shown in Table 4.11. The initial degradation rate of 2,4-dichlorophenol was decreased due to an increase in 2,4-dichlorophenol concentration from 0.5 to 5 mM. The high initial rate at low concentration of 2,4-dichlorophenol was possibly due to •OH rapidly oxidized 2,4-dichlorophenol in a low concentration.

Table 4.11 Initial rate of 2,4-dichlorophenol degradation and the removal efficiency of 2,4-dichlorophenol under the different hydrogen peroxide concentration with the condition of [2,4-DCP] = 1 mM, $[Fe^{2+}]$ = 0.25 mM , pH =3 and 100 grams of $SiO_2$.

| 2,4-dichlorophenol concentration (mM) | Initial rate * (x $10^{-1}$ mM/ min) | 2,4-dichlorophenol ** removal efficiency (%) |
|---|---|---|
| 0.5 | 0.0901 | 99.67% |
| 1 | 0.1784 | 99.38% |
| 2 | 0.2838 | 98.62% |
| 5 | 0.4363 | 82.28% |

* After 5 minutes of reaction, ** After 120 minutes of reaction

Since increasing 2,4-dichlorophenol concentration, a large amount of 2,4-dichlorophenol presence in the solution. Form this reason, there was not enough •OH to oxidize 2,4-dichlorophenol and lead to the decline in the removal efficiency and initial degradation rate as well.

Further analysis illustrated a linear relationship between the initial rate and 2,4-dichlorophenol concentration on a log-log scale with a slope of 0.68 as presented in Figure 4.18. Therefore, the rate equation regarding on 2,4-dichlorophenol concentration can be written as the following equation:

$$\frac{d[2,4\text{-DCP}]}{dt} = -k_{2,4\text{-DCP}}\,[2,4\text{-DCP}]^{0.68} \qquad (4\text{-}14)$$

Where $k_{2,4\text{-DCP}}$ is the apparent rate constants for 2,4-dichlorophenol degradation with respect to 2,4-dichlorophenol concentration in the range between 0.5 and 5 mM of 2,4-dichlorophenol.

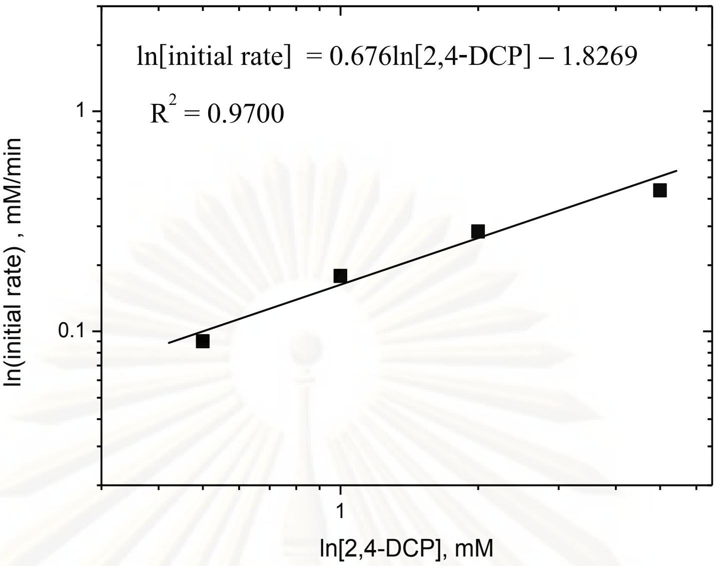


Figure 4.18 Relationship between initial 2,4-dichlorophenol concentration and initial rate of 2,4-dichlorophenol degradation on a log-log scale; with the condition of $[Fe^{2+}]$ =0.25 mM, $[H_2O_2]$ = 10 mM, pH =3 and 100 grams of $SiO_2$.

### 4.5.4 The overall degradation kinetic

The reaction rate of each individual component was determined in the previous parts. The overall rate equation for 2,4-dichlorophenol degradation by fluidized-bed Fenton process can be written as

$$\frac{-d[2,4\text{-DCP}]}{dt} = k[Fe^{2+}]^{0.51}[H_2O_2]^{0.19}[2,4\text{-DCP}]^{0.68} \qquad (4\text{-}15)$$

Where “k” is the overall rate constant for 2,4-dichlorophenol degradation by fluidized-bed Fenton process. The “k” value was determined by using a non-linear least square regression which minimizing the sum of error squares between the observed initial rates obtained from the experiment and the calculated initial rate generated by Equation (4-15). From the calculation, the k was equal to 0.184. Therefore, the overall reaction rate equation could be described as follows;

$$\frac{-d[2,4\text{-DCP}]}{dt} = 1.84 \times 10^{-1}[\mathrm{Fe}^{2+}]^{0.51}[\mathrm{H_2O_2}]^{0.19}[2,4\text{-DCP}]^{0.68} \qquad (4\text{-}16)$$

From above equation, it can be indicated that 2,4-dichlorophenol concentration have influences on the degradation rate of 2,4-dichlorophenol rather than ferrous ion and hydrogen peroxide.

This equation is valid under the degradation of 2,4-dichlorophenol in 5 minutes with the experimental conditions as follows: pH 3, 100 grams of $SiO_2$, initial $Fe^{2+}$ concentration between 0.1 to 1 mM, initial $H_2O_2$ concentration between 1 to 20 mM, initial 2,4-dichlorophenol concentration between 0.5 to 5 mM and this experiment was conducted at room temperature.

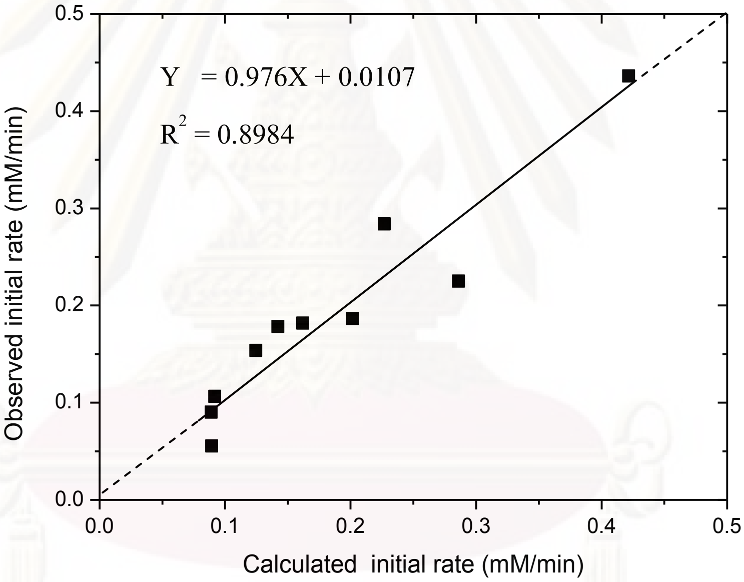


Figure 4.19 Relationship between observed initial rate and calculated initial rate of 2,4-dichlorophenol.

## 4.6 Intermediates from 2,4-dichlorophenol degradation

From the previous study, Even though 2,4-dichlorophenol was completely degraded at the end of 120 minutes of reaction time, it may be oxidized to other intermediates which possibly have more toxic than this compound. Therefore, the mineralization of 2,4-dichlorophenol may be not achieved. In this part, the identification of anions during 2,4-dichlorophenol oxidation were performed by Ion Chromatography(IC). The result shows that many intermediates were detected namely; chloride ions at 6.47 minute, maleic acid at 15.1 minute and oxalic acid at 18.6 minute.

The profile of anions generated during the degradation of 2,4-dichlorophenol was shown in Figure 4.20. The chloride ion and oxalic acid were found after 2 minutes of the reaction time and their concentration increased as the reaction time increased. For maleic acid was also found after 2 minutes and its concentration decreased after 10 minutes of reaction.

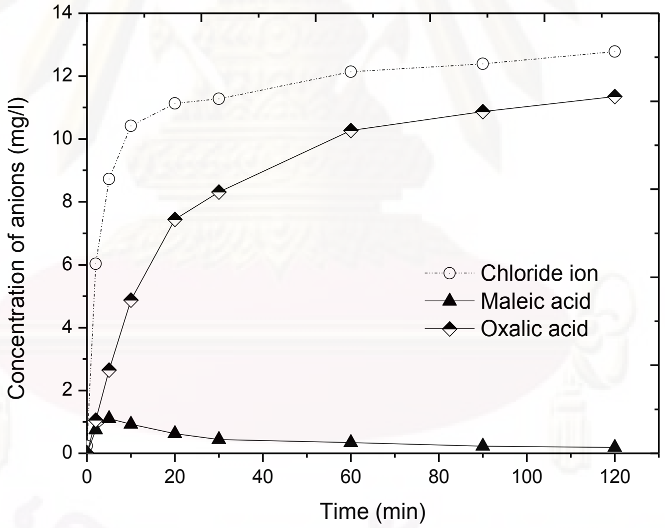


Figure 4.20 The generation of anions during the degradation of 2,4-dichlorophenol by fluidized-bed Fenton process at the optimum condition.

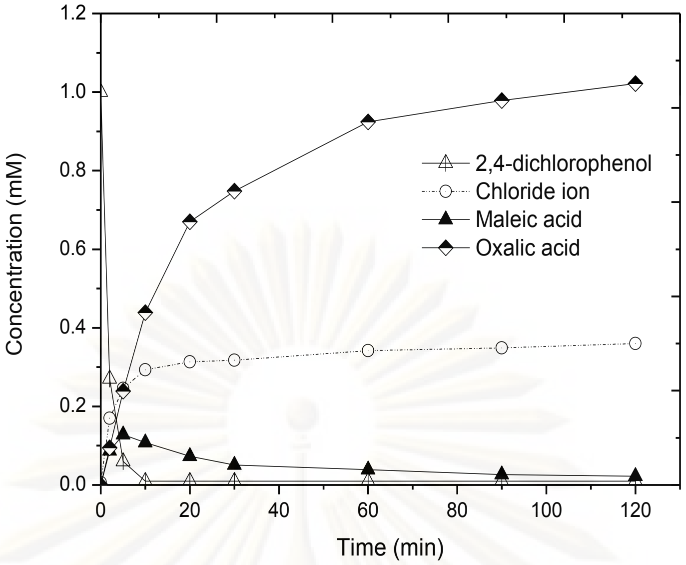


Figure 4.21 The profile of 2,4-dichlorophenol, chloride ion, maleic acid and oxalic acid generated during the reaction time by fluidized-bed Fenton process at the optimum condition.

Figure 4.21 illustrate the profile of 2,4-dichlorophenol, chloride ion, maleic acid and oxalic acid that generated during the reaction period at the optimum condition. The occurring of chloride ion came from 2,4-dichlorophenol molecule. It can be observed from Figure 4.21 that the chloride ion and oxalic acid increased whereas 2,4-dichlorophenol decrease. It indicated that 2,4-dichlorophenol could transform to some intermediates during the oxidation.

From the calculation, oxalic acid and maleic acid yield COD less than 10% of COD total which means that they are not the main intermediates occur during the degradation. In addition, the degradation pathway of 2,4-dichlorophenol by fluidized-bed Fenton process can be written as shown in figure 4.22. Therefore, the chlorine ion, maleic acid and oxalic acid were some part of intermediates which found in 2,4-dichlorophenol degradation. The complete oxidization was not achieved in this study because 2,4-dichlorophenol was not completely degraded to carbon dioxide and water during the reaction period.

