AMOXICILLIN COMBINED WITH CLAVULANIC ACID DEGRADATION BY ELECTRO-FENTON PROCESS

Miss Paranee Boonchuay

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2014

การย่อยสลายสารผสมอะม็อคซี่ซิลินกับกรดคลาวูลานิค ด้วยกระบวนการอิเล็กโตรเฟนตัน

นางสาวปารนีย์ บุญช่วย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

Thesis Title	AMOXICILLIN COMBINED WITH CLAVULANIC ACID DEGRADATION BY ELECTRO-FENTON PROCESS
By	Miss Paranee Boonchuay
Field of Study	Environmental Management
Thesis Advisor	Assistant Professor Kitirote Wantala, Ph.D.

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

....Dean of the Graduate School

(Associate Professor Sunait Chutintaranond, Ph.D.)

THESIS COMMITTEE

....Chairman

(Assistant Professor Chantra Tongcumpou, Ph.D.)

....Thesis Advisor

(Assistant Professor Kitirote Wantala, Ph.D.)

....Examiner

(Associate Professor Patiparn Punyapalakul, Ph.D.)

....Examiner

(On-anong Larpparisudthi, Ph.D.)

....External Examiner

(Visanu Tanboonchuy, Ph.D.)

ปารนีย์ บุญช่วย : การย่อยสลายสารผสมอะม๊อคซี่ซิลินกับกรดคลาวูลานิค ด้วยกระบวนการอิเล็กโตรเฟนตัน (AMOXICILLIN COMBINED WITH CLAVULANIC ACID DEGRADATION BY ELECTRO-FENTON PROCESS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: กิติโรจน์ หวันตาหลา, 147 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาการย่อยสลายสารอะม๊อคซี่ซิลิน ด้วยกระบวนการ ออกซิเดชั่นขั้นสูง โดยมุ่งศึกษากระบวนการอิเล็กโตรเฟนตัน ในแง่ของการศึกษาสภาวะที่เหมาสมสำหรับการดำเนินระบบให้เกิดประสิทธิภาพสูงสุดในรูปของซีโอดี และศึกษากลไกทางจลน์ศาสตร์ของกระบวนการภายในระบบ อีกทั้งมีการประเมินคุณภาพของน้ำที่ผ่านกระบวนการในระบบและนอกจากนี้ การศึกษายังรวมไปถึง การศึกษาผลกระทบของปริมาณสารโปรแทสเซียม คาวูลาเนต ที่มีต่อการย่อยสลายของสารอะม๊อคซี่ซิลินเช่นกัน และยิ่งไปกว่านั้นการออกแบบการทดลองถูกนำมาใช้เพื่อหาสภาวะที่ดีที่สุดด้วย ตัวแปรในการศึกษาครั้งนี้ได้แก่ พีเอช, อัตราส่วนปริมาณความเข้มข้นของไฮโดรเจนเปอร์ออกไซค์ ต่อ ปริมาณสารอะม๊อคซี่ซิลิน และ เฟอรัส และ ค่ากระแสไฟฟ้าต่อหน่วยพื้นที่ผลการศึกษาเมื่อนำผลการทดลองทั้งหมด 27 ชุด มาวิเคราะห์ผลโดยใช้เทคนิคพื้นที่ผิวผลตอบแบบ Box-Benkehn Design พบว่าพีเอช, อัตราส่วนปริมาณความเข้มข้นของ ไฮโดรเจนเปอร์ออกไซค์ ต่อ ปริมาณสารอะม๊อคซี่ซิลิน และต่อเฟอรัส และ ค่ากระแสไฟฟ้าต่อหน่วยพื้นที่เป็น 2.5, 40 (MR) ,15 (MR) และ 0.1 มิลลิแอมแปร์ต่อตารางเซนติเมตร ตามลำดับโดยสามารถกำจัดสารอินทรีย์ในรูปของซีโอดีได้สูงสุดถึง 65% นอกจากนี้การประเมินคุณภาพของน้ำที่ผ่านระบบไป ยังเป็นตัวชี้ให้เห็นว่า กระบวนการอิเล็กโตรเฟนตันสามารถที่จะเพิ่มอัตราความสามารถการออซิไดซ์ ทำให้เพิ่มการย่อยสลายทางชีวภาพให้แก่น้ำตัวอย่างได้เช่นกัน ทำให้น้ำนั้นสามารถที่จะปล่อยลงสู่ระบบบำบัดขั้นต่อไปที่เป็นระบบบำบัดทางชีวภาพได้ และนอกจากนี้ ได้มีการศึกษาผลกระทบของกรดวูลานิค ในรูปแบบของการเติมสารโพแทสเซียมคาวูลาเนตลงไป จากการทดลอง ทำให้เห็นว่าปริมาณของโพแทสเซียมคาวูลาเนต ไม่มีผลกระทบต่อการย่อยสลายอะม๊อคซี่ซิลิน แต่การเพิ่มสารชนิดลงไปในอัตราส่วน 1 : 8 (โพแทสเซียมคาวูลาเนต : อะม๊อคซี่ซิลิน) เพิ่มอัตราความสามารถการออซิไดซ์ และอัตราการย่อยสลายทางชีวภาพเล็กน้อย

สาขาวิชา การจัดการสิ่งแวดล้อม

ปีการศึกษา 2557

ลายมือชื่อนิสิต ....

ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5587574120 : MAJOR ENVIRONMENTAL MANAGEMENT

KEYWORDS: ELECTRO-FENTON / ADVANCE OXIDATION PROCESS / BOX-BEHNKEN DESIGN / PHARMACEUTICALS / HYDROXYL RADICAL

PARANEE BOONCHUAY: AMOXICILLIN COMBINED WITH CLAVULANIC ACID DEGRADATION BY ELECTRO-FENTON PROCESS. ADVISOR: ASST. PROF. DR. KITIROTE WANTALA, Ph.D., 147 pp.

The objectives of this study are to investigate the removal efficiency, effect of operating parameters of Amoxicillin using electro-Fenton process by using response surface methodology based on Box-Benkehn design. Using response surface methodology helps to optimize process efficiency including main effects, interaction effect, significant effect and experimental accuracy. Then, kinetic in term of COD on Amoxicillin degradation by electro-Fenton process was determined. 27 sets of experimental runs were performed and exhibited the optimal condition for this process. At pH 2.5, 40, 15 molar ratio of H_2O_2/AMX and $H_2O_2/Fe^{2+}$and 0.1 $mAcm^{-2}$ of current were the appropriate operating parameters to achieve 65% of COD removal. After that, rate constant of COD removal was established by using graphical method and finding order of rate reaction. In addition, treated water was evaluated average oxidation state. The tendency of average oxidation state was improved along the time interval of electro-Fenton process. This implied that there was biodegradable ability of treated water. Finally, the evaluation of Clavulanic acid of Amoxicillin degradation expressed that no difference on the degradation of these combination

Field of Study:	Environmental Management	Student's Signature	....
		Advisor's Signature	....
Academic Year:	2014		

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere appreciation to my professor, Dr. Kitirote Wantala, for supporting me to work in his laboratory and sympathize with me. All of your suggestion, recommend, enthusiasm, assistance and speech, I felt and realized. Their comments are so vary precious. Thanks to the committee members that give me many piece of advices. Furthermore, many thanks to Mr. & Mrs Ratpakdi, I appreciated their valuable suggestion and Dr.thanakorn Methatham as well.

I would like to thank for the accommodation of the Department of Chemical and Environmental Engineering, Khon Kaen University for laboratory supports. Special thanks got to Center of Excellence on Hazardous Substance Management (HSM) and Research Center for Environmental and Hazardous Substance Management (EHSM) for financial support on my research works. Without these financial assistances, my research should not totally fulfillment.

I want to give a big thanks my parents, grandmother, aunt, uncle, my younger brother and sister for the biggest supporting, understanding me and pushing me further.

I want to to thank you my lovely sisters, brothers and friends at EHWM, Envi Eng, CKCL, YW and MVSK. We worked and laugh together, helped each other and shared either good or bad times. I have no words to define this appreciate I am much appreciated. At the last, I thanks destiny, I always believe that whatever it happened, it happened for a reason.

CONTENTS

Page

LIST OF FIGURE

Page

LIST OF TABLE

Page

CHAPTER I

INTRODUCTION

1.1 State of problem

Nowadays, medical technologies have the trend of continuous advancement. Pharmaceuticals have been used so far for analysis, prevention, treatment and recovery of diseases (USEPA, 2012). There are many types of pharmaceutical compounds, for example antipyretics, analgesics, antimafarial drugs, antiseptics and antibiotics. The presence of antibiotics in the first time was the mid-1990s during World War II. Even though antibiotics have been used so far, the residual antibiotics just become the concerned problems that we should take it in account in recent years (Hernando, Mezcua, Fernández-Alba, & Barceló, 2006). The research reports the amount of pharmaceutical compounds existing in different range from mg L^{-1} to ng L^{-1} (Schwab et al., 2005). These residuals should be concerned because they have been identified as pollutants in ecosystem. Exposure of bacteria in water to antibiotic residues may induce antibiotic resistance, bacteria develop themselves to resist in changed condition and endure in the new environment. This concern will gradually increases and become risk to human health (Schwab et al., 2005). Problems of antibiotics presented led to resistant bacteria. In fact, simple biological treatment cannot completely treat these kinds of substances which consist of many non-biodegradable substances or toxic chemicals causing decrease of the number of native bacteria (Halling-Sørensen et al., 1998). Wastewater treatment plant partially remove pharmaceutical compound. The potential for these compounds consistently present in effluents. Accordingly, wastewater treatment plant did not design for directly removing pharmaceutical products so antibiotics still exit there.

Amoxicillin, ß-lactam antibiotic in penicillin class, is highly effective used for resisting pathogens regarding respiratory, excretory and gastrointestinal systems in both human and veterinary medicine. Clavulanic acid, ß-lactamase inhibitor promotes antibiotic’s activities against ß-lactamase’s activities. Recently, Amoxicillin is mostly used along with Clavulanic acid for improving medical treatment and promoting ß-lactamase’s ineffectiveness (Sirisomboon, 2003). Approximately 50-70 % of amoxicillin and 25-40% clavulanic acid are excreted by human body via urine and it still remains in those forms for 6 hours after excretion (McEvory, 2001). As a resulted to antibiotics can be consistently present in effluents. From releasing the residues, they can spread out to the environmental matrix according to food chain. Besides, they exist in the environmental phases depending on their properties (Homem & Santos, 2011). WHO classified amoxicillin as extremely potent bioactive substance, according to their low K_{ow} value, possibility that amoxicillin transform to hydrophobic phase such as fish and aquatic issue (Dahdouh, 2013).

To control the residual antibiotics and avoid pollutants accumulated in water and wastewater, the developed powerful methods and also effective technologies as advance oxidation process (AOPs) are applied as one choice. AOPs were installed at the pretreatment process in order to change forms of organic pollutants to biodegradable or less toxic forms and then convert them reactive free radicals, typically use hydroxyl radical ($^{\bullet}OH$), in ambient temperature. AOPs have been identified as effective method because they can produce strong oxidizing agent by themselves. The high potential of hydroxyl radicals reacts as nonselective compounds. Therefore, AOPs were widely applied in pre-treatment for prevention of loss of microorganism in subsequent biological treatment. Moreover, it is a easy method compared with other methods (e.g., activated carbon adsorption, air stripping and reverse osmosis) (Elmolla & Chaudhuri, 2010). There are many techniques to generate them (e.g. chemical oxidation, ultraviolet based process, photo-catalytic process, supercritical water oxidation, sonolysis electron beams x–ray irradiation and also Fenton reaction process) (Nidheesh & Gandhimathi, 2012). Among AOPs, Fenton process is identified as one of the useful method owing to their efficiency, simple method, low cost and nontoxic of reagent (H_2O_2/Fe^{2+}) (Elmolla & Chaudhuri, 2010). Currently, electrochemical advance oxidation process namely electro-Fenton has been known as an alternative method for wastewater treatment. Electro Fenton process is a modified Fenton process that uses electrochemical and Fenton reagent to react with pollutants.

The advantages of Electro Fenton are the environmentally friendly method due to generation of in situ Fenton’s reagent and cost effective method because it reduces operation cost of added reagent. There are no sludge generation in Electro Fenton process (Nidheesh & Gandhimathi, 2012).

For this research, the mixing of Amoxicillin with Clavulanic acid was chosen to be target compounds. The performances of Amoxicillin with Clavulanic acid degradation were performed by electro-Fenton process. The effects of operating parameters were determined. In addition, the optimum condition was operated to carry out the kinetic of COD removal.

1.2 Objectives

1. To investigate the removal efficiency of Amoxicillin using electro-Fenton process.
2. To determine the effect of operating parameters on Amoxicillin by using electro-Fenton process.
3. To determine the kinetic in term of COD on Amoxicillin degradation by electro-Fenton process.
4. To investigate the effect of Clavulanic acid on COD removal

1.3 Hypotheses

1. Amoxicillin combined with Clavulanic acid can be degraded by electro-Fenton process to smaller molecules, which can be continuously decomposed with biological treatment process.
2. Electrical current in electro-Fenton process can help to improve amoxicillin degradation.

1.4 Scopes of study

1. This experiment will be performed in laboratory scale and be operated in batch mode.
2. The experiment will be conducted at room temperature and control temperature and pH for kinetic experiment.
3. Using Amoxicillin and Amoxicillin mixed with Clavulanic acid as synthetic wastewater.

1.5 The Advantage of the study

1. To know the removal efficiency of electro-Fenton process on amoxicillin removal.
2. To access to the effect of operating parameters that effect on amoxicillin removal by electro-Fenton process in synthetic wastewater.

3. To achieve the maximum condition for amoxicillin degradation by electro-Fenton process.
4. To know the kinetic of amoxicillin degradation in term of COD removal by electro-Fenton process.