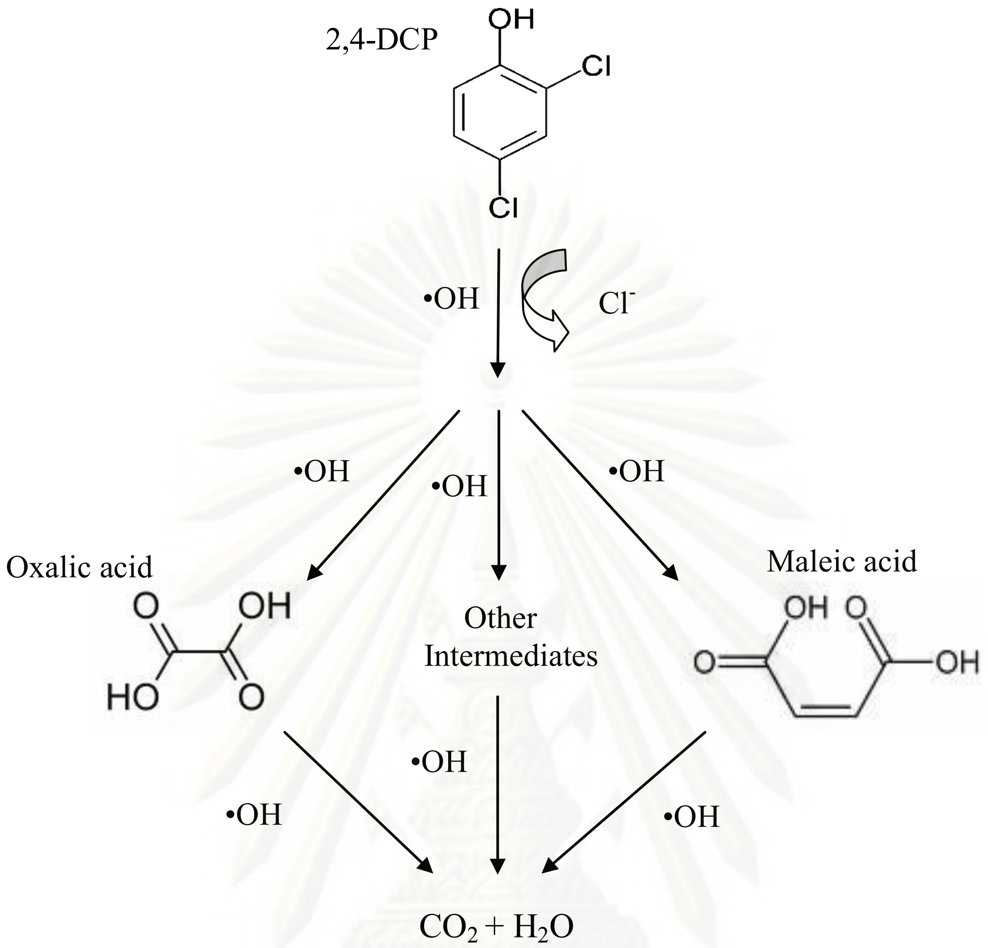


Figure 4.22 The degradation pathway of 2,4-dichlorophenol by fluidized-bed Fenton process.

# CHAPTER V

# CONCLUSION AND SUGGESTION FOR FUTURE WORK

## 5.1 Conclusion

The removal of 2,4-dichlorophenol has been investigated by fluidized-bed Fenton process. The following conclusion can be derived from this study.

- The fluidized-bed Fenton process was found to be an efficient method for treating the synthetic wastewater containing 2,4-dichlorophenol.
- The Box-Behnken design was proven to yield a reliable statistically result for determined the optimum condition in the removal of 2,4-dichlorophenol by fluidized-bed Fenton process, including the prediction of the interaction between process variable.
- The 2,4-dichlorophenol was very fast degraded by Fenton and fluidized-bed Fenton process. The removal efficiencies above 99% could be obtained in 10 minute.
- Under the studied conditions, hydrogen peroxide concentration was found to be the significant factor affecting on 2,4-dichlorophenol removal while the other factors had less significant affect on 2,4-dichlorophenol removal.
- pH, ferrous ion concentration and the amount of $SiO_2$ played an important role on the total iron removal.
- The optimum condition for removal of 1 mM of 2,4-dichlorophenol were pH 3, 100 grams of $SiO_2$, 0.25 mM of $Fe^{2+}$ and 10 mM of $H_2O_2$ which predicted to obtain the removal efficiency of 99.86%, 60.49% and 14.38 % for 2,4-dichlorophenol , COD and total iron, respectively.
- The removal efficiency of 2,4-dichlorophenol with the optimum condition from Fenton process and fluidized-bed Fenton process were almost the same , However, the higher total iron removal was found in fluidized-bed Fenton process Due to the advantage of fluidized-bed Fenton process which reduce the iron sludge via crystallization process.

- Overall kinetic equation for removal of 2,4-dichlorophenol by fluidized-bed Fenton process was :

$$\frac{-d[2,4\text{-DCP}]}{dt}\ (\text{mM/min}) = 1.84\text{x } 10^{-1}[\text{Fe}^{2+}]^{0.51}[\text{H}_2\text{O}_2]^{0.19}[2,4\text{-DCP}]^{0.68}$$

This equation is valid under the degradation of 2,4-dichlorophenol in 5 minutes with the experimental conditions as follows: pH 3, 100 grams of $SiO_2$, initial $Fe^{2+}$ concentration between 0.1 to 1 mM, initial $H_2O_2$ concentration between 1 to 20 mM, initial 2,4-dichlorophenol concentration between 0.5 to 5 mM and this experiment was conducted at room temperature.

- The intermediates from 2,4-dichlorophenol degradation were chloride ion, maleic acid and oxalic acid.

## 5.2 Recommendations for future work

This study focus on determination the optimum condition for removal of 2,4-dichlorophenol. There are many unexplored areas that need further investigation. Future studies may be conducted in the following:

- Identification of oxidation intermediates producing during the degradation of 2,4-dichlorophenol in order to establish a pathway of 2,4-dichlorophenol.
- Using the different type of carrier to compare the removal efficiency of organic pollutant and total iron.
- Optimization experiment for other operational parameters such as temperature, presence of anion, flow velocity, initial concentration of 2,4-dichlorophenol etc.
- Application of fluidized-bed Fenton process to the real wastewater.
- Investigate the behavior of fluidized-bed Fenton process under a continuous operation.

# REFERENCES

Ahlborg, U.G. and Victori, K. 1987. Impact on health of chlorinated dioxins and other trace organic emissions. Waste Management & Research 5: 203-224.

Agency for Toxic Substances and Disease Registry (ATSDR). 1999. Toxicological profile for chlorophenols. U.S., Department of Health and Human Services, Public Health Services Agency for Toxic Substances and Disease Registry. Atlanta, Georgia.

American Public Health Association. 1992. Standard methods for the examination of water and wastewater. 18th ed. Washington, DC: American Public Health Association.

Arslan-Alaton, I., Tureli, G. and Olmez-Hanci, T. 2009. Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: Optimization by response surface methodology. Journal of Photochemistry and Photobiology A: Chemistry 202: 142-153.

Ay,F., Catalkaya, E.C. and Kargi, F. 2009. A statistical experiment design approach for advanced oxidation process of Direct Red azo-dye by photo-Fenton treatment. Journal of Hazardous Materials 162: 230-236.

Bell, L.S., Devlin J.F., Gillham R.W. and Binning, P. J. 2003. A sequential zero valent iron and aerobic biodegradation treatment system for nitrobenzene. Journal of Contaminant Hydyology 66: 201- 207.

Bishop, D.F., Stern G.F., Fleishman, M. and Marshall, L.S. 1968. Hydrogen Peroxide Catalytic Oxidation of Refractory Organics in Municipal Waste Waters. Industrial Engineering Chemical Process Design and Development 7: 1110-1170.

Buxton, G.V., Greenstock, C.L., Helman, W.P. and Ross, A.B. 1998. Critical review of rate constants for reaction of hydrated electrons atoms and hydroxyl radical ($OH^{\bullet}/O^{\bullet}$) in aqueous solution. Journal of Physical Chemistry Reference Data 17: 513-886.

Catalkaya, E.C. and Kargi, F. 2007. Effects of operating parameters on advanced oxidation of diuron by the Fenton's reagent : A statistical design approach. Chemosphere 69: 485-492.

Chamarro, E., Marco, A. and Esplugas, S. 2001. Use of Fenton reagent to improve organic chemical biodegradability. Water Research 35: 1047-1051.

Chen, R. and Pignattello, J. 1997. Role of quinine intermediates as electron shuttles in Fenton and photoassisted Fenton oxidation of aromatic compounds. Environmental Science Technology 31: 2399-3406.

Chen, S., Sun, D. and Chung, S.J. 2007. Treatment of pesticide wastewater by moving-bed biofilm reactor combined with Fenton-coagulation pretreatment. Journal of Hazardous Materials 144: 577-584.

Chintitanun, S. 2007. Oxidation of Nitrobenzene by Fluidized-bed Fenton Process in the presence of chloride ion. Master's Thesis. Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University.

Chou, S. and Huang, C. 1998. Application of a support iron oxyhydroxide catalyst in oxidation of benzoic acid by hydrogen peroxide. Chemosphere 38: 2719-2731.

Chou, S. and Huang, C. 1999a. Effect of $Fe^{2+}$ on the catalytic oxidation in Fluidized-bed reactor. Chemosphere 39: 1997-2006.

Chou, S., Huang, C. and Huang, Y.H. 2001. Heterogeneous and homogeneous catalytic oxidation by supported $\gamma$ -FeOOH in a fluidized-bed reactor: Kinetic approach. Environmental ScienceTechnology 35: 1247-1251.

Chou, S., Huang, G.H., Liao, C.C., Hsu, S.F. and Huang, Y.H. 2003. Fenton family-Advanced Oxidation Technologies for Wastewater Treatment. Asian-Pacific Regional Conference on Practical Environmental Technologies Tainan, Taiwan, pp. (A2-17)-(A2-24).

Chou, S., Liao, C.C., Perng, S.H. and Chang, S.H. 2004. Factors influencing the preparation of supported iron oxide in Fluidized-bed crystallization. Chemosphere 54: 859-866.

CERAM Research Ltd. 2001. Silica-silicon dioxide [Online]. Available from: http://www.azom.com/Details.asp?ArticleID=1114#_Background[20 April 2009]

De Laat, J. and Gallard, H. 1999. Catalytic decomposition of hydrogen peroxide by Fe(III) in Homogeneous aqueous solutions: mechanism and kinetic modeling. Environmental ScienceTechnology 33 (16): 2726-2732.

Deng, Y. and Englehardt, J.D. 2006. Treatment of landfill leachate by the Fenton process. Water Research 40 (20): 3683-3694.

Diz, H.R. and Novak, P.E. 1998. Fluidized bed for removing iron and acidity from acid mine drainage. Journal of Environmental Engineering 124: 701-708.

Doocey, J.D. and Sharratt, N.P. 2004. Zeolite-mediated advanced oxidation of model chlorinated phenolic aqueous waste Part 1: Aqueous Phase Fenton Catalysis. Trans I Chemical E

82(B5): 352-358.

Eisenberg, G. 1943. Colorimetric determination of hydrogen peroxide. Industrial and Engineering Chemistry. Analytical Edition 15(5): 327-328.

Ferreira, S.L.C., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandao, G.C., Silva, E.G.P., Portugal, L.A., Reis, P.S., Souza, A.S. and Santos, W.N.L. 2007. Box-Behnken design: An alternative for the optimization of analytical method. Analytica Chimica Acta 597: 179-186.

Francis, F., Sabu, A., Nampoothiri, K.M., Ramachandran, S., Ghosh, S., Szakacs, G. and Pandey, A. 2003. Use of response surface methodology for the optimizing process parameters for the production of a-amylase by Aspergillus oryzae. Biochem Engineering Journal 15: 107-115.

Gallard, H., De Laat, J. and Legube, B. 1998. Effect of pH on the oxidation rate of organic compounds by Fe-II/$H_2O_2$, mechanisms and simulation. New Journal of Chemistry 22 (3): 263-268.

Glaze, W.H., Kang, J.W. and Chapin, D.H. 1987. The Chemistry of water treatment processes involving ozone. Science Engineering 9: 335-352.

Gogate, P.R. and Pandit, A.B. 2004. A review of imperative technologies for wastewater treatment I : oxidation technologies at ambient conditions. Advances in Environmental Research 8: 501-551.

Greenwood, N.N. and Earnshaw, A. 1997. Chemistry of the Elements. 2nd ed. UK : Butterworth-Heinemann.

Haag, W.R. and Yao, C.D. 1992. Rate constant for chromate and other inorganic anions by Organo-Zeolite. Environmental Science Technology 8: 452-458.

Hsueh, C.L., Huang, Y.H., Wang, C.C. and Chen, C.Y. 2006. Photoassisted fenton degradation of nonbiodegradable azo-dye (Reactive Black 5) over a novel supported iron oxide catalyst at neutral pH. Journal of Molecular Catalysis A: Chemical 245: 78-86.

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

Huang, C.P., Dong, C. and Tang, Z. 1993. Advanced chemical oxidation: Its present role and potential future in hazardous waste treatment. Water Management 13: 361-377.