CHAPTER II

THERETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Pharmaceutical residues

Pharmaceutical compounds are broadly used for preventing, treating infection in humans and animals. Moreover, they promote the growth rate in animals (Fent, Weston, & Caminada, 2006). There are many ways of pharmaceutical products can that be discharged to the environment for example, flushing expired drugs from households, using drugs in veterinary, leachate expired drugs from landfills and organic fertilizer, excretion of drugs via urine and feces, wastewater discharged from hospitals and pharmaceutical industries as shown in Figure1.

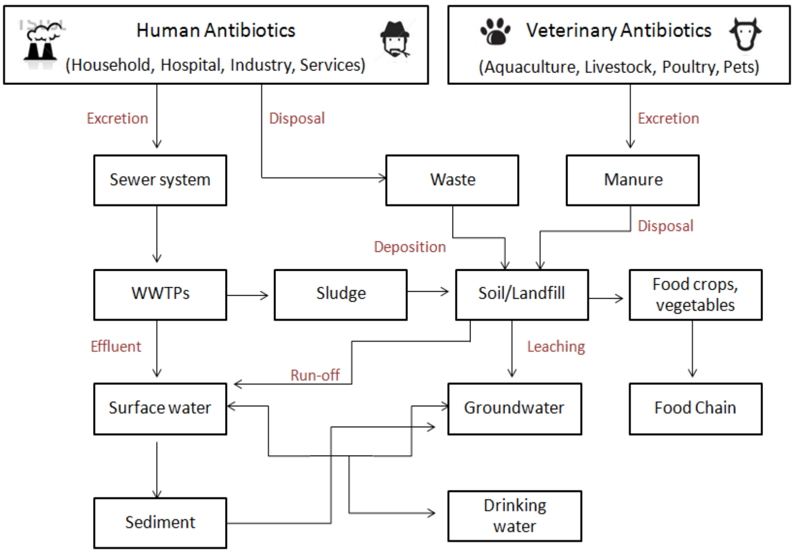


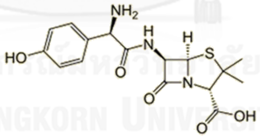
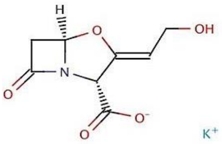
Figure 1 Pathways of pharmaceutical expose the environment

As this reason pharmaceutical compounds contaminated in river, ground water, water resources for drinking water and wastewater are presented (Kümmerer, 2009).

2.2 Amoxicillin

Amoxicillin (AMX), ß-lactam antibiotics, is effective against to inhibit biochemical process in cell wall synthesis both gram positive and gram negative bacteria. Therefore, Amoxicillin is broad spectrum of bacterial activity. The structure of amoxicillin that is ß-lactam ring (4 membered cyclic amide) with free amino led to improve adsorption properties than traditional penicillin. There are a variety of amoxicillin hydrated forms namely monohydrate, dihydrate, and trihydrate but the most stable hydrate form is trihydrate (Idrees Ala Khail, 2009). The physiochemical properties and molecular structures of amoxicillin are presented in the table below.

Table 1 Physiochemical properties and molecular structures of amoxicillin and Potassium Clavulanate (Lee, Kim, Ahn, & Scholtz, 2010; Pubchem, 2014)

Pharmaceutical	**Amoxicillin**	**Potassium Clavulanate**
Chemical formula	$C_{16}H_{19}N_3O_5S$	$C_8H_8NO_5{\bullet}K$
Molecular weight (g/mol)	365.41	237.25
pKa	3.39	2.7 at 25 °C
Log Kow[a]	0.87	-2.04
Melting point (°C)	194	237.25
Henry's law constant (-)	2.73×10^{-19} at 20 °C	>1700°C
Water solubility (mg/l)	3,430 at 20 °C	300
Molecular structure		

2.3 Clavulanic acid

Clavulanic acid (CA) was discovered by Brown and Napier as ß-lactamase inhibitor (Saudagar, Survase, & Singhal, 2008). Clavulanic acid molecules consist of two ß-lactam combined rings with 2R and 5R stereochemistry. The main central similar penicillin but oxygen at five membered rings is substituted Sulphur and at C6 side chain position disappears. The chemical structure of CA consists of ß-lactam ring as similar as penicillin class does. Thus, CA are used for develop antibiotic efficiency by combine with antibiotic as amoxicillin, ticarcillin, piperacillin. Beta lactamase enzyme will attach they instead of antibiotic because the same in some part of CA and antibiotic**.** Their ability can reduce ß-lactamase enzymes activity both Gram-positive and Gram-negative bacteria (Lee et al., 2010). Using CA alone exhibit weak antibiotic activity. It hardly found only CA was used as reactive against because the low activity of CA comparing to other antibiotics.

2.4 The combination of Amoxicillin and Clavulanic acid

Since 1974s, AMX were indicated treat capability effective against to *S. pneumoniae* and *H. influenza.* Due to low side effects of AMX, AMX trend to be prefer using of ß-lactam antibiotics than others in ß-lactam group. The increasing in demand of using antibiotics led to increasing high amount of antibiotic resistance. Previous research indicated the data obtained in Europe that demonstrated a quantity of ß-lactam antibiotics sale is correlated with penicillin non-susceptible *S. pneumonia* and *H. influenza* (HPSC, 2014). CA, ß-lactamase inhibitor was added to combine with AMX. Adding CA with AMX Improve efficiency of AMX, according to these combination induced ß-lactamase enzymes attached with CA instead of AMX.

The combination of AMX and CA was first used in the United Kingdom in 1981's as Augmentin. Normally, AMX and CA are available as a fixed AMX trihydrate combine with potassium salt of CA. Various dosages typically are as 250 - 875 mg of AMX and 125 mg of CA (Lee et al., 2010).

2.5 Pharmaceutical contamination in environment

A large number of pharmaceutical are consumed per year regarding their advantages. The highest consumption class in European countries was antibiotic (Adriaenssens et al., 2011). It is not surprising that antibiotic frequently found in the environment. Previous research reported many categories of antibiotics contaminated in environment for example anti-inflammatory substances antihistamines and antibiotics. Water sample from lake which located close to pharmaceutical industries in Hyderabad, India contaminated with ciprofloxacin, cetirizine, norfloxacin and enoxacin up to 6.5, 1.2 , 0.52 and 0.16, respectively(Fick et al., 2009). While river sediment of up and down stream where received effluent from same pharmaceutical industries is also detected. The concentration of upstream was 7.1 μgg^{-1} and 914 μmg^{-1} for downstream (Kristiansson et al., 2011). In addition, other environment phase also determined. The concentration of ciprofloxacin, sulfamethoxazole and carbamazepinein in manure slurry soil sample were detected at levels of 1.4, 4.3 and 5.4 $mgkg^{-1}$, respectively (Haller, Müller, McArdell, Alder, & Suter, 2002).

This contamination was toxic to bacteria community because they enhance bacterial resistant in environment. This reason caused human can affect to resistant gene by transformation of resistant gene to human pathogen by food, animal or directly expose.

AMX concentration in natural water was not frequency occurred in order to the properties of penicillin class that ß-lactam ring able to open easily by ß-lactamase. Therefore, low concentration of AMX in low level always detected. Many Sewage treatment effluent in Italy were detected amount of AMX in range 15 – 120 ngL-1 (Castiglioni, Bagnati, Calamari, Fanelli, & Zuccato, 2005) while AMX be detected in sea water in Hong Kong as 0.64-76 ng L^{-1}.

However; high concentration still present, it depended on type and characteristic of water. The highest concentration of AMX frequency found in effluent from pharmaceutical industry in range of several hundreds of milligrams per liter (Schreiber & Szewzyk, 2008).

2.6 Human exposed and toxicology effects

Maximum dosage of AMX suggesting for adult is 2-3 g/day. If over dosage was consumed, many effects both hypersensitivity and electrolyte imbalance can be gotten, for example neuromuscular hypersensitivity (hallucination, asterixis, agitation, encephalopathy, seizures and confusion). Moreover, environmental impacts can be occurring. Accordingly, WHO reported that AMX was classified as extremely potent bioactive substance because of their low K_{ow} value. AMX maybe transform to hydrophobic phase such as fish and aquatic issue. Even if AMX was found in a small amount in ecosystem because it was decomposed by hydrolysis process, small amount of their residual has the potential effect to biota.

The present of antibiotic not only the presence of antibiotic affects to resistant strains of infection, but also can affect to living microorganism that importance to ecosystem. For example; the study on toxicity of AMX in unicellular green-fresh water alga, the indicator for chemical water pollution, demonstrated that AMX risked to blue-green alga *S.lepoliensis* with 0.78, 1.56 and 2.22 μgL^{-1}, NOEC LOEC and EC_{50}, respectively. (Andreozzi et al., 2004). Moreover, short term effects of bacteria that expose to AMX was evaluated, the result indicated that it was caused decreasing in dominant bacterial communities (Binh et al., 2007; Boxall et al., 2004). In addition AMX also affected to Juvenile goldfish and mosquito The study of ecosystem toxicity on animal investigated the effects of AMX in both Juvenile goldfish and mosquito with LC_{50} value equals to 35.72 μg L^{-1} (Dahdouh, 2013). Eventthough, the toxicity of AMX impacts to organism in low level, these level not far from detected level in the environment.

2.7 Processes for pharmaceutical removal

Although, occurrence of low concentrations ranging from levels of ngL^{-1} to mgL^{-1} of pharmaceutical residual in the environment, scientists have concerned the toxic of these residual. They suggested that the increasing of pharmaceutical residual led to bacteria community decrease and resulted to ecological negative effect increase (Kümmerer, 2011).

Recently, There are many method have been developed for achieve high rate of pharmaceutical removal. Adsorption by organobentonite and activated carbon for remove 300 mgL^{-1} initial concentration of AMX. 88.01 and 94.67% of AMX removal was achieved by using bentonites and activated carbon (Putra, Pranowo, Sunarso, Indraswati, & Ismadji, 2009).

Other publishes used almond shell ashes to adsorb amoxicillin contaminated in aqueous solution at low level (μgL^{-1}). Even the low concentration was performed in this study, the percentage of AMX removal still high. About 97% AMX removal in term of Langmuir equation also achieved. Although high percentage removal of absorption obtained, Searching, handle, storage and disposal a large amount of absorbent material in adsorption process should be considered. Moreover, using nano filtration membrane was investigated. 97% of amoxicillin rejection was achieves as well and they suggested flow rate and pressure affect to amount of amoxicillin penetrate through nano filtration membrane. Even though nanomembrane filtration has good percentage of removal, fouling of membrane pore can be occurring during the operation by chemical precipitation and microbial growth on membrane surface.

2.8 Advance oxidation processes (AOPs)

“Advance oxidation processes (AOPs) are defined as those which involve the generation of hydroxyl radicals ($^{\bullet}OH$) in sufficient quantity to affect water purification”(Glaze, Kang, & Chapin, 1987). This is the accepted definition from 1987. AOPs come up with the objective to generate highly reactive free radicals in ambient temperature and pressure for oxidize organic pollutant or target compound to acceptable form or less toxic. AOPs are applied for treat many types of wastewater for example treating contaminated in groundwater, drinking water, water supply and also industrial wastewater include pharmaceutical industry. AOPs are installed as pretreatment process to enhance biodegradation ability. For this method, the larger molecule is oxidized to smaller one caused microorganism to easily degrade them. The combination with another treatment process such as biological treatment process is one way for upgrade the process efficiency and cost effective reason.

Hydroxyl radicals are identified as powerful oxidizing agent and their oxidation power versus standard hydrogen electrode (SHE) is 2.8 V, which is the second powerful oxidation potential next to fluorine as shown in Table 2.

Table 2 Oxidation potential of chemical (Buxton, Greenstock, Phillip Helman, & Ross, 1998)

Chemical	**Redox potential (Volt)**
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Hypobromous acid	1.59
Chloride dioxide	1.50
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chlorine	1.36
Bromide	1.09

In the present, AOPs have been used as alternative treatment method. Although, conventional wastewater treatment system is the treatment process that use to improve wastewater quality, it is not efficient to complete non-biodegradable substance. Pharmaceutical wastewater contain large molecular weight compound, non-biodegradable substance and directly toxic to microorganism (Homem & Santos, 2011). Thus, the conventional wastewater treatment system is not an appropriate treatment system to remove this kind of substance. Advance wastewater treatment process were developed for control this problem.

Recent progress in the removal of AMX by pharmaceutical wastewater had been applied AOPs in to treatment process with regarded their ability of $^{\bullet}OH$. Roberto Andreozzi studied amoxicillin degradation by ozonation process in sewage treatment plant effluents. They found pH was the influence on kinetics constant for hydroxyl radical attack to amoxicillin. At pH 5.5 kinetics constant was 3.93×10^{9} $M^{-1}s^{-1}$. During 4 minutes first operating time, 90% of AMX was changed to other form. Resulted from TOC at the beginning was few decreased (Andreozzi, Canterino, Marotta, & Paxeus, 2005). Despite high percentage of AMX removal expressed in ozonation process, cost effectiveness should be considered.

Among AOPs, Using catalyst showed good results on AMX degradation than only used solar photolysis (Pereira et al., 2013). TiO_2 catalyst was used for improve solar photolysis efficiency. Providing solar energy just 3.1 $KJ_{UV}L^{-1}$ for 60 min was enough for totally AMX degradation in the present of TiO_2. Nonetheless, using TiO_2 as catalyst, rapid recombination of electro-hold in some type of TiO_2 may induce inefficient catalyst. Removal of AMX by others, AOPs is interested, due to high oxidizing abilities of $^{\bullet}OH$. Moreover, AOPs are the best methods to treat non-biodegradable pollutant. AOPs can be installed as either separately or combined with other process to improve the efficiency of process.

Moreover, their rate constants for ability to oxidize organic compounds and inorganic compounds are in range 10^6 - 10^{10} $M^{-1}s^{-1}$ (Haag & Yao, 1992). There are many techniques to generate $^{\bullet}OH$ such as chemical oxidation, ultraviolet (UV)-based processes, photo-catalytic redox process, supercritical water oxidation, sonolysis electron beams X–ray irradiation and also Fenton reaction processes.