International Agency for Research on Cancer (IARC) .1999. Polychlorophenols and their Sodium Salts Group 2B) [Online]. Available from:

http://monographs.iarc.fr/ENG/Monographs/vol71/volume71.pdf [17 July 2008]

International Chemical Safety Cards (WHO/IPCS/ILO)/ CDC/NIOSH .1997. 2,4-dichlrophenol [Online].Available from: http://www.cdc.gov/niosh/ipcsneng/neng0438.html[2 June, 2008]

Kang, N., Lee, D.S. and Yoon, J. 2002. Kinetic Modeling of Fenton Oxidation of Phenol and Monochlorophenols. Chemosphere 47: 915-924.

Kang, S.H., Liao, C.H. and Chen, M.C. 2002. Pre-oxidation and coagulation of textile wastewater by Fenton process. Chemosphere 46: 923-928.

Khan, E. Wirojanagud, W. and Sermsai, N. 2009. Effects of iron type in Fenton reaction on mineralization and biodegradability enhancement of hazardous organic compounds. Journal of Hazardous Materials 161: 1024-1034.

Khunikakron, L. 2005. Oxidation of Aniline and Nitrobenzene in Fluidized-bed Fenton process. Master's Thesis. Science Program in Environmental Management (Inter-Department), Graduated School, Chulalongkorn University.

Kintz, P., Tracqui, A. and Mangin, P. 1992. 2,4-dichlorophenol. Wikipedia.[Online].Available from: http://en.wikipedia.org/wiki/2,4-dichlorophenol [3 June,2008]

Kitis, M., Adams, C.D. and Daigger, G.T. 1999. The effects of Fenton's reagent pretreatment on the biodegradability of non-ionic surfactants. Water Resource 33 (11): 2561-2568.

Kitngzett, CT. 1880. Chemistry New. 41: 76.

Kitmongkonsak, M. 2006. Textile Dyeing wastewater treatment by Fluidized-bed Fenton process. Master's Thesis. Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University.

Korbahti, B.K. 2007. Response surface optimization of electrochemical treatment of textile dye wastewater. Journal of Hazardous Materials 145: 227-286.

Korbahti, B.K. and Rauf, M.A. 2009. Determination of optimum operating conditions of carmine decoloration by UV/$H_2O_2$ using response surface methodology. Journal of Hazardous Materials 161: 281-286.

Krishna, S.H., Manohar, B., Divakar,S., Prapulla,S.G. and Karanth, N.G. 2000. Optimization of isomyl acetate production by using immobilized lipase from, Mucor miehei by response surface methodology. Enzyme Microbial Technologies 26: 131-136.

Laat, J. and Gallard, H. 1999. Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solutions: mechanism and kinetic modeling. Environmental

Science Technology 33(16): 2726-2732.

Lauderdale, Ft., Babson, P. and Savannah, FL. 2003. Spectrum Chemical Fact Sheet Cas#120832. Spectrum Laboratories [Online]. Available from: http://www.speclab.com/compound/c120832.htm[25 July 2008]

Lelesias, C.S. 2002. Degradation and biodegradability enhancement of nitrobenzene and 2,4-dichlorophenol by means of advance oxidation processes base on ozone. Doctoral dissertation. Department of D'Enfinyeria Quimica I Metallurgia. Facultat de Quimica Universitat de Barcelona, Bellaterra, Spain

Li, X.Z., Zhao, B.X. and Wang, P. 2007. Degradation of 2,4-dichlorophenol in aqueous solution by hybrid oxidation process. Journal of Hazardous Materials 147: 281-287.

Lide, D.R. 1992. CRC Handbook of Chemistry and Physicals, 73rd ed. Boca Raton, Florida : CRC Press.

Lin, S.H. and Lo, C.C. 1997. Fenton process for treatment of desizing wastewater. Water Research 31(8): 2050-2056.

Liu, J.Z., Weng, L.P. and Zhang, Q.L. 2003. Optimization of glucose oxidase production by Aspergillus niger in a benchtop bioreactor using response surface methodology. Journal Microbiol Biotechnol 19: 317-323.

Lu, M.C., Chen, J.N. and Chang, P. 1997. Effect of inorganic ions on the oxidation of dichlorvos insecticide with Fenton's reagent. Chemosphere 35(10): 2285-2293.

Lu, M.C., Chen, J.N. and Chang, P. 1999. Oxidation of dichlorovos with hydrogen peroxide using ferrous ion as catalyst. Journal of Hazardous Materials B65: 277-288.

Lu, M.C., Lin, C.J., Liao, C.H., Ting, W.P. and Huang, R.Y. 2001. Influence of pH on the dewatering of activated sludge by Fenton's reagent. Water Science Technology 44(10): 327-332.

Khunikakron, L. 2005. Oxidation of Aniline and Nitrobenzene in Fluidized-bed Fenton process. Master's Thesis. Science Program in Environmental Management (Inter-Department), Graduated School, Chulalongkorn University.

Masomboon, N. 2008. Degradation of 2,6-dimethylaniline and aniline by Fenton technologies. Doctoral dissertation. Department of Environmental Science (Interdisciplinary Program), Graduated School, Chulalongkorn University.

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

Mentasti, E., Pelizzetti, E. and Saini, G. 1973. Reactions between iron(III) and catechol(*o*-dihydroxybenzene). Part I. Equilibria and kinetics of complex formation in aqueous acid solution, Part II. Equilibria and kinetics of the Redox reaction in aqueous acid solution. Journal Chem Soc. Dalton Trans 3: 2605-2608.

Momani, A.F., Sans, C. and Esplugas, S. 2004. A comparative study of the advanced oxidation of 2,4-dichlorophenol. Journal of Hazardous Materials B107: 123-129.

Montgomery, D.C. 2001. Design and analysis of experiments. 5th ed. NewYork : John Wiley & Sons.

Munter, R. 2001. Advanced Oxidation Processes-Current Status and Prospects. Process Estonian Academic Science Chemistry 50: 59-80.

Muralidhar, R.V., Chirumamila, R.R. and Marchant, R. 2001. A response surface approach for the comparison of lipase production by Candida cylindracea using two different carbon sources. Biochem Engineering Journal 9: 17-23.

National Toxicology Program (NTP). 1989. Toxicology and carcinogenesis studies of 2,4-Dichlorophenol in F344/N rats and BC3F1 mice. (Feed Studies).Technical Report Series 353.

Neyens, E. and Baeyens, J. 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials B98: 33-50.

Olalla, M. J. F. 2007. Combination of Advanced Oxidation Processes with biological treatment for the remediation of water polluted with herbicides. Doctoral dissertation. Department of de Quimica Universitat Autonoma de Barcelona, Bellaterra, Spain.

Oliveira, R., Almedia, F.M., Santos, L. and Madeira, M. L. 2006. Experimental design of 2,4-dichlorophenol oxidation by Fenton's reaction. Industrial and Engineering Chemistry Research 45: 1266-1276.

Parson, S. 2004. Advanced oxidation processes for water and wastewater treatment. 1st ed. London: IWA Publishing.

Paterlini, W. C. and Nogueira, R.F.P. 2005. Multivariate analysis of photo-Fenton degradation of the herbicides tebuthiuron, diuron and 2,4-D. Chemosphere 58: 1107-1116.

Pignatello, J.J. 1992. Dark and photoassisted $Fe^{3+}$- catalysed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environmetal Science Technology 26(5): 944-951.

Prengle, H.W, Symons, M.J. and Belhateche, D. 1978. $H_2O_2$/vis UV Process for Photo-Oxidation of Waterborne Hazardous Substances C1-C6 Chlorinated Hydrocarbons. Waste

Management 16: 327-333.

Ramirez, J.H., Costa, C.A., and Madeira, L.M. 2005. Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent. Catalysis Today 107-108: 68-76.

Ramirez, J.H., Lampinen, M., Vicente, M.A., Costa,C.A. and Madeira, L.M. 2008. Experimental design to optimized the oxidation of orange II dye solution using a clay-based Fenton-like catalyst. Industrial Engineering Chemistry Research 47: 284-294.

Rodgers, J.D. and Bunce, N.J. 2001. Review Paper, Treatment methods for the remediation of nitroaromatic explosives. Water Research 35(9): 2101-2111.

Rodriques, C.S.D., Madeira, L.M. and Boaventura, R.A.R. 2009. Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design. Journal of Hazardous Materials 164: 987-994.

Scheidegger, A., Borkovec, M. and Sticher, H. 1993 . Coating silica sand with goethite: preparation and analytical identification. Geoderma 58: 43-65.

Sellers, R. M. 1980. Spectrophotometric determination of hydrogen peroxide using potassium titanium (IV) oxalate. The Analyst 105(1255): 950-954.

Sun, J.H, Sun, S.P, Fan, M.H., Guo, H.Q., Qiao, P.L. and Sun, R.X. 2007. A kinetic study on the degradation of *p*-nitroaniline by Fenton oxidation process. Journal of Hazardous Materials 148: 172-177.

Sun, J.H., Sun, S.P., Fan, M.H., Guo, H.Q., Lee, Y.F. and Sun, R.X. 2008. Oxidative decomposition of ρ-nitroaniline in water by solar photo-Fenton advanced oxidation process. Journal of Hazardous Materials 153: 187-193.

Sun, S.P., Li, C.J., Sun, J.H., Shi, S.H., Fan, M.H. and Zhou, Q. 2009. Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study. Journal of Hazardous Materials 161: 1052-1057.

U.S. Department of Labor Occupational Safety & Health Administration (OSHA). 2002. Chemical Sampling Information 2,4-Dichlorophenol [Online].Available from http://www.osha.gov/dts/chemicalsampling/data/CH_234100.html [17June,2008]

U.S. Environmental Protection Agency [U.S. EPA]. 2008. 2,4-Dichlorophenol; CASRN 120-83-2[Online].Available from: http://www.epa.gov/iris/subst/0041.htm [2 June,2008]

U.S. National Library of Medicine. 2001. Hazard assessment of 2,4-Dichlorophenol [2,4-Dichlorophenol, CAS No. 120-83-2] [Online]. Available from:

http://www.meti.go.jp/english/report/downloadfiles/gED0307e.pdf [5 June, 2008]

U.S. Peroxide. 2008. Fenton's Reagent iron-catalyzed hydrogen peroxide [Online]. Available from:http://www.h2o2.com/applications/industrialwastewater/fentonsreagent.html [22 May,2008]

Venkatadri, R. and Peters, R.W. 1993. Chemical oxidation technologies: ultraviolet light/hydrogen peroxide, Fenton's reagent and titanium dioxide-assisted photocatalysis. Hazardous Waste and Hazardous Material 10: 107-149.

Vohra, A. and Satyanarayna , T. 2002. Statistical optimization of medium components by response surface methodology to enhance phytase production by Pichia anomala. Process Biochem 37: 999-1004.

Walling C, 1975. Fenton's reagent revisited. Accounts of Chemical Research 8: 125-131.

Walling, C. and Goosen, A. 1973. Mechanism of the ferric ion catalysed decomposition of hydrogen peroxide: effects of organic substrate. The Journal of the American Chemical Society 95 (9): 2987-2991.

Walling, C. and Kato, S. 1971. The oxidation of alcohols by Fenton's reagent: the effect of copper ion. The Journal of the American Chemical Society 93: 4275-4281.

Wang, H. and Wang, J. 2008. Electrochemical degradation of 2,4-dichlorophenol on a palladium modified gas-diffusion electrode. Electrochimica Acta 53: 6402-6409.

Wang, J.X., Song, Y. and Mai, S.J. 2008. Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate. Journal of Hazardous Materials 148: 172-177.

Wang, X., Zheng, G. and Zhu, J. 2008. Treatment of jean–wash wastewater by combined coagulation, hydrolysis/acidification and Fenton oxidation. Journal of Hazardous Materials 153: 810-816.

Wells, A.F. 1984. Structural Inorganic Chemistry. 5th ed. UK: Oxford University Press.

Zhao, B.X., Li, X.Z. and Wang, P. 2007. Degradation of 2,4-dichlorophenol with a novel $TiO_2$/ Ti-Fe graphite felt photoelectrocatalytic oxidation process. Journal of Environmental Sciences 19: 1020-1024.