2.9 Fenton reaction process

In 1894 Fenton reaction was discovered by H.J.H Fenton (Nidheesh & Gandhimathi, 2012). This reaction is referred to using hydrogen peroxide with iron to generate $^{\bullet}OH$. The potential of $^{\bullet}OH$ does like nonselective substance to react with other organic pollutants or target compounds and form smaller, easily degrade, less toxic substance or mineralization (Nidheesh & Gandhimathi, 2012). This process also reduces carbon content in wastewater in term of both chemical oxygen demand (COD) and total organic carbon (TOC).

The main reaction involves with using hydrogen peroxide (H_2O_2) combine with ferrous ion (Fe^{2+}) to produce $^{\bullet}OH$ follow reaction 2.1. Therefore, these reagents are called “Fenton’s reagents”

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad k_1 = 76\ M^{-1}s^{-1} \qquad \text{Reaction 2.1}$$

Fenton reaction while H_2O_2 decomposition, using Fe^{2+} as catalysts in acidic solution in dark and without organic compound, is shown in the equation below(Barreiro, Capelato, Martin-Neto, & Bruun Hansen, 2007).

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet}$ $k_2 = 0.02$ Reaction 2.2

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-}$ $k_3 = 4.3 \times 10^{-6}$ Reaction 2.3

$Fe^{2+} + O_2^{\bullet -} \rightarrow Fe^{3+} + O_2^{-}$ $k_4 = 1 \times 10^{-7}$ Reaction 2.4

$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2$ $k_5 = 1.2 \times 10^{-6}$ Reaction 2.5

$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$ $k_6 = 2.7 \times 10^{-7}$ Reaction 2.6

$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$ $k_7 = 8.3 \times 10^{-5}$ Reaction 2.7

${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ $k_8 = 5.3 \times 10^{-9}$ Reaction 2.8

$RH + {}^{\bullet}OH \rightarrow RH^{\bullet} + OH^{-} \rightarrow product / CO_2 + H_2O$ Reaction 2.9

Neutralization is needed after Fenton reaction treatment process. Iron hydroxide sludge will occur during neutralization step, so further separation or sludge disposal is needed. Using Fenton's reagent has been reported that successfully degrade antibiotic contained wastewater.

The performance of Fenton reaction process depends on many factors. Operating parameters included pH, applied current, supporting electrolyte and Fenton's reagent amount are the main parameter on process efficiency. The key factors in Fenton process is pH. Because pH related with iron form that directly affect to iron solubility. The appropriate pH for operate Fenton reaction is around 2-4. The changing in both side optimal pH will impacts to process performance. Ferrous ion especially ferric ion will precipitate when pH increase. In contrast, H_2O_2 is not stable in acid pH. When pH decrease, the scavenging effect of $^{\bullet}OH$ by H^+ will occurs. $^{\bullet}OH$ will be reactd with H^+ to form $H_3O_2^+$ that reduced of $^{\bullet}OH$ amount of $^{\bullet}OH$ generation (Sun et al., 2008). Using Fenton's reagent to degrade wastewater that contained AMX at pH 3 was found high amount of COD and TOC removal (Arslan-Alaton & Dogruel, 2004). TOC removal decrease in range of 73 -81 % were met as operated photo-Fenton process after 240 minute as pH 2.5-2.8 (Trovó, Pupo Nogueira, Agüera, Fernandez-Alba, & Malato, 2011).

The ratio of Fenton's reagent is an important factor as well because it is responsible to generate $^{\bullet}OH$. Increased Fe^{2+} concentration led to COD removal increase but too much of theirs would reduce efficiency as a results of ferrous and ferric (Anotai, Singhadech, Su, & Lu, 2011). Using excessive unilaterally of Fenton's reagent is not acceptable due to side reaction (Reaction 2.1, 2.6). Thus, using suitable ratio of Fe^{2+} and H_2O_2 is necessary. The increased ratio of Fenton's reaction led to enhance process efficiency (Elmolla & Chaudhuri, 2010). The best condition for degrade Amoxicillin, Ampicillin and Cloxacillin in wastewater was obtained as 10 molar ratio H_2O_2/Fe^{2+} (Elmolla & Chaudhuri, 2010). These can confirm by increase H_2O_2/Fe^{2+} trended to improve mineralization (Mavronikola et al., 2009).

2.10 Electro-Fenton process

Eelectro-Fenton process refer to the process that applied electricity to produce the in-situ Fenton’s reacgent depending on suitable electrode. The advantage of insitu Fenton’s reagent is continuously produce $^{\bullet}OH$ and destroyed organic pollutant followed the objective of Fenton process.

This process can use for waste water treatment for example pulp bleaching, dye and also pharmaceutical waste water (Anotai, Su, Tsai, & Lu, 2010).

Base on Fenton process to achieve $^{\bullet}OH$ generation, these electrochemical reaction can be occurred.

On cathode side:

$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$ Reaction 2.11

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ Reaction 2.12

$H_2O + e^- \longrightarrow 1/2H^+ + OH^-$ Reaction 2.13

On anode side:

$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ Reaction 2.14

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ Reaction 2.15

Regarding the ability of $^{\bullet}OH$, electro-Fenton reaction was developed to be the method to treat wastewater. Some of the operating parameters of Fenton and electro-Fenton process are alike but there are additional compartment in electro-Fenton that involved with electro chemical oxidation process. Much research informed about them. Electrode material (anode and cathode) is important tool that are responsible for produce target chemical. Because Electro-Fenton process can be classified as 3 types depending on the purpose of electrical current supply (Qiang, Chang, & Huang, 2003).

The EF-H_2O_2 method

For this type, Fe^{2+} is added and H_2O_2 is electro-generated via the two electro reduction of sparked oxygen on cathodes (i.e. graphite, reticulated vitreous carbon and carbon-PTFE). O_2 is supplied into the process which can be superoxide ion ($O_2\cdot^-$) and continuously form H_2O_2 at cathode side.

On cathode side:

$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$ Reaction 2.16

On anode side:

$1/2O_2 + H_2O^+ \longrightarrow 2{}^\bullet OH$ Reaction 2.17

The EF-FeOx method

For this type, H_2O_2 were added and Fe^{2+} was generated by oxidation of sacrificial iron anode. The electrode that employed in this type was used as Fe^{2+}source led to Fe^{3+} continuously present at cathode side.

Fenton sludge recycling (FSR) system

For this type, Fe^{2+} and H_2O_2 were added to be initial source at the first time of operating. Electrical current was provided to the system for induce Fe^{2+}

regeneration from ferric hydroxide sludge. This concept can help the process to reduce sludge generation and sludge disposal cost also.

On cathode side:

$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$ Reaction 2.18

$H_2O + e^{-} \longrightarrow 1/2H_2 + OH^{-}$ Reaction 2.19

On anode side:

$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$ Reaction 2.20

$H_2O \longrightarrow 2H^{+} + 1/2O_2 + 2e^{-}$ Reaction 2.21

The work of Sires proposed that the different electrodes exhibited different performance, the high rate of oxidation power was presented on Pt/carbon felt than BDD/carbon felt than Pt/O_2 diffusion and more than BDD/O_2 diffusion (Sirés et al., 2007). Pt is high potential media and preferred usage but it is expensive. Therefore, the other types of anode (i.e. Boron-dropped diamond, Titanium coated IrO_2/RuO_2 and Iron) are used practical purpose (Nidheesh & Gandhimathi, 2012).

The important factor in electro-Fenton process is current density because applied current directly involve with the objective of electro Fenton. Normally, low current was suggested not larger than 6.4 A/m^2 (Nidheesh & Gandhimathi, 2012). Because the occurring of side reaction (i.e. the oxygen discharge and hydrogen evolution) at electrodes caused reduce the process performances.

The study of Thirugnanasambandham was reported 10 mAcm^{-2} as a the optimal current density of treated poultry wastewater by using electro-Fenton. The process achieved 97 and 93% of COD and turbidity removal, respectively (Thirugnanasambandham, Kandasamy, Sivakumar, kumar, & Mohanavelu). Especially, in electro Fenton electrolyte is very importance. This necessary for enhance solution conductivity and allow electron transfer. The supporting electrolyte sodium sulfate is normally used respect their electrolytic efficiency allowing high current density dramatically drop in efficiency also meet when 0.2 M sodium sulfate was applied, as a result of too much of SO_4^{2-} The scavenging effect of $^{\bullet}OH$ present as high of sulfate ion contained solution.

In addition, the work of Ghonein compared NaCl and Na_2SO_4 electrolyte. They demonstrated that during decolorization of sun set, yellow SO_4^{2-} provide higher rate than Cl^- (Ghoneim, El-Desoky, & Zidan, 2011). Previous work mentioned about electrolyte impacted to electro-Fenton performance but the study of Daneshvar reported that in the electro-Fenton of orange II degradation did not affect from supporting electrolyte using $NaClO_4$ 0.05-0.1 M (Daneshvar, Aber, Vatanpour, & Rasoulifard, 2008).Furthermore, ferrous catalyst from iron was suggested that there were most effective catalyst as 0.1 mM of $FeSO_4$ soluble solution than other metal cations such as copper, cobolt and manganess for 100% TOC removal of phenol solution

Because of Electro Fenton efficiency, a large deal of research is interested in applied electro-Fenton in waste water treatment process to treat organic matter such as phenolic compound, leachate, dye and pharmaceuticals as well. Sires used electro Fenton to treat antibiotic chlorophene for observe the behavior of different catalyst form. ß-Blocker antibiotic was degraded by electro-Fenton process. Complete mineralization was achieve and almost of nitrogen was accumulate in form of NH^{4+} (Sirés, Oturan, & Oturan, 2010). Previous work concluded that the generation of $^{\bullet}OH$ from Fenton process rapidly destroyed aromatic pollutants coming from the formation of ferrous and the others such as oxalic and oxamic producing from carboxylic (Isarain-Chávez et al., 2010).

2.11 Response surface methodology (RSM)

In the present, the education widely spread worldwide, the combination of two related fields is possible. Response surface methodology (RSM) is the collection method that applied statistical and mathematical model for use in model analysis. The Box-Behnken design (BBD), one type in RSM, is considered at the middle of edges of the experimental region and center point also for achieve process optimization. RSM have been used in many field of education such as biotechnology, biochemical, science, engineering pharmacy, industry and environmental application also (Sairiam, 2008).

BBD have been used to find the optimal condition on process performance of electro-Fenton process. The work of Guven et al (2008) applied RSM to optimized applied voltage and waste electrolytic in electro-Fenton process as set COD removal and waste concentration as response. At 25 °C, they found the optimal condition including 11.29 V of voltage and 19.87 gL^{-1} of electrolytic concentration for remove 100 % of waste concentration and 100 % COD (Güven, Perendeci, & Tanyolaç, 2008).

Homem et al (2010) investigated the degradation of AMX in water in ppb (450 μgL^{-1}) level by Fenton reaction using central composite design. Three factors were evaluated i.e. Fe^{2+}, H_2O_2 concentration and temperature, while the dimensionless concentration (C/C_0) was set as response. Under the optimal condition including, AMX completely degrade in 30 minute of operating time (Homem, Alves, & Santos, 2010).

In 2013, the team of Homem also applied RSM to improve Fenton reaction process by micro wave assistance. The highest efficiency was met during short time just in 5 minute of operating time. The optimal condition included 162 watt, 2.35 mgL^{-1} and 95 μgL^{-1} for power, H_2O_2 and Fe^{2+} concentration, respectively (Homem, Alves, & Santos, 2013).

CHAPTER III

MATERIAL AND METHODS

3.1 Experimental framework

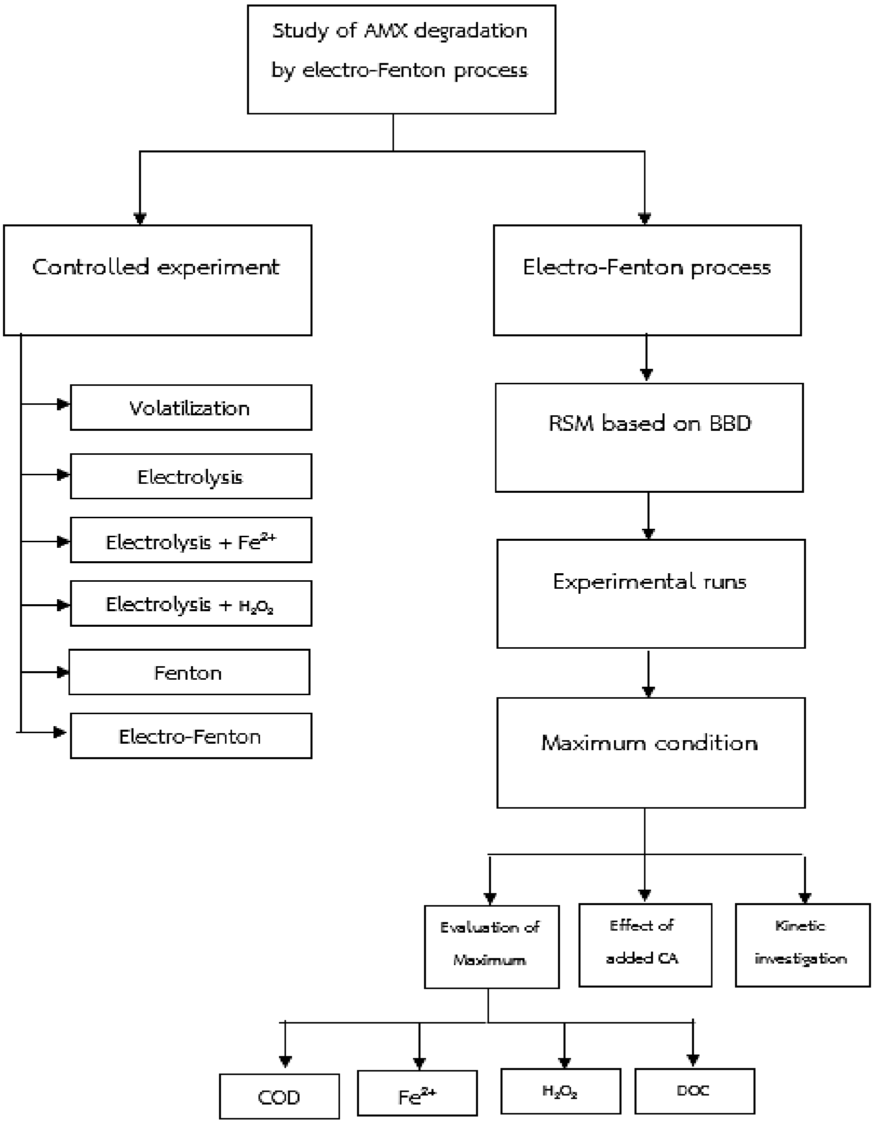


Figure 2 Experimental framework.

3.2 Materials

Amoxicillin: $C_{16}H_{19}N_3O_5S$ (≥ 900 μg mg^{-1}, Sigma Aldrich)

Potassium clavulanate: $C_8H_8NO_5K$ (99.8%, Sigma Aldrich)

Ferrous sulfate heptahydrate: $FeSO_4 \cdot 7H_2O$ (Merck)

Hydrogen peroxide: H_2O_2, (35%, Merck)

Sodium hydroxide: NaOH (98%, Ajex)

Sulfuric acid: H_2SO_4 (98%, RCI Labscan)

Hydrochloric acid: HCl (37%, RCI Labscan)

Ammonium acetate: $NH_4C_2H_3O_2$ (Ajex)

Potassium titanium (IV) oxalate: K_2TiO (≥ 90%, Sigma Aldrich)

Deionized water

3.3 Experimental Equipment

pH meter

UV-VIS Spectrophotometer (Analytic jena, specord 200 plus)

TOC analyzer (Analytic jena, Multi N/C 2100s)

Thermometer 0-100 °C

Weighing Machine (4-Digits Balance)

Magnetic Stirrer

Thermal controller

1L of electro-Fenton reactor with recycle pump

Stainless steel electrodes and Ti/RuO_2/IrO_2 electrodes

Clock Timer

Membrane Filter 0.2 and 0.45 μm

DC power supply

Ultra sonicator

3.4 Electro-Fenton reactor setup

The experiment was performed in an Electro-Fenton reactor batch reactor. 1 liter of glass jacketed batch reactor was used in this study. To protect reactor from light, aluminum foil were used to wrap it. Electrodes in electro-Fenton process consisted of Ti/RuO_2/IrO_2 as anode and stainless steel as cathode. Both of electrodes were connected with a DC power supply for provide electricity. Magnetic stirrer bar was used for provide complete mixing. The temperature was controlled by using cooling system. The schematic experiment set up of this study shows in Figure 3.

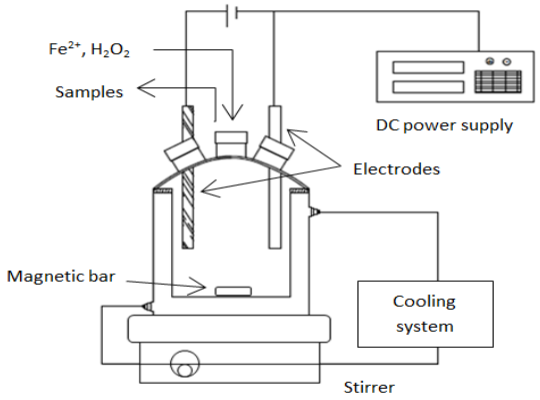


Figure 3 Schematic diagram of electro-Fenton reactor.

3.5 Electro-Fenton procedures

Antibiotic aqueous solution containing 0.3 mM of AMX was prepared by dissolving AMX powder in water. After that, dissolved solution was sonicated for completely dissolved for 20 min. AMX synthetic solution has the initial COD 110-130 mgL^{-1}. The pH of the solution was adjusted to desired pH with H_2SO_4 and NaOH. Then, a mount of Ferrous sulfate was added into solution. After added ferrous ion caused pH may be changed, therefore rechecking pH again is necessary. Subsequently, both H_2O_2 and electricity were supplied to solution. Supplying of H_2O_2 and electricity means to start reaction. The electrical current and pH were maintained during operating time period. 10 mL of aqueous solution was kept at time interval and NaOH was added to reach pH than 10 for stop the reaction. In order to meet H_2O_2 decompose, sample was left for 10 hours before COD analysis. Then, the sample was filtered with 0.45 μm membrane filter.

3.6 Analytical method

Using preliminary setup AMX was detected by using high performance liquid chromatography (HPLC) with UV detector following previous AMX analysis (Rajesh et al., 2013) as describe below.

Column	Hypersil ODS C_{18}
Column size	250mm×4.6nm, 5µm
Detection	UV 228 nm
Mobile phase	Acetate buffer : Methanol (94:6 v/v) *pH 4.0 Acetate buffer (Dissolve 2.86 ml of glacial acetic acid and 1 mL of 50% w/v of sodium hydroxide, dilute with water to make 1,000 mL)
Flow rate	1 mL min^{-1}
Temp	25 °C
Injection size	20 µL

Using electro-Fenton experiment these analytical methods were used as summarized in Table 3.

Table 3 Summary of analytical method

Variables	Method	Reference
Temperature	Thermometer	APHA*
Analysis of Chemical oxygen demand (COD)	Close reflux method	
Analysis of Dissolve organic carbon (TOC)	TOC analyzer	
Analysis of Fe^{2+} concentration	Phenanthroline method	
Analysis of H_2O_2 concentration	Spectrophoto method	
pH measurement	pH meter	

APHA* Standard Methods for the Examination of Water and Wastewater, 20th edition. American Public Health Association, Washington, D.C. (Apha & Wef, 2012).

3.7 Experimental design and statistical analysis

Response Surface Methodology (RSM) is the collection method that applied statistical and mathematical model for use in model analysis. The model was used to estimate correlation of independent variables and experimental results. The Box-Behnken design, one type in RSM, is considered at the middle of edges of the experimental region and center point also. In this study researcher used RSM experiment based on Box-Behnken design for find the maximum optimal condition for AMX degradation by electro-Fenton process. In the section of statistical analysis, Minitab 16 software (Minitab Inc.) was employed. Moreover, the analysis from Box-Behnken design can help to reduce a number of experimental runs. Therefore, the results were carried out by effectiveness and take no longer time. The levels of variables are displayed in Table 4.

Table 4 The range of levels of independent variables

Variables	Variable level		
	Low	Center	High
pH	2.5	3	3.5
H_2O_2/AMX (MR)	10	25	40
H_2O_2/Fe^{2+} (MR)	5	10	15
Current density ($mAcm^{-2}$)	0.1	0.55	1

Accordingly, the calculation of amount of Fenton's reagent following different molar ratio of Fenton's reagent is shown in Table5.

Table 5 Amount of Fenton's reagent

Fenton's reagent	Fe^{2+} (Ratio)	5	10	15
H_2O_2 (Ratio)	Amount of H_2O_2 (mM)	Amount of Fe^{2+} (mM)		
10	3	0.6	0.3	0.2
25	7.5	1.5	0.75	0.5
40	12	2.4	1.2	0.8

In this study COD removal was set as response. Accordingly, The COD removal of each experimental runs was calculated following Equation3.1.

$$\% \, COD \; removal = \frac{COD_0 - COD_t}{COD_0} \times 100 \qquad \text{Equation 3.1}$$

Where COD_0 is initial concentration of COD (mg O_2 L^{-1})

COD_t is COD is concentration of COD at interval time.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preliminary setup

To investigate AMX degradation by electro-Fenton process, AMX concentration was measured by HPLC for identify amount of AMX concentration. Peak of 0.3 mM standard concentration of AMX, showed in Figure 4, while peak of AMX concentration after operated time was displayed in Figure 5 (a) and (b).

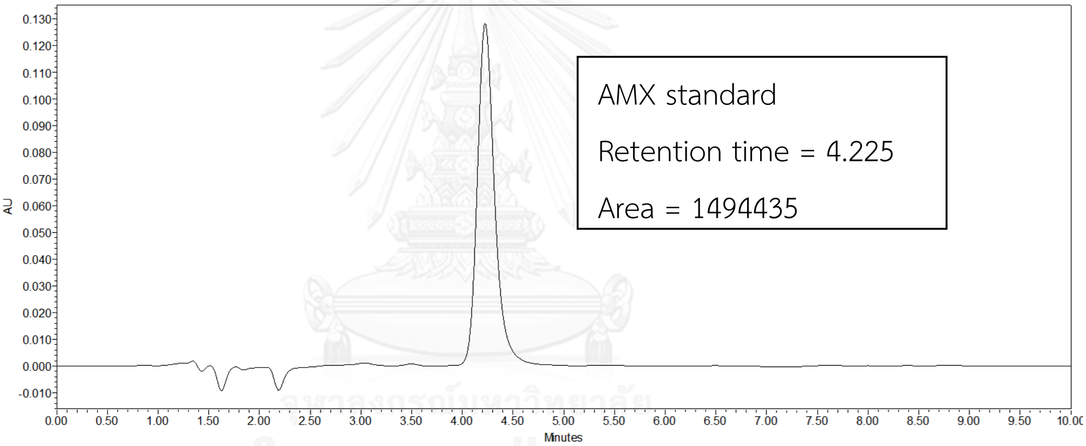
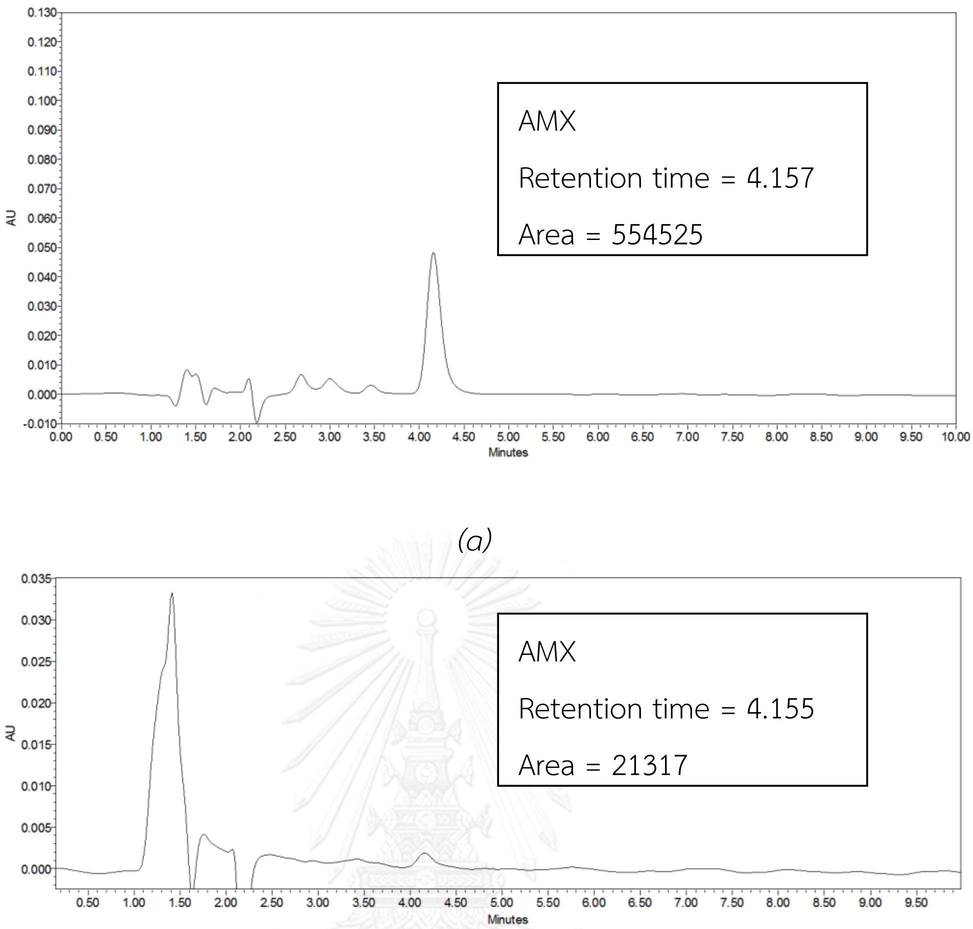


Figure 4 Spectrum peak of AMX 0.3 mM standard concentration by HPLC.



(a)

(b)

Figure 5 (a) Spectrum peak of AMX after 3 minute operating reaction, (b) Spectrum peak of AMX after 5 minute operating reaction.

The retention time of AMX standard spectrum showed in 4.20 minute. For 0.3 mM of AMX their high presented around 1.27 AU (area =1494435). After started reaction, AMX did detect well. There was low AMX remained in solution after operated electro-Fenton in 3 minute as displayed in Figure 5 (a) and few AMX remained in solution after 5 minute as displayed in Figure 5 (b). However, there was some intermediate presented during AMX degradation as retention time about 1.5 minute as displayed in Figure 5 (b). Accordingly, COD was used as parameter that represented overall organic carbon contained in solution in next step.

4.2 Controlled experiment

In this part to make sure that the removal of COD did not significantly remove via non-Fenton reaction. The controlled experiments were performed for observe these results. The initial concentration of controlled experiment were as follows AMX 0.3 mM, 1.2 mM of H_2O_2, 0.8 mM of Fe^{2+} and 0.1 $mAcm^{-2}$of current density. Because the property of AMX that easily hydrolysis by breaking β-lactam ring structure. Thus AMX hydrolysis should be considered as a controlled experiment.

The reaction at 5 minute represented Fenton reaction that main Fe^{2+} came from ferrous salt, adding from outside. This reaction mainly form $^{\bullet}OH$ by the combination of Fe^{2+} and H_2O_2. While reaction time at 5-30 minute represented Electro-Fenton that Fe^{2+} came from ferrous regeneration regarding electro-Fenton principle. Therefore reaction was divided into two parts (0-5 and 5-30 minute) for observe experimental results.