Zhao, X.K., Yang, G.P., Yang, Y.J., Wang, X. and Gao, C. 2004. Photochemical degradation of dimethly phthalate by Fenton reagent. Journal Photochemical Photobiol A:Chem 161: 215-220.

Zhou, T., Li, Y., Wong S.F. and Lu, X. 2008. Enhanced degradation of 2,4-dichlorophenol by ultrasound in a new Fenton-like system (Fe/EDTA) at ambient circumstance. Ultrasonics Sonochemistry 15: 782-790.

Yoon, J., Lee, Y. and Kim, S. 2001. Investigation of the reaction pathway of OH radicals produced by Fenton oxidation in the conditions of wastewater treatment. Water Science Technology 44 (5): 15-21.

# Appendices

# Appendix A

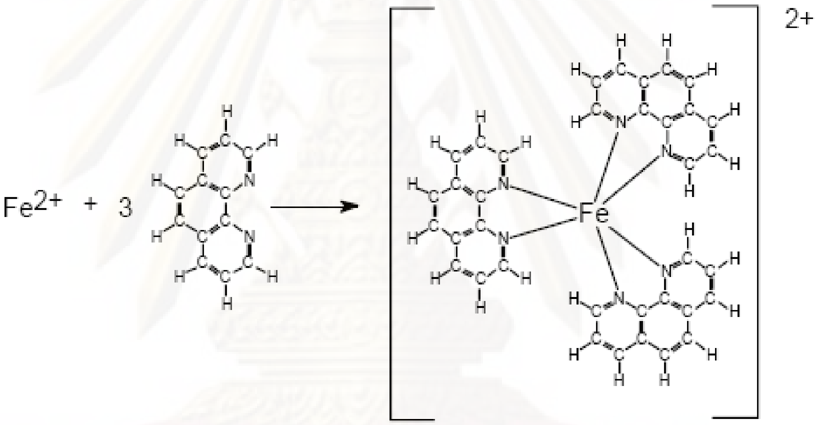
## Analytical method

# Appendix A-1

## **Analysis of ferrous ions** (APHA, 1992)

### Principle

The phenanthroline method is the preferred standard procedure for the measurement of iron in water at the present time, except when color, turbidity, phosphate, or heavy metal interferences are present. The method depends upon the fact that 1,10-phenanthroline combine with ferrous to form a complex iron that is orange-red in color. Three molecules of 1,10-phenanthroline are required to sequester or form a complex ion with each ferrous ion. The reaction may be represented as shown in the following equation:



### Reagents

1. Hydrochloric acid, HCl: 20 ml of concentration hydrochloric acid was diluted to 1,000 ml with DI water.
2. Ammonium Acetate Buffer Solution: 500 g of $NH_4C_2H_3O_2$ was dissolved in 300 ml of DI water. Then 1,400 ml of concentrated acetic acid was filled up to the mark of 2,000 ml.
3. Phenanthroline Solutions: 5 g of 1,10 – phenanthroline monohydrate, $C_{12}H_8N_2.H_2O$, was dissolved and 1 ml of concentrated hydrochloric acid was added. Then, DI waster was used to make the mark of 1000 ml.

**Apparatus**

1. Spectrophotometer (Shimadsu UV-1201). The absorbance used for ferrous ion analysis was 510 nm.
2. Acid-washed Glassware: All glass wares were washed with conc. HCl and rinsed with DI water to remove deposit of iron oxide. 50 ml Erlenmeyer flask
3. Membrane Filter: a 0.45 μm membrane filter was used to filter the sample to remove precipitation particle on solution.
4. Medicine dropper

**Procedure**

1. 25 ml of HCl from stock solution was prepared in 50 ml volumetric flask. Then, 10 ml of phenanthroline solution and 5 ml of ammonium acetate solution were added with vigorous stirring.
2. 2 ml of sample was filled and diluted to 50 ml with DI water. After that, it had to stand for 20 min. Do not expose to sunlight. (Color develop was rapid in the presence of excess phenanthrolines.)
3. Measured the absorbance of samples by spectrophotometer at 510 nm.

**Preparing for Calibration Curve**

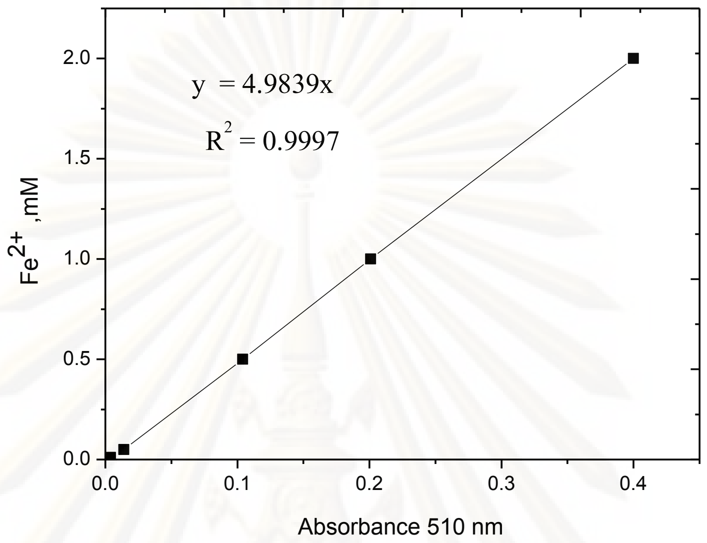
The standard ferrous solution were prepared in the range of 0.01 to 2 mM of $Fe^{2+}$ concentration.

1. 25 ml of HCl from stock solution was prepared in five 50 ml volumetric flasks. Then, 10 ml of phenanthroline solution and 5 ml of ammonium acetate solution were added with vigorous stirring.
2. 1 ml of 0.01, 0.05, 0.5,1 and 2 mM of $Fe^{2+}$ concentration were pipetted, respectively.
3. The samples were diluted to 50 ml with DI water, mixed thoroughly. After that, it had to stand for 20 min.
4. Measured the absorbance of samples by spectrophotometer at 510 nm.

**Calculation**

$Y = 4.9839X$

Where X = absorbance at 510 nM, Y = $Fe^{2+}$ concentration(mM)



# Appendix A-2

## Spectrophotometric determination of hydrogen peroxide

(Eisenberg, 1943 and Sellers, 1980)

### Principle

The method is based on photoelectric measurement of color intensities of hydrogen peroxide solution treated with potassium titanium (IV) oxalate reagent in the acid solution. The yellow color produced in the reaction due to the formation of pertitanic acid complex as $TiO_2.H_2O_2$, showing a true peroxide structure. The reaction equation is usually written:

$$Ti^{4+} + H_2O_2 + 2H_2O \longrightarrow H_2TiO_4 + 4H^+$$

### Reagents

Potassium titanium (IV) oxalate solution is prepared by mixed 27.2 mL of concentrated sulfuric acid ($H_2SO_4$ (conc.)) with about 300 mL of dionized water, then dissolve in this mixture 35.4 g of potassium titanium (IV) oxalate ($K_2TiO(C_2O_4)_2{\cdot}2H_2O$) and make up to 1 L with dionized water.

### Apparatus

1. Spectrophotometer capable of measuring absorption at a wavelength of 400 nm and fitted with 10 mm and 40 mm pathlength glass cells.
2. 25 ml Erlenmeyer flask
3. Medicine dropper

### Procedure

1. 5 mL of titanium oxalate reagent was prepared into 25 mL volumetric flask.
2. Transfer 1 mL of sample to 25 mL Erlenmeyer flask.
3. Adjust the volume to 25 mL with DI water, mixed thoroughly. After that, it had to stand for 15 min for the stable coloration.
4. Measured the absorbance of samples by spectrophotometer at 400 nm.

## Preparing for Calibration Curve

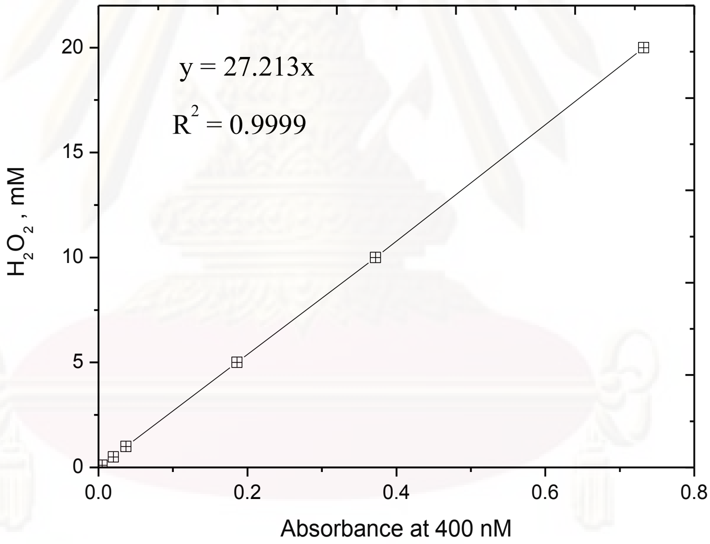
The standard ferrous solution were prepared in the range of 0 to 5 mg/l as $Fe^{2+}$

1. 5 ml of titanium oxalate reagent was prepared into 25 ml volumetric flasks.
2. 1 ml of 0.1, 0.5, 1, 5, 10 and 20 mM of $H_2O_2$ concentration were pipetted, respectively.
3. The samples were diluted to 25 ml with DI water, mixed thoroughly. After that, it had to stand for 15 min for the stable coloration.
4. Measured the absorbance of samples by spectrophotometer at 400 nm.

## Calculation

$Y = 27.213X$

Where X = absorbance at 400 nM, Y = $H_2O_2$ (mM)



# Appendix B

# Experimental data

# Appendix B

### B.1 Experimental data for Control experiment data

Table B-1 2,4-dichlorophenol remaining of control experiment

| Time | 2,4-dichlorophenol remaining ($C/C_0$) | | |
|---|---|---|---|
| (min) | Absorption | 0.25 mM of $Fe^{2+}$ | of 10 mM $H_2O_2$ |
| 0 | 1.0000 | 1.000 | 1.000 |
| 2 | 0.9934 | 0.9480 | 0.9337 |
| 5 | 0.9769 | 0.9110 | 0.8915 |
| 10 | 0.9492 | 0.8701 | 0.8629 |
| 20 | 0.9356 | 0.8468 | 0.8368 |
| 30 | 0.9155 | 0.8234 | 0.8132 |
| 60 | 0.9106 | 0.8134 | 0.7892 |
| 90 | 0.9083 | 0.8073 | 0.7766 |
| 120 | 0.9053 | 0.7946 | 0.7750 |

Note ; 2,4-DCP = 1 mM , $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 100 gram, pH initial = 3

Table B-2 COD remaining of control experiment

| Time | COD remaining ($C/C_0$) | | |
|---|---|---|---|
| (min) | Absorption | 0.25 mM of $Fe^{2+}$ | of 10 mM $H_2O_2$ |
| 0 | 1.0000 | 1.0000 | 1.000 |
| 2 | 0.9989 | 0.9725 | 0.9757 |
| 5 | 0.9817 | 0.9560 | 0.9709 |
| 10 | 0.9773 | 0.9560 | 0.9563 |
| 20 | 0.9692 | 0.9396 | 0.9272 |
| 30 | 0.9609 | 0.9396 | 0.9078 |
| 60 | 0.9485 | 0.9286 | 0.9175 |
| 90 | 0.9509 | 0.9341 | 0.9417 |
| 120 | 0.9609 | 0.9396 | 0.9320 |

Note ; 2,4-DCP = 1 mM , $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 100 gram, pH initial = 3

Table B-3 2,4-dichlorophenol remaining of control experiment

| Time | 2,4-dichlorophenol remaining ($C/C_0$) | |
|---|---|---|
| (min) | 2,4-DCP : $Fe^{2+}$ : $H_2O_2$ = 1 :1 :1 | 2,4-DCP : $Fe^{2+}$ : $H_2O_2$ = 1 :1 :12 |
| 0 | 1.0000 | 1.0000 |
| 2 | 0.4218 | 0.0934 |
| 5 | 0.3964 | 0.0450 |
| 10 | 0.3950 | 0.0231 |
| 20 | 0.3849 | 0.0046 |
| 30 | 0.3792 | 0.0037 |
| 60 | 0.3555 | 0.0024 |
| 90 | 0.3279 | 0.0011 |
| 120 | 0.3083 | 0.0007 |

Note ; 2,4-DCP = 1 mM , $Fe^{2+}$ = 1 mM , $SiO_2$ = 100 gram, pH initial = 3

Table B-4 COD remaining of control experiment

| Time | COD remaining ($C/C_0$) | |
|---|---|---|
| (min) | 2,4-DCP : $Fe^{2+}$ : $H_2O_2$ = 1 :1 :1 | 2,4-DCP : $Fe^{2+}$ : $H_2O_2$ = 1 :1 :12 |
| 0 | 1.0000 | 1.0000 |
| 2 | 0.9218 | 0.8070 |
| 5 | 0.8189 | 0.6579 |
| 10 | 0.6955 | 0.5702 |
| 20 | 0.6337 | 0.5439 |
| 30 | 0.5926 | 0.5263 |
| 60 | 0.5761 | 0.4912 |
| 90 | 0.5679 | 0.4561 |
| 120 | 0.5597 | 0.4211 |

Note ; 2,4-DCP = 1 mM , $Fe^{2+}$ = 1 mM , $SiO_2$ = 100 gram, pH initial = 3

## B.2 Experimental data in Box-Behnken design

Table B-5 Chemical remaining for Run#1 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.9523 | 0.9363 | 0.8261 | 0.9456 | 0.9564 |
| 5 | 0.8440 | 0.8676 | 0.6957 | 0.9207 | 0.8637 |
| 10 | 0.7751 | 0.8039 | 0.6087 | 0.8859 | 0.8526 |
| 20 | 0.7149 | 0.7745 | 0.6522 | 0.8411 | 0.9152 |
| 30 | 0.6703 | 0.7206 | 0.6957 | 0.8261 | 0.9532 |
| 60 | 0.4325 | 0.5245 | 0.6957 | 0.7465 | 0.8978 |
| 90 | 0.2098 | 0.4657 | 0.6957 | 0.7017 | 0.8811 |
| 120 | 0.0699 | 0.4363 | 0.6957 | 0.5922 | 0.8875 |

Note ; 2,4-DCP = 1 mM , $Fe^{2+}$ = 0.1 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 2

Table B-6 Chemical remaining Run#2 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.8419 | 0.9320 | 0.3500 | 0.9705 | 0.7735 |
| 5 | 0.7731 | 0.8738 | 0.3000 | 0.9406 | 0.7469 |
| 10 | 0.6855 | 0.8058 | 0.3000 | 0.8709 | 0.7229 |
| 20 | 0.5570 | 0.7573 | 0.4000 | 0.8112 | 0.7096 |
| 30 | 0.4482 | 0.7087 | 0.4500 | 0.7714 | 0.7638 |
| 60 | 0.1738 | 0.6699 | 0.5000 | 0.7067 | 0.7691 |
| 90 | 0.1067 | 0.6408 | 0.5000 | 0.6320 | 0.8393 |
| 120 | 0.0692 | 0.6311 | 0.5000 | 0.5723 | 0.8295 |

Note ; 2,4-DCP = 1 mM , $Fe^{2+}$ = 0.1 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 4

Table B-7 Chemical remaining Run#3 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.1434 | 0.8036 | 0.5364 | 0.4230 | 0.9743 |
| 5 | 0.1170 | 0.7857 | 0.4818 | 0.1841 | 0.9674 |
| 10 | 0.1122 | 0.7500 | 0.4500 | 0.0697 | 0.9679 |
| 20 | 0.1102 | 0.7232 | 0.5227 | 0.0547 | 0.9880 |
| 30 | 0.1053 | 0.6875 | 0.5818 | 0.0448 | 0.9827 |
| 60 | 0.0780 | 0.6518 | 0.6273 | 0.0348 | 0.9767 |
| 90 | 0.0754 | 0.6429 | 0.6455 | 0.0299 | 0.9809 |
| 120 | 0.0724 | 0.6339 | 0.6727 | 0.0299 | 0.9835 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 1 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 2

Table B-8 Chemical remaining Run#4 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.1656 | 0.6810 | 0.5946 | 0.1543 | 0.9471 |
| 5 | 0.0978 | 0.6207 | 0.4550 | 0.0498 | 0.9296 |
| 10 | 0.0877 | 0.5948 | 0.5180 | 0.0398 | 0.9091 |
| 20 | 0.0848 | 0.5690 | 0.5901 | 0.0348 | 0.8844 |
| 30 | 0.0817 | 0.5517 | 0.6216 | 0.0299 | 0.8659 |
| 60 | 0.0780 | 0.5345 | 0.6757 | 0.0249 | 0.8522 |
| 90 | 0.0767 | 0.5172 | 0.7072 | 0.0249 | 0.8454 |
| 120 | 0.0750 | 0.5172 | 0.7297 | 0.0299 | 0.8506 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.1 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 4

Table B-9 Chemical remaining Run#5 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.4356 | 0.9615 | 0.9219 | 0.2190 | 0.9956 |
| 5 | 0.4061 | 0.9038 | 0.8906 | 0.1916 | 0.9593 |
| 10 | 0.3641 | 0.8750 | 0.8828 | 0.1916 | 0.9351 |
| 20 | 0.3622 | 0.7885 | 0.8828 | 0.1642 | 0.9547 |
| 30 | 0.3527 | 0.7115 | 0.8750 | 0.1642 | 0.9557 |
| 60 | 0.3336 | 0.5673 | 0.8828 | 0.1369 | 0.9405 |
| 90 | 0.3335 | 0.5577 | 0.8906 | 0.1369 | 0.9469 |
| 120 | 0.3091 | 0.5192 | 0.9219 | 0.1369 | 0.9492 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 1 mM , $SiO_2$ = 50 gram, pH = 3

Table B-10 Chemical remaining Run#6 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.0221 | 0.9435 | 0.8110 | 0.7171 | 0.9897 |
| 5 | 0.0031 | 0.8629 | 0.6614 | 0.4681 | 0.9839 |
| 10 | 0.0015 | 0.7903 | 0.5118 | 0.3175 | 0.9773 |
| 20 | 0.0014 | 0.6855 | 0.3622 | 0.2381 | 0.9759 |
| 30 | 0.0007 | 0.5887 | 0.2677 | 0.2217 | 0.9597 |
| 60 | 0.0008 | 0.5484 | 0.2520 | 0.1423 | 0.9440 |
| 90 | 0.0012 | 0.5081 | 0.1732 | 0.1013 | 0.9382 |
| 120 | 0.0016 | 0.4355 | 0.1969 | 0.0821 | 0.9363 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 150 gram, pH = 3

Table B-11 Chemical remaining Run#7 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.3390 | 0.8851 | 0.9355 | 0.3558 | 0.9579 |
| 5 | 0.2164 | 0.8161 | 0.8871 | 0.2737 | 0.9484 |
| 10 | 0.2151 | 0.7356 | 0.8710 | 0.2463 | 0.9408 |
| 20 | 0.2135 | 0.6322 | 0.8548 | 0.2190 | 0.9373 |
| 30 | 0.2100 | 0.6092 | 0.8871 | 0.1916 | 0.9306 |
| 60 | 0.2131 | 0.5632 | 0.9032 | 0.1642 | 0.9497 |
| 90 | 0.2135 | 0.5402 | 0.9032 | 0.1369 | 0.9503 |
| 120 | 0.2100 | 0.5402 | 0.9032 | 0.1369 | 0.9466 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 1 mM , $SiO_2$ = 250 gram, pH = 3

Table B-12 Chemical remaining Run#8 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.0254 | 0.9219 | 0.6720 | 0.7308 | 0.9289 |
| 5 | 0.0034 | 0.8281 | 0.5360 | 0.5310 | 0.9245 |
| 10 | 0.0048 | 0.7656 | 0.4480 | 0.4188 | 0.8992 |
| 20 | 0.0031 | 0.7031 | 0.3200 | 0.3093 | 0.8795 |
| 30 | 0.0029 | 0.6641 | 0.2560 | 0.2682 | 0.8548 |
| 60 | 0.0022 | 0.6328 | 0.1680 | 0.1916 | 0.8516 |
| 90 | 0.0021 | 0.5703 | 0.1680 | 0.1478 | 0.8370 |
| 120 | 0.0018 | 0.5234 | 0.1520 | 0.0849 | 0.8634 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 250 gram, pH = 3

Table B-13 Chemical remaining Run#9 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.2745 | 0.9266 | 0.7600 | 0.6669 | 0.9981 |
| 5 | 0.1070 | 0.8165 | 0.6560 | 0.4927 | 0.9715 |
| 10 | 0.0639 | 0.6606 | 0.6000 | 0.2190 | 0.9740 |
| 20 | 0.0471 | 0.6239 | 0.5680 | 0.0647 | 0.9534 |
| 30 | 0.0500 | 0.6147 | 0.5840 | 0.0448 | 0.9541 |
| 60 | 0.0460 | 0.5963 | 0.6320 | 0.0348 | 0.9458 |
| 90 | 0.0445 | 0.5872 | 0.6800 | 0.0299 | 0.9294 |
| 120 | 0.0402 | 0.5688 | 0.7200 | 0.0249 | 0.9300 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 50 gram, pH = 2

Table B-14 Chemical remaining Run#10 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.2113 | 0.5685 | 0.7426 | 0.5226 | 0.8823 |
| 5 | 0.1122 | 0.5000 | 0.6040 | 0.3135 | 0.8479 |
| 10 | 0.0930 | 0.4932 | 0.5347 | 0.1692 | 0.8218 |
| 20 | 0.0793 | 0.4658 | 0.5644 | 0.0647 | 0.8190 |
| 30 | 0.0592 | 0.4247 | 0.6139 | 0.0299 | 0.7902 |
| 60 | 0.0497 | 0.3973 | 0.6634 | 0.0249 | 0.8038 |
| 90 | 0.0249 | 0.4041 | 0.7129 | 0.0249 | 0.7803 |
| 120 | 0.0242 | 0.4110 | 0.7030 | 0.0199 | 0.7835 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 50 gram, pH = 4

Table B-15 Chemical remaining Run#11 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.3749 | 0.6380 | 0.7438 | 0.8112 | 0.9652 |
| 5 | 0.1772 | 0.5951 | 0.5950 | 0.7117 | 0.9416 |
| 10 | 0.0670 | 0.5706 | 0.5620 | 0.4778 | 0.9291 |
| 20 | 0.0410 | 0.5337 | 0.5455 | 0.2090 | 0.9478 |
| 30 | 0.0386 | 0.5399 | 0.5207 | 0.1393 | 0.9636 |
| 60 | 0.0358 | 0.5153 | 0.4628 | 0.0896 | 0.9531 |
| 90 | 0.0278 | 0.4847 | 0.4876 | 0.0846 | 0.9652 |
| 120 | 0.0349 | 0.4663 | 0.5124 | 0.0846 | 0.9565 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 250 gram, pH = 2

Table B-16 Chemical remaining Run#12 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.2615 | 0.7766 | 0.6809 | 0.7465 | 0.8952 |
| 5 | 0.0429 | 0.7128 | 0.5426 | 0.6320 | 0.8254 |
| 10 | 0.0426 | 0.6702 | 0.5851 | 0.3285 | 0.7826 |
| 20 | 0.0386 | 0.6170 | 0.6383 | 0.1692 | 0.7530 |
| 30 | 0.0385 | 0.5957 | 0.6915 | 0.0896 | 0.7680 |
| 60 | 0.0378 | 0.5851 | 0.7128 | 0.0448 | 0.7678 |
| 90 | 0.0349 | 0.5957 | 0.7340 | 0.0448 | 0.7663 |
| 120 | 0.0319 | 0.5957 | 0.7340 | 0.0448 | 0.7643 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 250 gram, pH = 4

Table B-17 Chemical remaining Run#13 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.8563 | 0.8944 | 0.6190 | 0.9306 | 0.9237 |
| 5 | 0.7923 | 0.8521 | 0.5714 | 0.8212 | 0.8863 |
| 10 | 0.7350 | 0.7676 | 0.5238 | 0.6569 | 0.8911 |
| 20 | 0.5788 | 0.6620 | 0.5714 | 0.4927 | 0.8585 |
| 30 | 0.4601 | 0.6338 | 0.6190 | 0.3558 | 0.8283 |
| 60 | 0.3284 | 0.5775 | 0.6190 | 0.2463 | 0.8331 |
| 90 | 0.3049 | 0.5845 | 0.6667 | 0.1916 | 0.8998 |
| 120 | 0.2926 | 0.5563 | 0.6667 | 0.1642 | 0.8967 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.1 mM , $H_2O_2$ = 1 mM , $SiO_2$ = 150 gram, pH = 3