Figure 6 displayed many processes that were considered as controlled experiment for electro-Fenton study. The results show slightly drop (1.82 – 18.33 %) in COD removal in controlled experiments. A mount of 1.83% of COD removal was caused by hydrolysis in the absence of Fenton’s reagent. Only 3.53% of COD removal was obtained from electrolysis. Furthermore, 18.33% and 12.05% were the results from electrolysis with the present of H_2O_2 and Fe^{2+}, respectively. All of controlled experiments were designed to investigate the impact of degradation, pH, current density, a mount of ferrous and hydrogen peroxide. Thereby, using only Fe^{2+}, H_2O_2 and current density have no significant effect to COD removal.

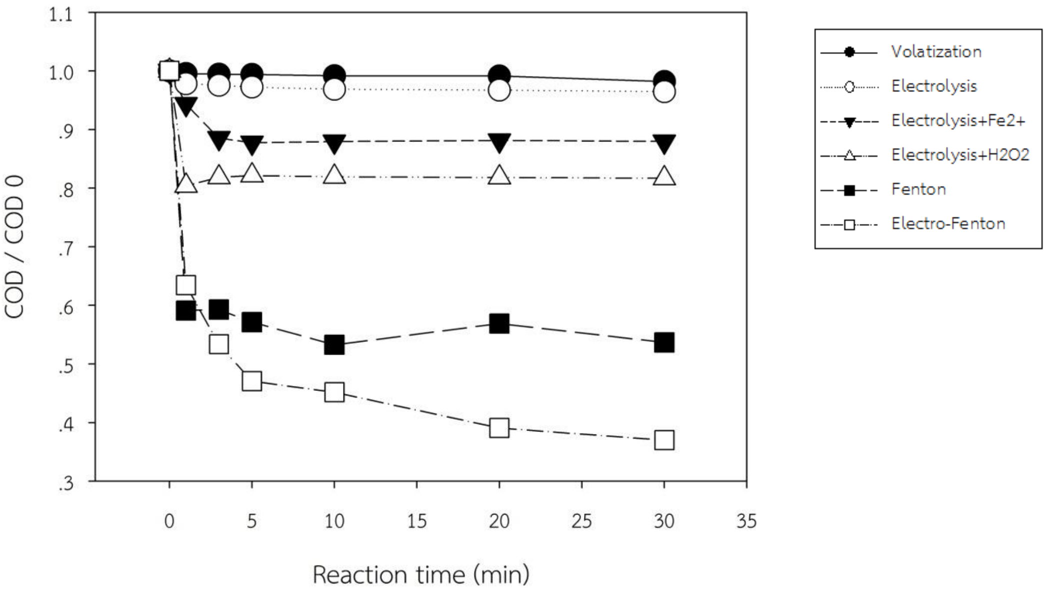


Figure 6 The comparison of COD/COD_0 versus time using different processes.

4.3 Electro-Fenton process

4.3.1 Experimental results

RSM is the collection method that applied statistical and mathematical model for use in model analysis. The Box-Behnken design (BBD), one type in RSM, is considered at the middle of edges of the experimental region and center point also for achieve process optimization. In this section BBD was used to determine the optimal condition with independent variable factors include pH, H_2O_2/AMX (MR), H_2O_2/Fe^{2+} (MR) and current density and response function was the percentage of COD removal.

To access the performance of COD removal and observe the variable effects at different time during reaction period by electro-Fenton process, the experimental results were classified as two groups. First group, initial stage, represents rapid reaction by Fenton process that occurs in 5 minute. The second represent the overall reaction of electro-Fenton process in 30 minute as shown in Figure 6.

In this study COD removal of each experimental runs was calculated following Equation 3.1 Results from experimental runs was displayed in Table 6 and detailed of experiment was displayed in Appendix C.

Table 6 Design of experimental runs with 0.3 mM of initial concentration AMX

Run order	Level of variables				Response	
	pH	H_2O_2/AMX (MR)	H_2O_2/Fe^{2+} (MR)	Current density (mAcm-2)	% Removal	
					5 min	30 min
1	3.0	25	15	0.10	51.57	70.29
2	3.0	40	15	0.55	60.48	70.75
3	3.5	25	5	0.55	67.61	75.33
4	2.5	40	10	0.55	64.91	70.45
5	2.5	25	10	1.00	46.94	59.09
6	3.5	10	10	0.55	43.05	46.62
7	2.5	25	5	0.55	65.56	67.57
8	3.5	25	15	0.55	54.97	67.26
9	3.0	25	5	1.00	49.50	53.57
10	3.0	40	10	1.00	51.43	54.58
11	3.0	40	10	0.10	61.20	63.10
12	3.0	10	10	0.10	33.16	47.35
13	3.0	25	5	0.10	59.06	60.53
14	3.5	25	10	0.10	49.64	53.74
15	3.0	10	10	1.00	25.36	40.33
16	2.5	25	10	0.10	62.70	71.66
17	3.0	25	10	0.55	55.34	58.79

Table 6 Design of experimental runs with 0.3 mM of initial concentration AMX (continue)

Run order	Level of variables				Response	
	pH	H_2O_2/AMX (MR)	H_2O_2/Fe^{2+} (MR)	Current density (mAcm-2)	% Removal 5 min	% Removal 30 min
18	3.5	25	10	1.00	51.23	56.69
19	3.0	25	10	0.55	54.83	55.57
20	2.5	25	15	0.55	58.13	68.88
21	2.5	10	10	0.55	33.01	41.85
22	3.0	40	5	0.55	61.65	62.30
23	3.0	10	15	0.55	29.04	44.43
24	3.5	40	10	0.55	61.88	58.60
25	3.0	10	5	0.55	36.17	45.07
26	3.0	25	15	1.00	49.80	59.48
27	3.0	25	10	0.55	52.43	56.93

4.3.2 Investigation of maximum condition for COD removals in initial stage.

4.3.2.1 The effects of operating parameters for COD removal in initial stage by electro-Fenton process

After finished experimental, the experimental results were evaluated by using empirical equation to establish relationship between independent factors and response. Table 8 showed the coefficient data.

Consequently, the equation, an empirical relationship between the response and independent variables, for COD removal in the initial stage by electro-Fenton process are displayed as Equation 4.1. Then established equation as

$$COD\ removal_{5\,m} = 54.201 - 0.239\mathrm{A} + 13.480\mathrm{B} - 2.963\mathrm{C} - 3.589\mathrm{D} + 4.184A^2 - 8.102B^2 - 4.320D^2 - 3.264AB + 4.339AD \qquad \text{Equation 4.1}$$

Where A is pH

B is molar ratio of H_2O_2/AMX

C is molar ratio of H_2O_2/Fe^{2+}

D is Current density ($mAcm^{-2}$)

Table 7 Coefficient data for COD removal for initial state

Source	Coefficient	P-value
Constant	54.201	0.000
A (pH)	-0.239	0.776
B (H_2O_2/AMX (MR))	13.480	0.000
C ($H_2O_2/Fe^{2+(}$MR))	-2.963	0.004
D (Current density (mAcm^{-2}))	-3.589	0.001
A^2	4.184	0.005
B^2	-8.102	0.000
C^2	2.173	0.103
D^2	-4.320	0.004
AB	-3.264	0.041
AC	-1.303	0.378
AD	4.339	0.010
BC	1.492	0.315
BD	-0.494	0.734
CD	1.949	0.196
R-Sq = 97.21%		
R-Sq(pred) = 84.44%		
R-Sq(adj) = 93.96%		

Since empirical equation had been established, it is necessary to check the fitted model for make sure that the predicted values are accepted. There are many ways to determine an accuracy of model. A normal probability plot is one choice that made from error value of predicated value and actual value. The residuals from experiment can be plotting to check the appropriate of the model. Generally, the residuals should fall on a straight line. If the residuals can be live nearly a straight line, normal assumption is satisfied. If the residuals leave from a straight line, normal assumption may be avoid. As a result of residuals plot, the results showed all points of residuals fall on a straight line. It indicated the experimental results are satisfied as shown in Figure 7.

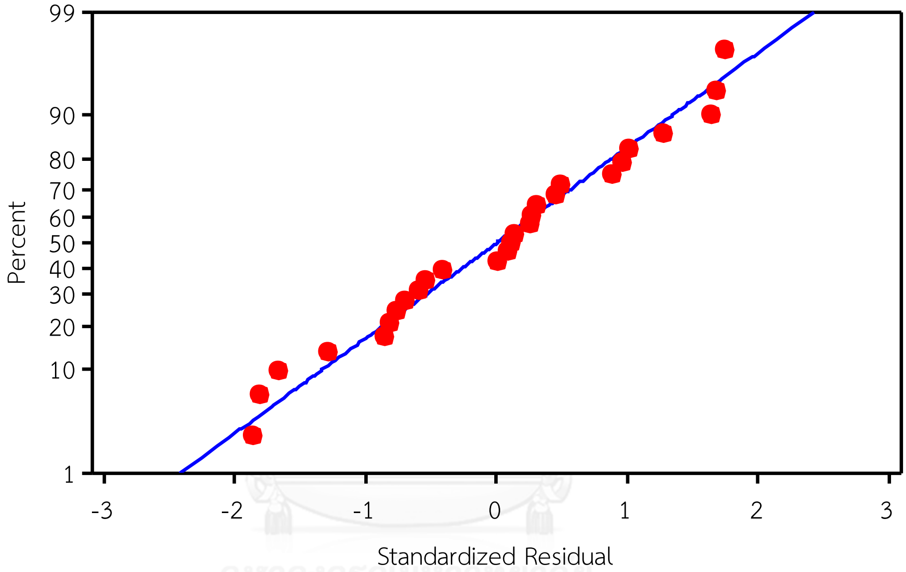


Figure 7 A normal probability plot for 5 minute of operating time.

Histogram was used to check the accuracy of predicted model also. The frequency of error distribution was in normal curve as shown in Figure 8. It denoted that the errors of experimental results are accepted.

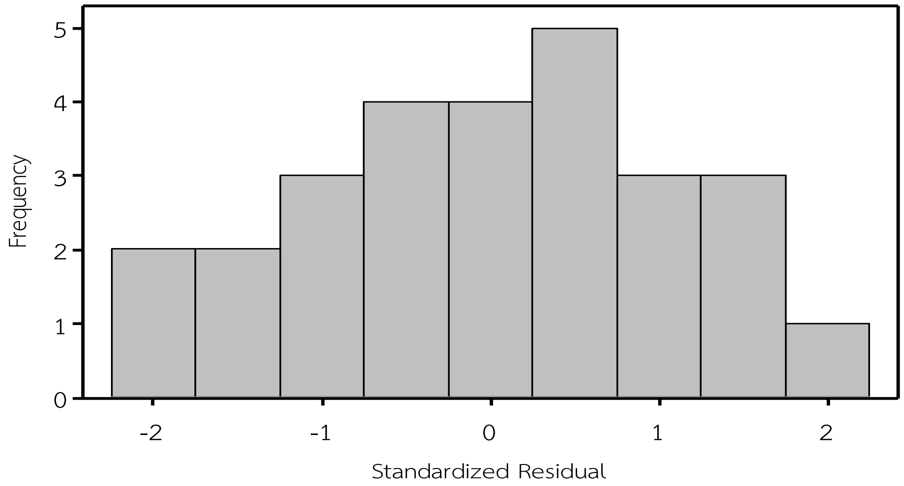


Figure 8 Histogram for 5 minute of operating time.

Subsequently, Analysis of variance (ANOVA) was applied to evaluate the results of variable factors from regress equation of COD removal.

Fischer's F test (F-value), dividing the mean square of regression by the mean sum square of residual error. In case of F-value is higher than critical value ($F_{0.95,\ 4,\ 12}$= 3.26) (Dinov, 2002), it means the model is satisfied. Critical value refers to the F-value that consider at 95% confidence with (4, 12) degree of freedom in linear and residual error. In this study, the model of COD removal in earliest stage is satisfied because the F-value of regression is equal to 29.91 as shown in Table .8

Table 8 ANOVA results for COD removal in the earliest stage by electro-Fenton

Source	Degree of freedom	F-value	P-value
Regression	14	29.91	0.000
Linear	4	75.29	0.000
A (pH)	1	0.08	0.776
B (H_2O_2/AMX (MR))	1	269.02	0.000
C (H_2O_2/$Fe^{2+(}$MR))	1	13.00	0.004
D (Current density ($mAcm^{-2}$))	1	19.07	0.001
Square	4	24.78	0.000
A^2	1	11.52	0.005
B^2	1	43.20	0.000
C^2	1	3.11	0.103
D^2	1	12.28	0.004
Interaction	6	3.08	0.046
AB	1	5.26	0.041
AC	1	0.84	0.378
AD	1	9.29	0.010
BC	1	1.10	0.315
BD	1	0.12	0.734
CD	1	1.87	0.196
Lack of fit	10	3.84	0.224
Residual Error	12		
R-Sq = 97.21%			
R-Sq(pred) = 84.44%			
R-Sq(adj) = 93.96%			

The other tool can be used for check the assumption of the model is value of probability (p-value). While consider at 95% confidence interval, P-value< 0.050 indicated that the assumption of model are acceptable. The significant factors, large significance of independent variables, are agreed with small P-values. If P-values less than 0.050 are argued that the model term is significant. While, P-values is more than 0.100 that means the model term are not significant. Accordingly, P-value from Table 8 demonstrated that the significant variables including H_2O_2/AMX (MR) (B), current density (D) and H_2O_2/Fe^{2+} (MR) (C). While the significant interaction of pH and H_2O_2/AMX (MR) and pH and current density are significant. Nevertheless, too much of pH, H_2O_2/AMX (MR) and current density are significant due to their small of p-value. Moreover, high value of Lack of fit also confirms this model has small noise model.

The empirical equation can be used to predict response thanks to statistical confirmation. The plotting between predicted values and actual values of COD removal in the earliest stage by electro-Fenton process is displayed in Figure 9. The tendencies come along the part of linear regression.