Table B-18 Chemical remaining Run#14 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.4342 | 0.8750 | 0.7991 | 0.4927 | 0.9547 |
| 5 | 0.4150 | 0.7426 | 0.7534 | 0.2190 | 0.9350 |
| 10 | 0.4092 | 0.6838 | 0.7169 | 0.1916 | 0.9355 |
| 20 | 0.3785 | 0.6544 | 0.7671 | 0.1642 | 0.9324 |
| 30 | 0.3747 | 0.6324 | 0.7900 | 0.1642 | 0.9090 |
| 60 | 0.3730 | 0.5809 | 0.8356 | 0.1369 | 0.8903 |
| 90 | 0.3531 | 0.5515 | 0.8676 | 0.1369 | 0.9015 |
| 120 | 0.3462 | 0.5074 | 0.8721 | 0.1369 | 0.9037 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 1 mM , $H_2O_2$ = 1 mM , $SiO_2$ = 150 gram, pH = 3

Table B-19 Chemical remaining Run#15 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.6577 | 0.9400 | 0.8500 | 0.8075 | 0.8867 |
| 5 | 0.5601 | 0.8667 | 0.7500 | 0.7582 | 0.8517 |
| 10 | 0.4347 | 0.8000 | 0.6500 | 0.7199 | 0.7781 |
| 20 | 0.1561 | 0.7467 | 0.7000 | 0.6131 | 0.7818 |
| 30 | 0.0475 | 0.6533 | 0.7500 | 0.5639 | 0.7965 |
| 60 | 0.0331 | 0.4933 | 0.8000 | 0.4489 | 0.8186 |
| 90 | 0.0256 | 0.4667 | 0.8000 | 0.4024 | 0.8250 |
| 120 | 0.0172 | 0.3867 | 0.8000 | 0.3887 | 0.8324 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.1 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 150 gram, pH = 3

Table B-20 Chemical remaining Run#16 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.0718 | 0.7921 | 0.4358 | 0.5146 | 0.9710 |
| 5 | 0.0263 | 0.7228 | 0.2752 | 0.2901 | 0.9555 |
| 10 | 0.0241 | 0.6535 | 0.2202 | 0.1943 | 0.9474 |
| 20 | 0.0236 | 0.6139 | 0.1651 | 0.1068 | 0.9283 |
| 30 | 0.0206 | 0.6040 | 0.1560 | 0.0630 | 0.9016 |
| 60 | 0.0207 | 0.6139 | 0.1055 | 0.0301 | 0.8907 |
| 90 | 0.0186 | 0.6139 | 0.1284 | 0.0246 | 0.8908 |
| 120 | 0.0163 | 0.5941 | 0.2431 | 0.0164 | 0.8770 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 1 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 150 gram, pH = 3

Table B-21 Chemical remaining Run#17 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.2572 | 0.7267 | 0.7787 | 0.3558 | 0.9727 |
| 5 | 0.1885 | 0.6832 | 0.6803 | 0.2190 | 0.9664 |
| 10 | 0.1804 | 0.6211 | 0.6148 | 0.1916 | 0.9617 |
| 20 | 0.1786 | 0.5528 | 0.4508 | 0.1642 | 0.9651 |
| 30 | 0.1739 | 0.5155 | 0.3525 | 0.1642 | 0.9581 |
| 60 | 0.1703 | 0.5093 | 0.2869 | 0.1369 | 0.9431 |
| 90 | 0.1647 | 0.4907 | 0.2705 | 0.1095 | 0.9454 |
| 120 | 0.1528 | 0.4783 | 0.2623 | 0.0821 | 0.9600 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 1 mM , $SiO_2$ = 150 gram, pH = 2

Table B-22 Chemical remaining Run#18 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.8060 | 0.9402 | 0.5149 | 0.5474 | 0.8735 |
| 5 | 0.5090 | 0.8632 | 0.3960 | 0.4106 | 0.8726 |
| 10 | 0.4447 | 0.7863 | 0.2772 | 0.3285 | 0.8918 |
| 20 | 0.4012 | 0.5641 | 0.2178 | 0.2737 | 0.8796 |
| 30 | 0.3815 | 0.4957 | 0.1980 | 0.2463 | 0.8784 |
| 60 | 0.3370 | 0.4957 | 0.1782 | 0.1916 | 0.8667 |
| 90 | 0.3321 | 0.4615 | 0.1485 | 0.1642 | 0.8609 |
| 120 | 0.3234 | 0.4530 | 0.0990 | 0.1369 | 0.8818 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 1 mM , $SiO_2$ = 150 gram, pH = 4

Table B-23 Chemical remaining Run#19 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.2378 | 0.9080 | 0.7541 | 0.8266 | 0.9432 |
| 5 | 0.0825 | 0.7241 | 0.6885 | 0.6651 | 0.9389 |
| 10 | 0.0289 | 0.5402 | 0.5984 | 0.4790 | 0.9416 |
| 20 | 0.0192 | 0.4368 | 0.4344 | 0.3640 | 0.9369 |
| 30 | 0.0060 | 0.4253 | 0.4016 | 0.3148 | 0.9262 |
| 60 | 0.0060 | 0.4253 | 0.3197 | 0.2026 | 0.9180 |
| 90 | 0.0046 | 0.4138 | 0.2295 | 0.1615 | 0.9193 |
| 120 | 0.0046 | 0.3793 | 0.2131 | 0.1259 | 0.9421 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 150 gram, pH = 2

Table B-24 Chemical remaining Run#20 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.1005 | 0.7755 | 0.7745 | 0.5830 | 0.9340 |
| 5 | 0.0454 | 0.7347 | 0.5980 | 0.4161 | 0.9069 |
| 10 | 0.0109 | 0.6735 | 0.4608 | 0.3339 | 0.8847 |
| 20 | 0.0071 | 0.6020 | 0.3529 | 0.2491 | 0.8663 |
| 30 | 0.0047 | 0.5714 | 0.2745 | 0.1998 | 0.8489 |
| 60 | 0.0026 | 0.5102 | 0.2157 | 0.1122 | 0.8341 |
| 90 | 0.0003 | 0.4796 | 0.1863 | 0.0411 | 0.8406 |
| 120 | 0.0003 | 0.4694 | 0.1373 | 0.0383 | 0.8487 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 150 gram, pH = 4

Table B-25 Chemical remaining Run#21 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.8034 | 0.9111 | 0.8400 | 0.9107 | 0.7601 |
| 5 | 0.7055 | 0.8611 | 0.8000 | 0.8809 | 0.7289 |
| 10 | 0.5606 | 0.7778 | 0.7600 | 0.8460 | 0.7270 |
| 20 | 0.3953 | 0.7222 | 0.8000 | 0.7963 | 0.6682 |
| 30 | 0.1842 | 0.6944 | 0.8000 | 0.7166 | 0.6323 |
| 60 | 0.0543 | 0.6278 | 0.8000 | 0.5176 | 0.6253 |
| 90 | 0.0334 | 0.5833 | 0.8000 | 0.4330 | 0.6216 |
| 120 | 0.0202 | 0.5278 | 0.8000 | 0.3782 | 0.5698 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.1 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 50 gram, pH = 3

Table B-26 Chemical remaining Run#22 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.1455 | 0.8571 | 0.4400 | 0.1941 | 0.9614 |
| 5 | 0.0946 | 0.8312 | 0.3867 | 0.0697 | 0.9408 |
| 10 | 0.0960 | 0.7922 | 0.3511 | 0.0498 | 0.9313 |
| 20 | 0.0930 | 0.7662 | 0.4667 | 0.0448 | 0.9089 |
| 30 | 0.0794 | 0.7208 | 0.5778 | 0.0448 | 0.9258 |
| 60 | 0.0791 | 0.6688 | 0.6578 | 0.0398 | 0.9327 |
| 90 | 0.0747 | 0.6299 | 0.6933 | 0.0348 | 0.9344 |
| 120 | 0.0695 | 0.6169 | 0.7200 | 0.0299 | 0.9405 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 1 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 50 gram, pH = 3

Table B-27 Chemical remaining Run#23 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.7138 | 0.9023 | 0.7941 | 0.9804 | 0.9672 |
| 5 | 0.5525 | 0.8647 | 0.7059 | 0.8759 | 0.9572 |
| 10 | 0.3236 | 0.8195 | 0.7059 | 0.7963 | 0.9418 |
| 20 | 0.0940 | 0.7444 | 0.7647 | 0.6121 | 0.9551 |
| 30 | 0.0370 | 0.7068 | 0.7941 | 0.4977 | 0.9638 |
| 60 | 0.0165 | 0.6842 | 0.8235 | 0.3036 | 0.9547 |
| 90 | 0.0150 | 0.6015 | 0.8529 | 0.2339 | 0.9456 |
| 120 | 0.0131 | 0.5865 | 0.8529 | 0.1891 | 0.9044 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.1 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 250 gram, pH = 3

Table B-28 Chemical remaining Run#24 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.1757 | 0.9338 | 0.5134 | 0.1244 | 0.9700 |
| 5 | 0.1499 | 0.8456 | 0.4063 | 0.0547 | 0.9477 |
| 10 | 0.1281 | 0.7279 | 0.4464 | 0.0498 | 0.9572 |
| 20 | 0.1208 | 0.6397 | 0.5357 | 0.0448 | 0.9584 |
| 30 | 0.1148 | 0.6103 | 0.5893 | 0.0398 | 0.9275 |
| 60 | 0.1042 | 0.6029 | 0.6518 | 0.0348 | 0.9142 |
| 90 | 0.0910 | 0.5368 | 0.6875 | 0.0299 | 0.9081 |
| 120 | 0.0900 | 0.5368 | 0.6920 | 0.0249 | 0.9029 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 1 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 250 gram, pH = 3

Table B-29 Chemical remaining Run#25 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.0583 | 0.7727 | 0.8696 | 0.5226 | 0.9516 |
| 5 | 0.0551 | 0.6000 | 0.7652 | 0.1344 | 0.9407 |
| 10 | 0.0531 | 0.5273 | 0.7043 | 0.0747 | 0.9330 |
| 20 | 0.0505 | 0.5273 | 0.7304 | 0.0398 | 0.9192 |
| 30 | 0.0438 | 0.4909 | 0.7826 | 0.0299 | 0.9028 |
| 60 | 0.0428 | 0.4636 | 0.8696 | 0.0199 | 0.9220 |
| 90 | 0.0347 | 0.4364 | 0.8522 | 0.0100 | 0.9226 |
| 120 | 0.0239 | 0.4091 | 0.8609 | 0.0100 | 0.8992 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 3

Table B-30 Chemical remaining Run#26 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.1607 | 0.7485 | 0.8655 | 0.3533 | 0.9488 |
| 5 | 0.0923 | 0.6257 | 0.7647 | 0.1493 | 0.9326 |
| 10 | 0.0733 | 0.5906 | 0.7227 | 0.0697 | 0.8938 |
| 20 | 0.0554 | 0.5673 | 0.7815 | 0.0498 | 0.8809 |
| 30 | 0.0356 | 0.5789 | 0.8151 | 0.0348 | 0.8859 |
| 60 | 0.0415 | 0.5965 | 0.8403 | 0.0348 | 0.8824 |
| 90 | 0.0266 | 0.5789 | 0.8571 | 0.0299 | 0.8885 |
| 120 | 0.0203 | 0.5380 | 0.8739 | 0.0249 | 0.8932 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 3

Table B-31 Chemical remaining Run#27 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.0530 | 0.8190 | 0.5089 | 0.5076 | 0.9656 |
| 5 | 0.0311 | 0.7069 | 0.3125 | 0.3235 | 0.9572 |
| 10 | 0.0210 | 0.6207 | 0.2500 | 0.2190 | 0.9446 |
| 20 | 0.0209 | 0.5431 | 0.1607 | 0.1344 | 0.9325 |
| 30 | 0.0113 | 0.5172 | 0.1607 | 0.0995 | 0.9272 |
| 60 | 0.0109 | 0.4914 | 0.1518 | 0.0348 | 0.9279 |
| 90 | 0.0086 | 0.4655 | 0.1964 | 0.0299 | 0.9262 |
| 120 | 0.0080 | 0.4483 | 0.2232 | 0.0249 | 0.9157 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 3

Table B-32 Chemical remaining Run#28 in Box-Behnken design.

| Time | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| (min) | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.1145 | 0.8641 | 0.6641 | 0.5673 | 0.9142 |
| 5 | 0.0870 | 0.8350 | 0.6328 | 0.2737 | 0.9080 |
| 10 | 0.0572 | 0.7961 | 0.5938 | 0.1543 | 0.8962 |
| 20 | 0.0513 | 0.6602 | 0.5391 | 0.0498 | 0.9005 |
| 30 | 0.0481 | 0.5631 | 0.5859 | 0.0398 | 0.9288 |
| 60 | 0.0368 | 0.6019 | 0.7266 | 0.0348 | 0.9380 |
| 90 | 0.0353 | 0.5922 | 0.7500 | 0.0299 | 0.9192 |
| 120 | 0.0345 | 0.5340 | 0.7969 | 0.0249 | 0.9172 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 3

Table B-33 Chemical remaining Run#29 in Box-Behnken design.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.4544 | 0.7485 | 0.8655 | 0.3533 | 0.9656 |
| 5 | 0.1660 | 0.6257 | 0.7647 | 0.1493 | 0.9572 |
| 10 | 0.0082 | 0.5906 | 0.7227 | 0.0697 | 0.9446 |
| 20 | 0.0081 | 0.5673 | 0.7015 | 0.0498 | 0.9325 |
| 30 | 0.0080 | 0.5789 | 0.6851 | 0.0348 | 0.9272 |
| 60 | 0.0025 | 0.5965 | 0.7203 | 0.0348 | 0.9279 |
| 90 | 0.0022 | 0.5789 | 0.7371 | 0.0299 | 0.9262 |
| 120 | 0.0001 | 0.5380 | 0.7539 | 0.0249 | 0.9157 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.55 mM , $H_2O_2$ = 5.5 mM , $SiO_2$ = 150 gram, pH = 3

## B.3 Experimental data for comparison of fluidized-bed Fenton process and Fenton process at the optimum condition.

Table B-34 Chemical remaining in Run optimum condition by fluidized-bed Fenton process.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.2842 | 0.8750 | 0.9355 | 0.7500 | 0.9129 |
| 5 | 0.0642 | 0.7989 | 0.9032 | 0.6788 | 0.9099 |
| 10 | 0.0088 | 0.7391 | 0.8710 | 0.5775 | 0.9014 |
| 20 | 0.0084 | 0.6630 | 0.7903 | 0.4790 | 0.8935 |
| 30 | 0.0080 | 0.6250 | 0.7258 | 0.4297 | 0.8814 |
| 60 | 0.0079 | 0.5652 | 0.5000 | 0.3449 | 0.8542 |
| 90 | 0.0075 | 0.5272 | 0.4032 | 0.3230 | 0.8500 |
| 120 | 0.0065 | 0.4946 | 0.4032 | 0.2929 | 0.8367 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM , $SiO_2$ = 100 gram, pH = 3

Table B-35 Chemical remaining in Run optimum condition by Fenton process.

| Time (min) | Chemical remaining ($C/C_0$) | | | | |
|---|---|---|---|---|---|
| | 2,4-DCP | COD | $Fe^{2+}$ | $H_2O_2$ | Total iron |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.3177 | 0.9456 | 0.9231 | 0.7336 | 0.9778 |
| 5 | 0.0288 | 0.8571 | 0.8846 | 0.6432 | 0.9873 |
| 10 | 0.0076 | 0.6871 | 0.8269 | 0.5529 | 0.9823 |
| 20 | 0.0077 | 0.6463 | 0.7115 | 0.4681 | 0.9753 |
| 30 | 0.0075 | 0.5782 | 0.6538 | 0.4325 | 0.9911 |
| 60 | 0.0071 | 0.5782 | 0.5385 | 0.3422 | 0.9405 |
| 90 | 0.0070 | 0.5442 | 0.4808 | 0.3011 | 0.9335 |
| 120 | 0.0058 | 0.5510 | 0.4038 | 0.2737 | 0.9278 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM and pH = 3

### B.4 Experimental data of kinetic study

**The effect of initial $Fe^{2+}$ concentration.**

Table B-36 The effect of initial ferrous ion on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; 2,4-dichlorophenol remaining

| Time (min) | 2,4-dichlorophenol remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| | $Fe^{2+}$ 0.10 mM | $Fe^{2+}$ 0.25 mM | $Fe^{2+}$ 0.50 mM | $Fe^{2+}$ 1.0 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.7670 | 0.2728 | 0.1292 | 0.0138 |
| 5 | 0.6711 | 0.0616 | 0.0049 | 0.0025 |
| 10 | 0.5362 | 0.0084 | 0.0041 | 0.0018 |
| 20 | 0.2892 | 0.0080 | 0.0035 | 0.0017 |
| 30 | 0.1361 | 0.0077 | 0.0035 | 0.0012 |
| 60 | 0.0318 | 0.0075 | 0.0027 | 0.0009 |
| 90 | 0.0270 | 0.0072 | 0.0026 | 0.0003 |
| 120 | 0.0172 | 0.0062 | 0.0011 | 0.0002 |

Note ; 2,4-DCP = 1 mM, $H_2O_2$ = 10 mM , $SiO_2$ = 100 gram, pH = 3

Table B-37 The effect of initial ferrous ion on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; COD remaining

| Time | COD remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | $Fe^{2+}$ 0.10 mM | $Fe^{2+}$ 0.25 mM | $Fe^{2+}$ 0.50 mM | $Fe^{2+}$ 1.0 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.9023 | 0.8750 | 0.9000 | 0.6833 |
| 5 | 0.8448 | 0.7989 | 0.7500 | 0.6063 |
| 10 | 0.8218 | 0.7391 | 0.6750 | 0.5837 |
| 20 | 0.7931 | 0.6630 | 0.6313 | 0.5294 |
| 30 | 0.7644 | 0.6250 | 0.6125 | 0.4751 |
| 60 | 0.7299 | 0.5652 | 0.5500 | 0.4434 |
| 90 | 0.7069 | 0.5272 | 0.5063 | 0.4208 |
| 120 | 0.6782 | 0.4946 | 0.4875 | 0.4163 |

Note ; 2,4-DCP = 1 mM, $H_2O_2$ = 10 mM , $SiO_2$ = 100 gram, pH = 3

Table B-38 The effect of initial ferrous ion on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; Total iron remaining

| Time | Total iron remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | $Fe^{2+}$ 0.10 mM | $Fe^{2+}$ 0.25 mM | $Fe^{2+}$ 0.50 mM | $Fe^{2+}$ 1.0 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.9153 | 0.9129 | 0.9647 | 0.9171 |
| 5 | 0.8764 | 0.9099 | 0.9569 | 0.9114 |
| 10 | 0.8654 | 0.9014 | 0.9610 | 0.8970 |
| 20 | 0.8136 | 0.8935 | 0.9472 | 0.8936 |
| 30 | 0.7707 | 0.8814 | 0.9316 | 0.9108 |
| 60 | 0.6869 | 0.8542 | 0.8970 | 0.9094 |
| 90 | 0.6690 | 0.8500 | 0.8923 | 0.9106 |
| 120 | 0.6461 | 0.8367 | 0.8714 | 0.9125 |

Note ; 2,4-DCP = 1 mM, $H_2O_2$ = 10 mM , $SiO_2$ = 100 gram, pH = 3

Table B-39 The effect of initial ferrous ion on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; $Fe^{2+}$ remaining

| Time (min) | $Fe^{2+}$ remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| | $Fe^{2+}$ 0.10 mM | $Fe^{2+}$ 0.25 mM | $Fe^{2+}$ 0.50 mM | $Fe^{2+}$ 1.0 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.9615 | 0.9667 | 0.8889 | 0.4927 |
| 5 | 0.9231 | 0.9333 | 0.7677 | 0.3463 |
| 10 | 0.8846 | 0.9000 | 0.5758 | 0.2195 |
| 20 | 0.8077 | 0.8333 | 0.4646 | 0.1951 |
| 30 | 0.7692 | 0.7500 | 0.3131 | 0.1756 |
| 60 | 0.6923 | 0.5167 | 0.2424 | 0.0878 |
| 90 | 0.6154 | 0.4167 | 0.1818 | 0.1122 |
| 120 | 0.5769 | 0.4167 | 0.1818 | 0.1951 |

Note ; 2,4-DCP = 1 mM, $H_2O_2$ = 10 mM , $SiO_2$ = 100 gram, pH = 3

Table B-40 The effect of initial ferrous ion on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; $H_2O_2$ remaining

| Time (min) | $H_2O_2$ remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| | $Fe^{2+}$ 0.10 mM | $Fe^{2+}$ 0.25 mM | $Fe^{2+}$ 0.50 mM | $Fe^{2+}$ 1.0 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.9389 | 0.7500 | 0.6734 | 0.5940 |
| 5 | 0.8923 | 0.6788 | 0.5693 | 0.3422 |
| 10 | 0.8540 | 0.5775 | 0.4544 | 0.2135 |
| 20 | 0.7692 | 0.4790 | 0.3558 | 0.1286 |
| 30 | 0.6952 | 0.4297 | 0.2956 | 0.1040 |
| 60 | 0.6159 | 0.3449 | 0.2053 | 0.0356 |
| 90 | 0.5748 | 0.3230 | 0.1670 | 0.0137 |
| 120 | 0.5474 | 0.2929 | 0.1314 | 0.0109 |

Note ; 2,4-DCP = 1 mM, $H_2O_2$ = 10 mM , $SiO_2$ = 100 gram, pH = 3

**The effect of initial $H_2O_2$ concentration**

Table B-41 The effect of initial hydrogen peroxide concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; 2,4-dichlorophenol remaining

| Time | 2,4-dichlorophenol remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | $H_2O_2$ 1 mM | $H_2O_2$ 5 mM | $H_2O_2$ 10 mM | $H_2O_2$ 20 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.6075 | 0.5118 | 0.2728 | 0.2825 |
| 5 | 0.4456 | 0.2093 | 0.0616 | 0.0462 |
| 10 | 0.3561 | 0.0386 | 0.0084 | 0.0084 |
| 20 | 0.3148 | 0.0362 | 0.0080 | 0.0067 |
| 30 | 0.3143 | 0.0352 | 0.0077 | 0.0065 |
| 60 | 0.2931 | 0.0343 | 0.0075 | 0.0058 |
| 90 | 0.2835 | 0.0331 | 0.0072 | 0.0053 |
| 120 | 0.2751 | 0.0320 | 0.0062 | 0.0052 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.25 mM , $SiO_2$ = 100 gram, pH = 3

Table B-42 The effect of initial hydrogen peroxide concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; COD remaining

| Time | COD remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | $H_2O_2$ 1 mM | $H_2O_2$ 5 mM | $H_2O_2$ 10 mM | $H_2O_2$ 20 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.8715 | 0.8939 | 0.8750 | 0.8555 |
| 5 | 0.8268 | 0.8232 | 0.7989 | 0.7919 |
| 10 | 0.7374 | 0.7727 | 0.7391 | 0.7225 |
| 20 | 0.7151 | 0.6818 | 0.6630 | 0.6416 |
| 30 | 0.6983 | 0.6465 | 0.6250 | 0.5665 |
| 60 | 0.6760 | 0.6313 | 0.5652 | 0.5260 |
| 90 | 0.6480 | 0.6162 | 0.5272 | 0.4740 |
| 120 | 0.6536 | 0.6212 | 0.4946 | 0.4277 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.25 mM, $SiO_2$ = 100 gram, pH = 3

Table B-43 The effect of initial hydrogen peroxide concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; Total iron remaining

| Time | Total iron remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | $H_2O_2$ 1 mM | $H_2O_2$ 5 mM | $H_2O_2$ 10 mM | $H_2O_2$ 20 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.9063 | 0.9543 | 0.9129 | 0.9763 |
| 5 | 0.9240 | 0.8640 | 0.9099 | 0.9548 |
| 10 | 0.9195 | 0.8544 | 0.9014 | 0.9418 |
| 20 | 0.9029 | 0.8386 | 0.8935 | 0.9164 |
| 30 | 0.9172 | 0.8324 | 0.8814 | 0.8983 |
| 60 | 0.9103 | 0.8409 | 0.8542 | 0.8932 |
| 90 | 0.9149 | 0.8527 | 0.8500 | 0.8870 |
| 120 | 0.9200 | 0.8589 | 0.8367 | 0.8949 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.25 mM , $SiO_2$ = 100 gram, pH = 3