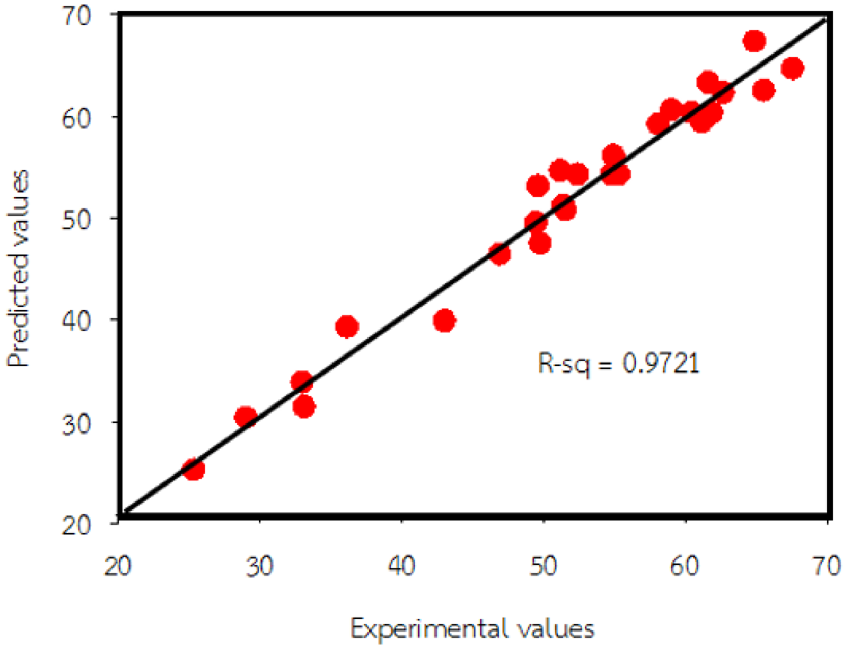


Figure 9 A parity plot of percentage of COD removal in the earliest stage.

To evaluate the quality of fitting equation, a coefficient of determination (R^2) was used. R^2 should in range of 0 to 1. If R^2 close to 1, it means the model well predict. In this results, R^2 was 0.9721 that closed to 1, thus this predicted is satisfied.

4.3.2.2 Main effect investigation for COD removal at initial stage

After checking the fitted model to confirm that was able to predict truthfully. The main effect plot of four variables for COD removal by the initial stage of electro-Fenton is displayed in Figure 10. According to the results from main effects plot showed that pH range in this study has rarely impact on COD removal, it can be summarized that pH used in this study did not have an effect on COD removal significantly.

In this study, the experiment was conducted on the range of pH 2.5-3.5. The result showed the highest COD removal was in pH 2.5, while the others showed a bit different. Thus, the results indicated the percentages of COD removal among different pH values were not differently. Similarly, the report of jiang et al., 2007 reported the appropriate pH for electro-Fenton process is at pH of 2 - 4.

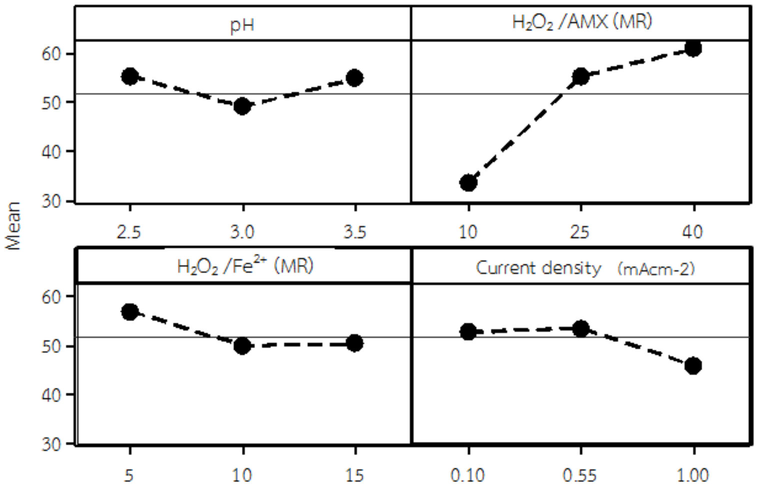


Figure 10 Main effect plots for COD removal at initial stage.

The increase in mole ratio of H_2O_2 and AMX exhibited the increase of COD removal from minimal level to maximum level. The molar ratio of H_2O_2 and AMX was proposed as 40 to achieve a highest COD removal. This is may be the true that H_2O_2 is one of Fenton's reagents as the results of $^{\bullet}OH$ generation. The suitable ratio providing the sufficient level of H_2O_2 concentration led to more produce $^{\bullet}OH$ according to reaction 2.1.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad k_1 = 76\ M^{-1}s^{-1} \qquad \text{Reaction 2.1}$$

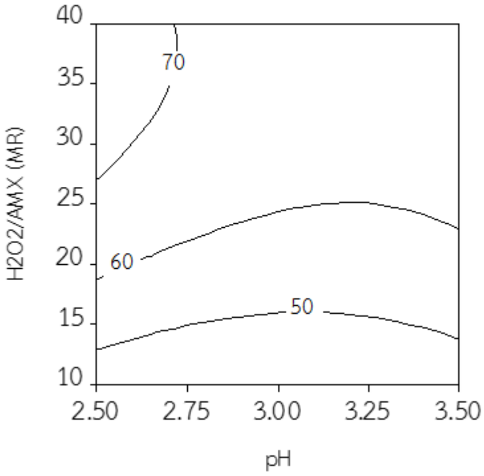
Nonetheless, too much of H_2O_2 may cause scavenging effect because $^{\bullet}OH$ will react with H_2O_2. Effect of H_2O_2/Fe^{2+} (MR) was shown that the low ratio of H_2O_2/Fe^{2+} (MR) showed the good performance on COD removal. The high

COD removal efficiency presented at the proportion of H_2O_2/Fe^{2+} (MR) equaled to 5. The increase H_2O_2/Fe^{2+} (MR) from 5 to 10 inhibited the efficiency of COD removal and trended to steady until 15.

The effect of current density also evaluates. The plot showed COD removal efficiency tended to be decrease with increase current density from 0.1 to 1 $mAcm^{-2}$. Supplying low current density (0.10 - 0.55 $mAcm^{-2}$) provided the good efficiency on COD removal, while high current density (1 $mMcm^{-2}$) did not present the same tendency. The percentage of COD removal dropped as the result of more Fe^{2+} regeneration from Fe^{3+} at high current density. Due to too much of Fe^{2+} regeneration caused scavenging effects.

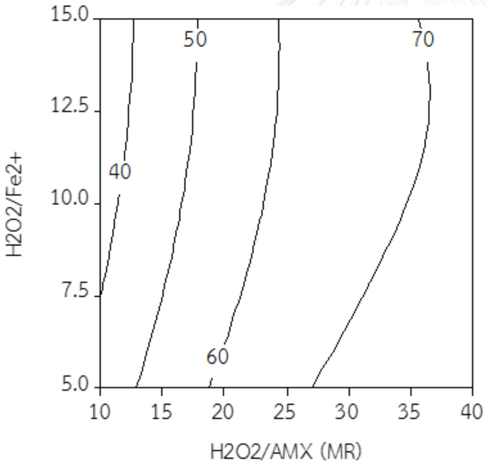
4.3.2.3 Interaction effect investigation for COD removal at initial stage

A contour graph helps to optimize process efficiency and to identification of interaction between variables. Accordingly, to access the response (% COD removal) and variables thus, a plotting of response and two independent factors was created in a single contour plot. In this study, response surface and contour graph shows in Figure 11 - 16.



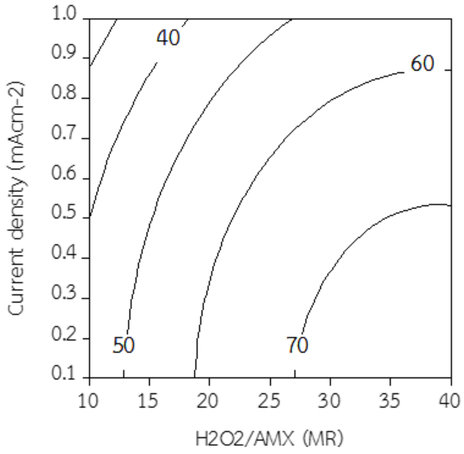
Hold Values	
H_2O_2/Fe^{2+}	5
Current density	0.1

Figure 11 Relationship between pH and H_2O_2/AMX (MR) for COD removal in initial stage of electro-Fenton process.



Hold Values	
pH	2.5
Current density	0.1

Figure 12 Relationship between H_2O_2/Fe^{2+} (MR) and H_2O_2/AMX (MR) for COD removal in initial stage of electro-Fenton process.



Hold Values

H_2O_2/Fe^{2+}	5
pH	2.5

Figure 13 Relationship between current density and H_2O_2/AMX (MR) for COD removal in initial stage of electro-Fenton process.

Hold Values

H_2O_2/AMX	40
Current density	0.1

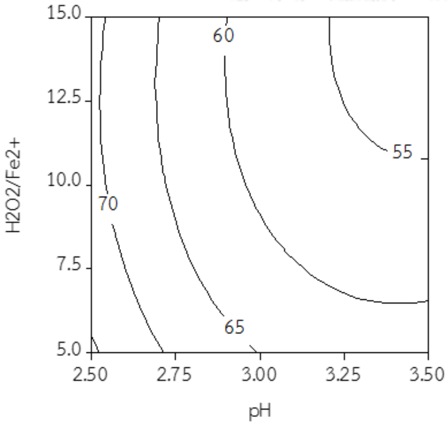
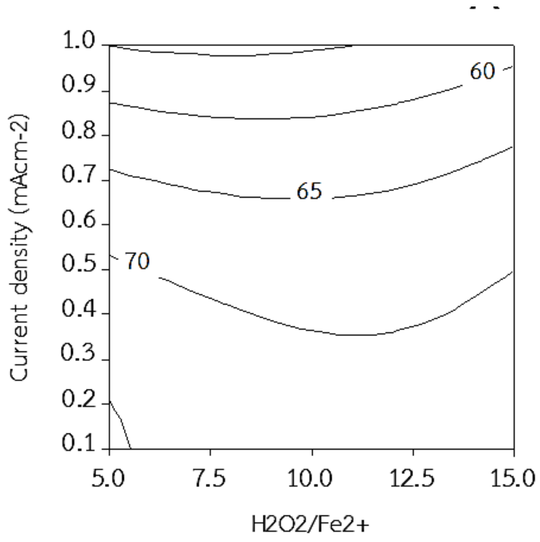
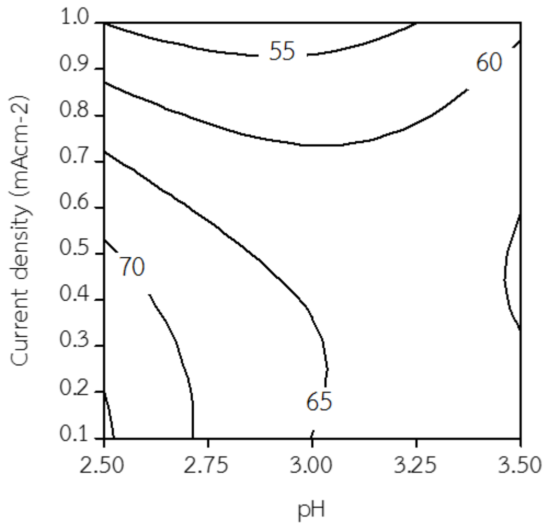


Figure 14 Relationship between H_2O_2/Fe^{2+} (MR) and pH for COD removal in initial stage of electro-Fenton process.



Hold Values	
H_2O_2/AMX	40
pH	2.5

Figure 15 Relationship between current density and H_2O_2/Fe^{2+} (MR) for COD removal in initial stage of electro-Fenton process.



Hold Values	
H_2O_2/AMX	40
H_2O_2/Fe^{2+}	5

Figure 16 Relationship between current density and H_2O_2/Fe^{2+} (MR) for COD removal in initial stage of electro-Fenton process.

Surface plots demonstrated that at pH range in this study slightly promote COD removal. There were slightly differences in COD removal efficiency for using various pH while keeping current density and H_2O_2/Fe^{2+} (MR) were constant as show in Figure 11. High level of H_2O_2 from 27 to 40 still exhibited the good performance on COD removal. Undoubtedly, the pH range in this study is close to optimal pH range for Fenton reaction. However, a great deal of H_2O_2/AMX (MR) was provided, high percentage of COD removal occurred at pH 2.5. This is because the good performance of COD removal always present at low pH, as the result of high reactive ferrous ion dissolution. Consequently, the low amounts of ferrous ion dissolution could react with H_2O_2. Sufficient ferrous ions may react with H_2O_2 to generate free radical toward, thus the COD removal efficiency would have been affected. These ranges were agreed with much previous research suggesting optimal pH should operate in acid condition. Similarly, some research indicated 2.8 was optimal pH for operate electro Fenton (Brillas, Sirés, & Oturan, 2009). Nonetheless, some research reported there was probably that H_2O_2 may affect from scavenging effect of the high concentration of H^+ when operate at low pH. H_2O_2 was influent by raising it stability to form more stable form following Reaction 4.1 (Methatham, Lu, & Ratanatamskul, 2013).

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \qquad \text{Reaction 4.1}$$

The high removal efficiency was observed in range of 26 – 40 molar ratio of H_2O_2/AMX with operated in low pH between 2.5 – 2.75. Similarly, the optimal pH was reported for degrade organic substance in Fenton reaction around 2.8 (Brillas et al., 2009). In addition, high H_2O_2 concentration also showed the better performance than other ratios did. Evidently, Figure 8, 9 and 10 demonstrated high of H_2O_2/AMX ratios were provide also showed high percentage of COD removal efficiency. This fact can describe as H_2O_2 is one of Fenton's reagent that can promote COD removal efficiency $^{\bullet}OH$ generation via Fe^{2+} catalyzed H_2O as shown in main reaction of Fenton process (Reaction 2.1). In the present of ferrous ion, more H_2O_2 led to more $^{\bullet}OH$ generation toward degradation of organic substance.