Table B-44 The effect of initial hydrogen peroxide concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; $Fe^{2+}$ remaining

| Time | $Fe^{2+}$ remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | $H_2O_2$ 1 mM | $H_2O_2$ 5 mM | $H_2O_2$ 10 mM | $H_2O_2$ 20 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.9123 | 0.9123 | 0.9667 | 0.9483 |
| 5 | 0.8596 | 0.8421 | 0.9333 | 0.9138 |
| 10 | 0.7895 | 0.8070 | 0.9000 | 0.8621 |
| 20 | 0.8070 | 0.7368 | 0.8333 | 0.7931 |
| 30 | 0.8246 | 0.7018 | 0.7500 | 0.7241 |
| 60 | 0.8772 | 0.7719 | 0.5167 | 0.4828 |
| 90 | 0.8947 | 0.8070 | 0.4167 | 0.3621 |
| 120 | 0.8947 | 0.8246 | 0.4167 | 0.3103 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.25 mM, $SiO_2$ = 100 gram, pH = 3

Table B-45 The effect of initial hydrogen peroxide concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; $H_2O_2$ remaining

| Time | $H_2O_2$ remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | $H_2O_2$ 1 mM | $H_2O_2$ 5 mM | $H_2O_2$ 10 mM | $H_2O_2$ 20 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.6022 | 0.8814 | 0.7500 | 0.8882 |
| 5 | 0.3832 | 0.6624 | 0.6788 | 0.8225 |
| 10 | 0.2190 | 0.4325 | 0.5775 | 0.7486 |
| 20 | 0.1642 | 0.2299 | 0.4790 | 0.7062 |
| 30 | 0.1095 | 0.1478 | 0.4297 | 0.6761 |
| 60 | 0.0821 | 0.0547 | 0.3449 | 0.6090 |
| 90 | 0.0547 | 0.0383 | 0.3230 | 0.5885 |
| 120 | 0.0547 | 0.0274 | 0.2929 | 0.5858 |

Note ; 2,4-DCP = 1 mM, $Fe^{2+}$ = 0.25 mM, $SiO_2$ = 100 gram, pH = 3

**The effect of initial 2,4-dichlorophenol concentration**

Table B-46 The effect of initial 2,4-dichlorophenol concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; 2,4-dichlorophenol remaining

| Time | 2,4-dichlorophenol remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | 2,4-DCP 0.5 mM | 2,4-DCP 1 mM | 2,4-DCP 2 mM | 2,4-DCP 5 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.2412 | 0.2728 | 0.4943 | 0.7683 |
| 5 | 0.0493 | 0.0616 | 0.1524 | 0.5853 |
| 10 | 0.0074 | 0.0084 | 0.0306 | 0.4085 |
| 20 | 0.0056 | 0.0080 | 0.0155 | 0.2654 |
| 30 | 0.0043 | 0.0077 | 0.0148 | 0.2025 |
| 60 | 0.0037 | 0.0075 | 0.0142 | 0.1833 |
| 90 | 0.0034 | 0.0072 | 0.0140 | 0.1813 |
| 120 | 0.0033 | 0.0062 | 0.0138 | 0.1772 |

Note ; $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM, $SiO_2$ = 100 gram, pH = 3

Table B-47 The effect of initial 2,4-dichlorophenol concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; COD remaining

| Time | COD remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | 2,4-DCP 0.5 mM | 2,4-DCP 1 mM | 2,4-DCP 2 mM | 2,4-DCP 5 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.8167 | 0.8750 | 0.8906 | 0.9464 |
| 5 | 0.7083 | 0.7989 | 0.8333 | 0.8929 |
| 10 | 0.6333 | 0.7391 | 0.7812 | 0.8016 |
| 20 | 0.5750 | 0.6630 | 0.7240 | 0.7500 |
| 30 | 0.5333 | 0.6250 | 0.6771 | 0.7262 |
| 60 | 0.5000 | 0.5652 | 0.6458 | 0.6786 |
| 90 | 0.4583 | 0.5272 | 0.6094 | 0.6905 |
| 120 | 0.4333 | 0.4946 | 0.5990 | 0.6984 |

Note ; $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM, $SiO_2$ = 100 gram, pH = 3

Table B-48 The effect of initial 2,4-dichlorophenol concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; Total iron remaining

| Time | Total iron remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | 2,4-DCP 0.5 mM | 2,4-DCP 1 mM | 2,4-DCP 2 mM | 2,4-DCP 5 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.9258 | 0.9129 | 0.9102 | 0.9270 |
| 5 | 0.9117 | 0.9099 | 0.8785 | 0.9047 |
| 10 | 0.8835 | 0.9014 | 0.8707 | 0.8853 |
| 20 | 0.8629 | 0.8935 | 0.8857 | 0.8505 |
| 30 | 0.8752 | 0.8814 | 0.9066 | 0.8192 |
| 60 | 0.8676 | 0.8542 | 0.8809 | 0.8448 |
| 90 | 0.8652 | 0.8500 | 0.8857 | 0.8722 |
| 120 | 0.8546 | 0.8367 | 0.8821 | 0.8756 |

Note ; $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM, $SiO_2$ = 100 gram, pH = 3

Table B-49 The effect of initial 2,4-dichlorophenol concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; $Fe^{2+}$ remaining

| Time | $Fe^{2+}$ remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | 2,4-DCP 0.5 mM | 2,4-DCP 1 mM | 2,4-DCP 2 mM | 2,4-DCP 5 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.7692 | 0.9667 | 0.8095 | 0.8947 |
| 5 | 0.6923 | 0.9333 | 0.6984 | 0.8070 |
| 10 | 0.5577 | 0.9000 | 0.6349 | 0.7368 |
| 20 | 0.4231 | 0.8333 | 0.6032 | 0.6842 |
| 30 | 0.3462 | 0.7500 | 0.6667 | 0.7018 |
| 60 | 0.2692 | 0.5167 | 0.6984 | 0.7719 |
| 90 | 0.1923 | 0.4167 | 0.7143 | 0.8246 |
| 120 | 0.1731 | 0.4167 | 0.7460 | 0.8421 |

Note ; $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM, $SiO_2$ = 100 gram, pH = 3

Table B-50 The effect of initial 2,4-dichlorophenol concentration on 2,4-dichlorophenol degradation in fluidized-bed Fenton process. ; $H_2O_2$ remaining

| Time | $H_2O_2$ remaining ($C/C_0$) | | | |
|---|---|---|---|---|
| (min) | 2,4-DCP 0.5 mM | 2,4-DCP 1 mM | 2,4-DCP 2 mM | 2,4-DCP 5 mM |
| 0 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 2 | 0.8622 | 0.7500 | 0.8403 | 0.8403 |
| 5 | 0.8239 | 0.6788 | 0.6432 | 0.7363 |
| 10 | 0.7582 | 0.5775 | 0.4571 | 0.5310 |
| 20 | 0.6870 | 0.4790 | 0.3285 | 0.3203 |
| 30 | 0.6487 | 0.4297 | 0.2409 | 0.1779 |
| 60 | 0.5885 | 0.3449 | 0.0985 | 0.0547 |
| 90 | 0.5447 | 0.3230 | 0.0246 | 0.0164 |
| 120 | 0.5173 | 0.2929 | 0.0219 | 0.0109 |

Note ; $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM, $SiO_2$ = 100 gram, pH = 3

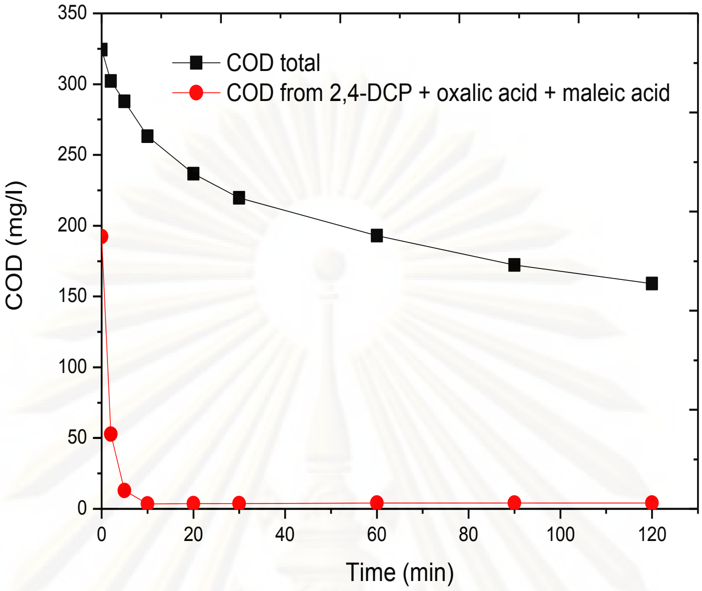
## B.5 Experimental data for intermediate detection of 2,4-dichlorophenol degradation.

Table B-51 The concentration of anion generated during the degradation of 2,4-dichlorophenol by fluidized-bed Fenton process at the optimum condition.

| Time (min) | Chemical remaining (mM) | | | |
|---|---|---|---|---|
| | 2,4-DCP | Chloride ion | Maleate ion | Oxalate ion |
| 0 | 0.9984 | 0.0065 | 0.000 | 0.000 |
| 2 | 0.2723 | 0.1697 | 87.146 | 92.738 |
| 5 | 0.0615 | 0.2459 | 127.900 | 233.405 |
| 10 | 0.0084 | 0.2933 | 107.718 | 429.212 |
| 20 | 0.0080 | 0.3136 | 73.101 | 654.798 |
| 30 | 0.0077 | 0.3177 | 51.004 | 731.254 |
| 60 | 0.0075 | 0.3419 | 39.264 | 903.850 |
| 90 | 0.0072 | 0.3491 | 26.282 | 956.944 |
| 120 | 0.0062 | 0.3600 | 22.097 | 999.252 |

Note ; 2,4-DCP = 1 mM , $Fe^{2+}$ = 0.25 mM , $H_2O_2$ = 10 mM, $SiO_2$ = 100 gram, pH = 3

# COD from of intermediates



# Appendix C

# Experimental Figure

Figure C.1 Operating Fluidized-bed Fenton reactor

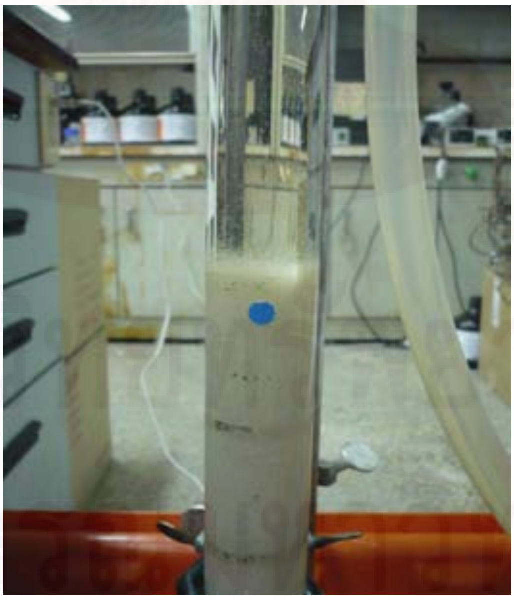


Figure C.2 Carriers in fluidized-bed reactor

# BIOGRAPHY

Miss Isara Muangthai was born on December 13, 1984 in Bangkok Thailand. She graduated Bacherlor's degree in Environmental Engineering form the faculty of Environmental Engineering, Kasetsart University 2007. She pursed her Master Degree in Environmental Engineering from the faculty of Engineering, Chulalongkorn University, Bangkok Thailand on May, 2007. She had attained oral presentation and submitted a publication with her advisor, Associate Professor Chavalit Ratanatamskul, Ph.D. and co-advisor, Professor Ming-Chun Lu, Ph.D., in the subject of "Study on 2,4-dichlorophenol degradation by fluidized-bed Fenton process using statistical experimental design" in the international conference on Environmental Quality Concern, Control and Conservation on May, 22, 2009, Kaohsiung, Taiwan.