Furthermore, results showed the increase in COD removal was met at low current density. In this study, COD removal was greater than 75% when low current density was applied. The decreasing of current density from 0.2 – 0.1 $mAcm^{-2}$ appeared to have high efficiency of COD removal at 5.0 molar ratio of H_2O_2/Fe^{2+}. At the same current density, low proportion of H_2O_2/Fe^{2+} (MR) exhibited the good performance than others as shown in Figure 11. The minimal ratio of H_2O_2/Fe^{2+} (MR) implied large amount of ferrous is more affective catalyst than the higher one. This because more ferrous can combine with H_2O_2 effectively in Fenton process. In the initial stage of electro-Fenton process Fe^{2+} mainly come from added $Fe(SO_4)$ from the outside. Therefore, electrical current did not responsibly. More supplied of current density led to lose in COD removal efficiency. In this study, COD removal was greater than 75% when low current density was applied. Even if current density did not play important role on COD removal, too much current density also inhibited COD removal efficiency as shown in Figure. 13, 17 and 19.

The increase in current density trended to reduce COD removal. The increase of current density caused more production of Fe^{2+} on the cathode following Equation 2.18 as described in previous chapter.

$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+} \qquad \text{Reaction 2.18}$$

Too much of Fe^{2+} increases scavenging effect from the excessed ferrous. Ferrous ion competitive reacts with hydroxyl radical following Equation 2.4. Although, much research report that more current density help to improve removal efficiency.

4.3.2.4 Optimization for COD removal in initial stage by electro-Fenton process

Finally, all of variables were consider determining the appropriate value to be maximum condition in initial stage of electro-Fenton process. Figure 18 displays the maximum value that was calculated from RSM.

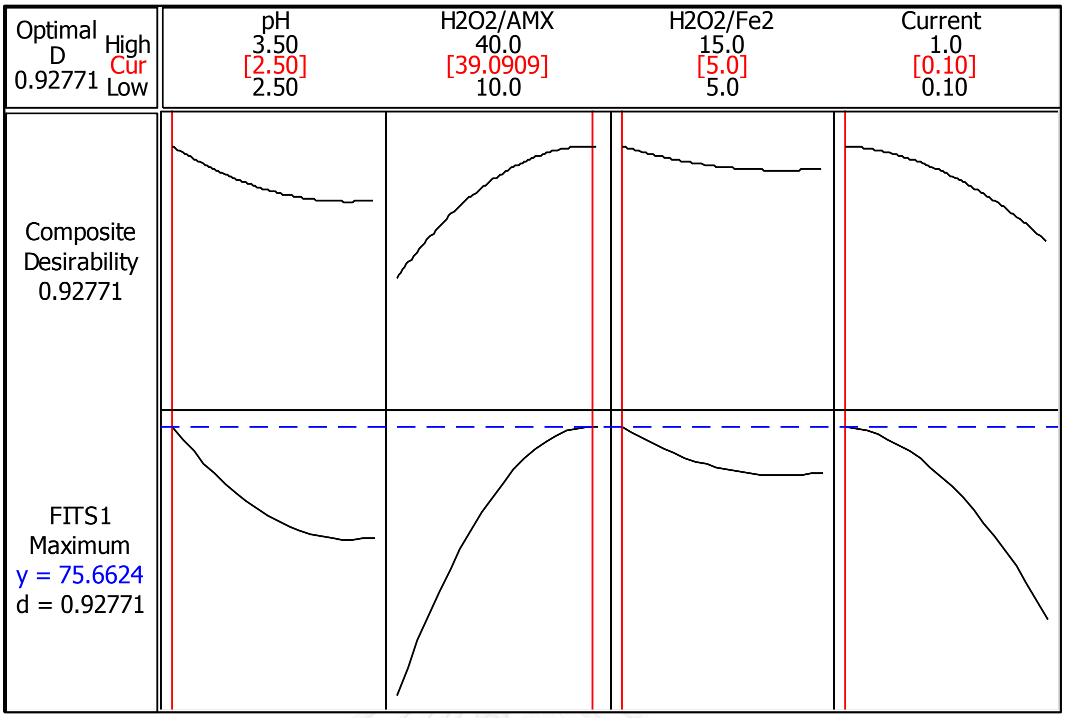


Figure 17 Maximum value in initial stage of electro-Fenton process.

The information form RSM that clearly explained the impacts of several operating parameter was evaluated the quality of each factor. The experimental results indicated all of pH in this study did not affect to process performance, while using pH at 2.5 showed the best results for COD removal in initial stage. This maximum pH was found in Fenton process for treatment of landfill leachate (Hermosilla, Cortijo, & Huang, 2009). This is pH the pH that consider all of influent effects form the others variables and the best performance of effective Fenton's reagent.

The effect of H_2O_2/AMX (MR) concentration for COD removal on electro-Fenton process demonstrated increasing the H_2O_2/AMX ratio from 10 to 40 enhance COD removal efficiency. The maximum concentration ratio of H_2O_2/AMX (MR) was pointed as the maximum ratio in initial stage of electro-Fenton. In this study, the concentration of AMX was fixed as 0.3 mM while suitable H_2O_2 concentration was 12 that is a deal of H_2O_2 as 40 molar ratio. This ratio was agreed with previous that demonstrated 40 was the effective ratio as high COD removal would obtain (Methatham et al., 2013). That mention about the excess ratio that was ineffective to process performance. The suitable ratio of H_2O_2 and Fe^{2+} catalyst resulted to continuously react of Fenton's reagent. Owing to the maximum H_2O_2 concentration was used, a mount of ferrous iron was expected at 5 molar ratio H_2O_2/Fe^{2+}. This appropriated ratio was changed to amount of Fe^{2+} equaling 2.4 mM. Finally, current density was evaluated to achieve high removal efficiency. The results indicated that low current density supplied supported high COD removal. A deal of 0.1 $mAcm^{-2}$ current density was selected to operate during initial stage of electro-Fenton process. Moreover, the most effective COD removal was found as low current density supplied Because of energy saving reason, 0.1 $mAcm^{-2}$ was chosen to be a suitable current density in this section.

Although, the effect of operating parameter of experimental result was described by using main and interaction plot, there was some detailed in experimental designed that can help to explain the result in deep.

Even though the same ration of H_2O_2/Fe^{2+} was used in experiment, using different molar of H_2O_2 also directly affected to COD removal efficiency as shown in Figure 18 - 20.

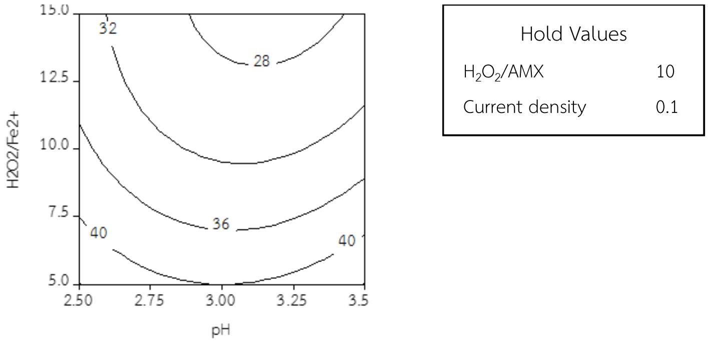


Figure 18 Interaction plot of pH versus H_2O_2/Fe^{2+} holding 10 H_2O_2/AMX (MR)

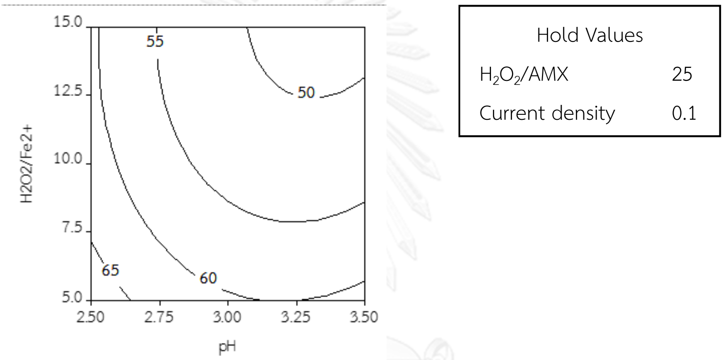


Figure 19 Interaction plot of pH versus H_2O_2/Fe^{2+} holding 25 H_2O_2/AMX (MR).

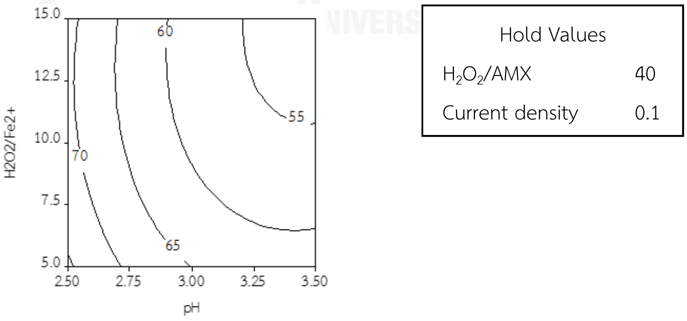


Figure 20 Interaction plot of pH versus H_2O_2/Fe^{2+} holding 40 H_2O_2/AMX (MR).

Using high molar ratio of H_2O_2/AMX means large deal of H_2O_2 was supplied, while using low molar ratio of H_2O_2/AMX implied that low amount of H_2O_2 was supplied. More H_2O_2 concentration directly affect to Fe^{2+} ratio. According to the different molar ratio of H_2O_2/AMX, amount of Fe^{2+} in each experiment was not same. The various amount of Fenton's reagent was shown in Table 5.

For example, using the same ratio of 10 H_2O_2/Fe^{2+} (MR) but different of H_2O_2/AMX was used referring to amount of H_2O_2 12 and 3 mM. While amount of Fe^{2+} was 1.2 and 0.3 for RUN 11 and RUN 12, respectively. The higher COD removal presented in the experiment that used high amount of H_2O_2. 61.2% and 33.16% of COD removal was presented as show in picture 15. This result indicated using high ratio of H_2O_2/AMX was better.

From the summary of main effect reported using low ratio of H_2O_2/Fe^{2+} (high amount of Fe^{2+}) was exhibited higher performance. Nonetheless, the ratio of H_2O_2 was influent. The result form RUN 22 and RUN 25 can describe this assumption. In these experimental results (RUN 22 and 25), the same ratio of H_2O_2/Fe^{2+} was used while different ratio of H_2O_2/AMX. Even though, same ratio of H_2O_2/Fe^{2+} was used in these experiment, different in amount of Fe^{2+} also applied. This because different H_2O_2/AMX ratio was amount of Fe^{2+} controller. High H_2O_2/AMX (MR) led to high $Fe^{2+.}$ It was no wonder that why there was different in COD removal result when applied the same ratio of H_2O_2/Fe^{2+}.

In addition, the COD removal performance with using different amount of Fenton’s reagent was shown in Figure 18-20. The high COD removal always presented at high H_2O_2 was applied. Moreover, this high result also present at supplied H_2O_2 about 6 mM and supplied high amount Fe^{2+}. These result can be mention that the high COD removal was presented not only using high of H_2O_2 but present when using high Fe^{2+} amount also. This can be describe that the appropriate ratio not only deepened on using H_2O_2 but amount of Fe^{2+} should be consider. Using 5-8 mM of H_2O_2 with amount of Fe^{2+} higher than 2 mM showed high COD removal reach to 70 %.

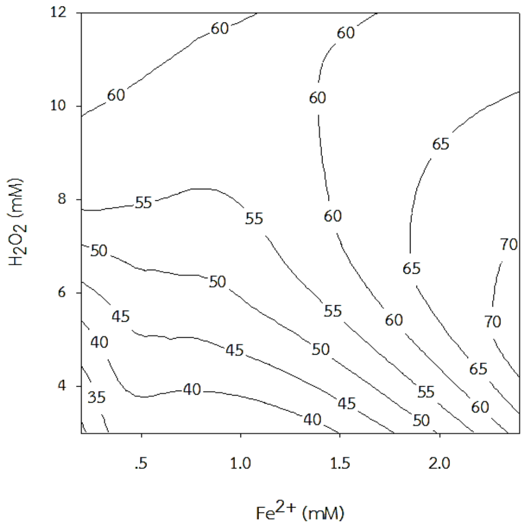


Figure 21 The COD removal performance with using different amount of Fenton’s reagent.

4.3.3 Investigation of maximum condition for COD removals in 30 minute.

4.3.3.1 The effects of operating parameters for COD removal by 30 minute of electro-Fenton process

In this section the overall COD removal was evaluated using RSM as same as initial stage did. In order to create empirical equation that correlated with relationship between independent factors and response. The results of overall electro-Fenton reaction were shown in Table 6. The coefficient data for overall process by using electro-Fenton process as shown in Table 9.

First of all, the experimental results in second group were evaluated by using statistic test as well. The way to check model following the principle of statistical analysis are described in previous section. The coefficient data for overall process by using electro-Fenton process as shown in Table 9.

Table 9 Coefficient data for COD removal

Source	Coefficient	P-value
Constant	57.094	0.000
A (pH)	-1.829	0.090
B (H_2O_2/AMX (MR))	8.854	0.000
C (H_2O_2/$Fe^{2+(}$MR))	1.525	0.151
D (Current density ($mAcm^{-2}$))	-3.333	0.006
A^2	4.115	0.017
B^2	-6.862	0.001
C^2	5.197	0.004
D^2	-0.618	0.686
AB	-3.167	0.091
AC	-0.717	0.684
AD	3.407	0.071
BC	1.292	0.467
BD	-0.376	0.831
CD	-0.708	0.688

Consequently, the equation, an empirical relationship between the response and independent variables, for COD removal by overall electro-Fenton process are displayed as Equation 4.3.

$$COD\ removal_{30\,m} = 57.094 - 1.829\mathrm{A} + 8.854\mathrm{B} + 1.525\mathrm{C} - 3.333\mathrm{D} + 4.115A^2 - 6.862B^2 + 5.197C^2 - 0.618D^2 - 3.167AB - 0.717AC + 3.407\mathrm{AD} + 1.292\mathrm{BC} - 0.376\mathrm{BD} - 0.708\mathrm{CD} \quad \text{Equation 4.3}$$

Where A is pH

B is molar ratio of H_2O_2/AMX

C is molar ratio of H_2O_2/Fe^{2+}

D is Current density ($mAcm^{-2}$)

The mathematics equation displays the relationship between variables in term of coefficient number. If consider at 95% confidence, p-value should less than 0.05. Many term of variables had p-value lower than 0.05 including H_2O_2/AMX (MR) and current density. Moreover the low p-value also met in square term (i.e. pH*pH, H_2O_2/AMX (MR)*H_2O_2/AMX (MR) and H_2O_2/Fe^{2+} (MR)*H_2O_2/Fe^{2+} (MR)). Therefore, these were significant factors affecting %Y response. Furthermore, some of the insignificant factors that slightly affect to COD removal efficiency may be eliminated for improve predicable capacity and model accuracy. However, some of insignificant factors should be existed because their provided large number of coefficient values such as pH*H_2O_2/AMX (MR) and pH*Current density ($mAcm^{-2}$). The coefficient data eliminated insignificant variables are shown in Table 10.

Table 10 Coefficient data for COD removal after modified

Source	Coefficient	P-value
Constant	56.545	0.000
A (pH)	-1.829	0.051
B (H_2O_2/AMX (MR))	8.854	0.000
C (H_2O_2/$Fe^{2+(}$MR))	1.525	0.099
D (Current density ($mAcm^{-2}$))	-3.333	0.001
A^2	4.321	0.003
B^2	-6.656	0.000
C^2	5.403	0.000
AB	-3.167	0.052
AD	3.407	0.038

The modified equation for COD removal by 30 minute of electro-Fenton process express as:

$$COD\ removal_{Over\ all} = 56.545 - 1.829A + 8.854B + 1.525C - 3.333D + 4.321A^2 - 6.656B^2 + 5.403C^2 - 3.167AB + 3.407AD \qquad \text{Equation 4.4}$$

Where A is pH

B is molar ratio of H_2O_2/AMX

C is molar ratio of H_2O_2/Fe^{2+}

D is Current density ($mAcm^{-2}$)

After that, this equation was used for evaluate COD removal in 30 minute by electro-Fenton process.

Since empirical equation had been established, it is necessary to check the fitted model for make sure that the predicted values are accepted. A normal probability plot and histogram, instrument to check the assumption, are displayed in Figure 23 and 23.

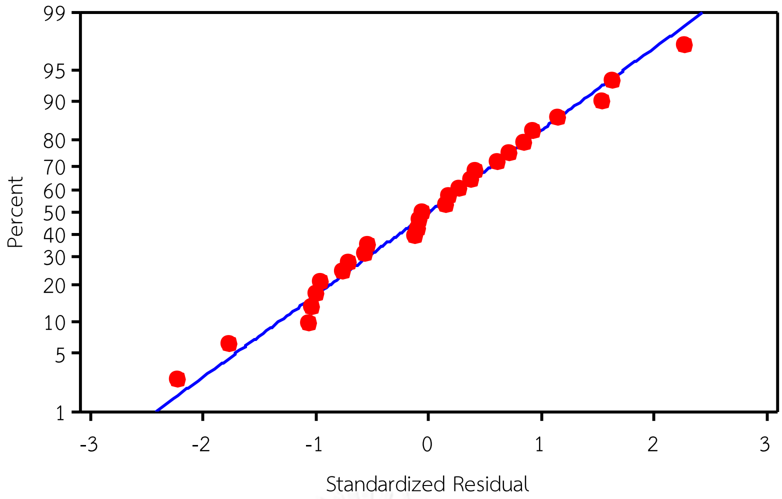


Figure 22 A normal probability plot.

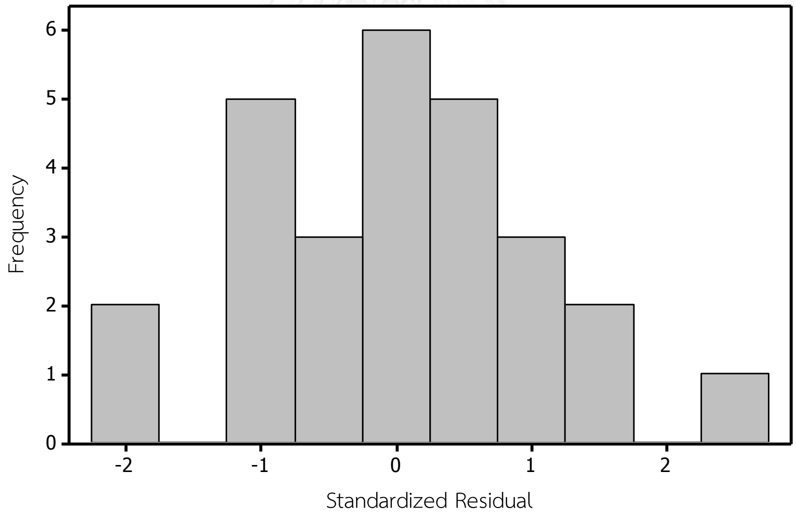


Figure 23 Histogram of residual error for COD removal in 30 minute of electro-Fenton.

After checking assumption to ensure that our experiment values would be in good agreement with predicted value, ANOVA were applied also. Critical value refers to the F-value (F-critical) that consider at 95% confidence with degree of freedom in linear and residual error. Fischer's F test (F-value) of experimental datum higher than critical value ($F_{0.95}$, 9, 17= 2.4943) (Dinov, 2002) as shown in Table 11.

Table 11 ANOVA test for COD removal for 30 minute

Source	Degree of freedom	F-value	P-value
Regression	9	23.73	0.000
Linear	4	31.22	0.000
A (pH)	1	4.39	0.051
B (H_2O_2/AMX (MR))	1	102.87	0.000
C (H_2O_2/$Fe^{2+(}$MR))	1	3.05	0.099
D (Current density (mAcm^{-2}))	1	14.58	0.001
Square	3	26.42	0.000
A^2	1	12.25	0.003
B^2	1	29.07	0.000
C^2	1	19.15	0.000
Interaction	2	4.73	0.023
AB	1	4.39	0.052
AD	1	5.08	0.038
Residual Error	17	155.44	9.144
Lack of fit	15	3.82	0.227
Pure Error	2		
R-Sq = 92.63%			
R-Sq(pred) = 77.81%			
R-Sq(adj) = 88.73%			

The other tool can be used for check the assumption of the model is value of probability (p-value). While consider at 95% confidence interval, P-value< 0.05 indicated that the assumption of model are acceptable. The significant factors, large significance of independent variables, are agreed with small p-values. If p-values less than 0.05 are argued that the model term is significant. While, p-values is more than 0.05 that means the model term are not significant. Accordingly, p-value from Table 11 demonstrated that the significant variables including H_2O_2/AMX (MR) (B), current density (D) and H_2O_2/Fe^{2+} (MR) (C). While the significant interaction of pH and H_2O_2/AMX (MR) and pH and current density are significant. Nevertheless, too much of pH, H_2O_2/AMX (MR) and current density are significant due to their small of p-value. Moreover, high value of Lack of fit also confirms this model has small noise model.

The empirical equation can be used to predict response thanks to statistical confirmation. The plotting between predicted values and actual values of COD removal in 30 minute by electro-Fenton process is displayed in Figure 24.

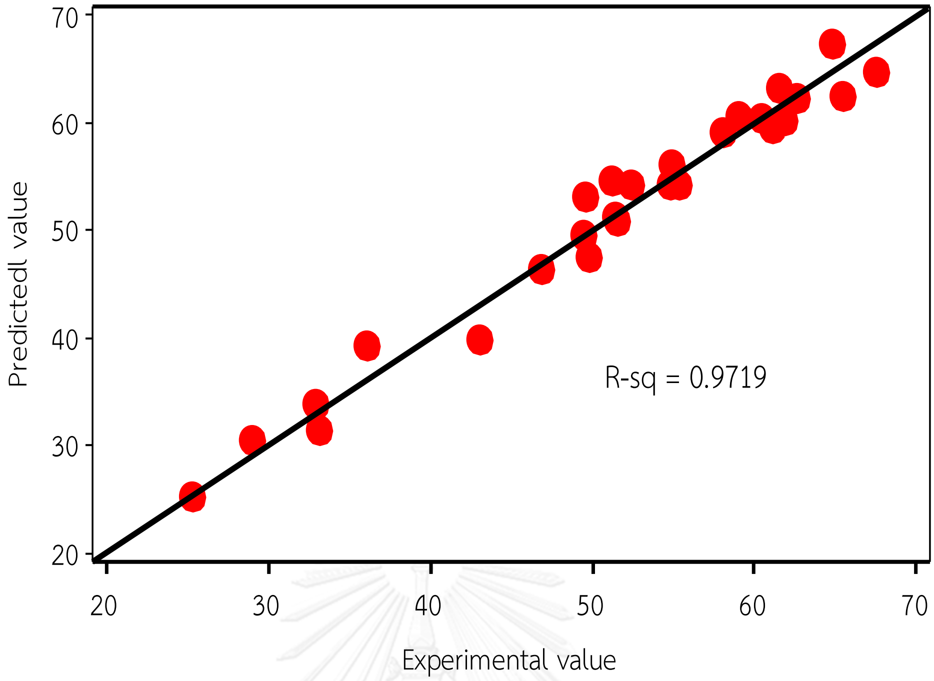


Figure 24 Predicted value versus experimental value.

The tendencies come along the part of linear regression. To evaluate the quality of fitting equation, a coefficient of determination (R^2) was used. R^2 should in range of 0 to 1. In this study, R^2 closed to 1, it means the model well predict.

4.3.3.2 Main effect investigation for COD removal at 30 minute

After checking the fitted model to confirm that was able to predict truthfully. The main effect plot of COD removal in 30 minute using electro-Fenton is displayed in Figure 25. There are four independent variable include pH, H_2O_2/AMX (MR), H_2O_2/Fe^2(MR) and current density.

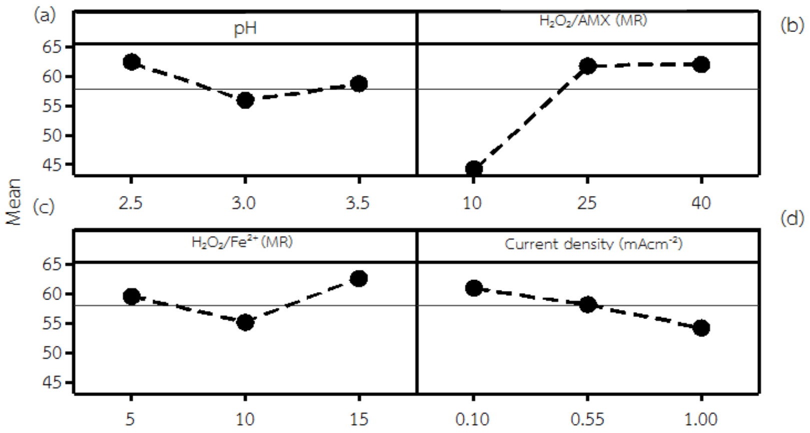


Figure 25 Main effects plot for COD removal in 30 minute using electro-Fenton process.

According to the results from main effects plot showed in Figure 25. The best result (61%) of response presented at pH 2.5, while COD removal little dropped at pH 3 (58%) and slightly increase at pH 3.5 (59%). A bit difference on COD removal obtained from the experimental results 5 and 18 are displayed in Figure 26.

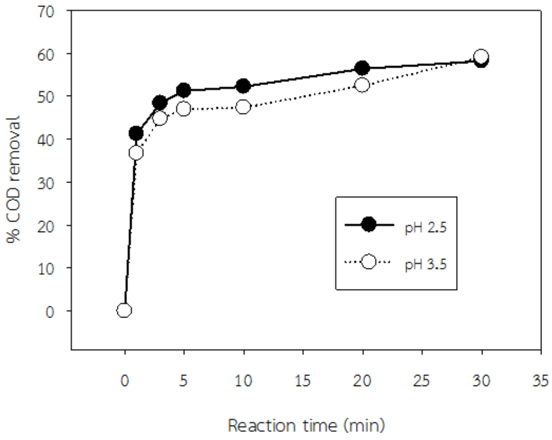


Figure 26 Influence of pH on COD removal as H_2O_2/AMX=25 (MR), H_2O_2/Fe^{2+} = 10 and current density = 0.1 $mAcm^{-2}$ by electro-Fenton process. RUN 5:pH 2.5 (•), RUN 18: pH 3.5(O)

Even if, various pH were used by holding the same condition for the others, the COD removal in RUN 5 that used pH 2.5 expressed the slightly higher than RUN 18 that used pH 3.5 did. However there were slightly different in COD removal efficiency in the response that using various pH. It can be summarized that pH range in this study did not have an effect on COD removal significantly. The tendency of electro-Fenton in initial stage and 30 min operating time were alike. It is possibly that pH range of 2-4 is the acid range pH that is recommended to find maximum amount of $^{\bullet}OH$ to oxidize organic compounds (Kavitha & Palanivelu, 2004).

Moreover, the molar ration of H_2O_2/AMX showed significant effect on COD removal. Figure 27 displayed the increase of H_2O_2/AMX ratio promoted COD removal efficiency. The Molar ratio in range of 10 – 25 dramatically affect to COD removal, more than 15 % of COD removal was obtained. After that the increase ratio slightly increased COD removal.

The clearly difference on COD removal using various H_2O_2/AMX are shown in Figure 27. The tendency for COD removal of higher H_2O_2/AMX ratio (40 MR) appeared that COD removal dramatically increased up to 60% in 5 minute and then kept continuously constant, while the lower presented the dramatically increased in 1 minute.

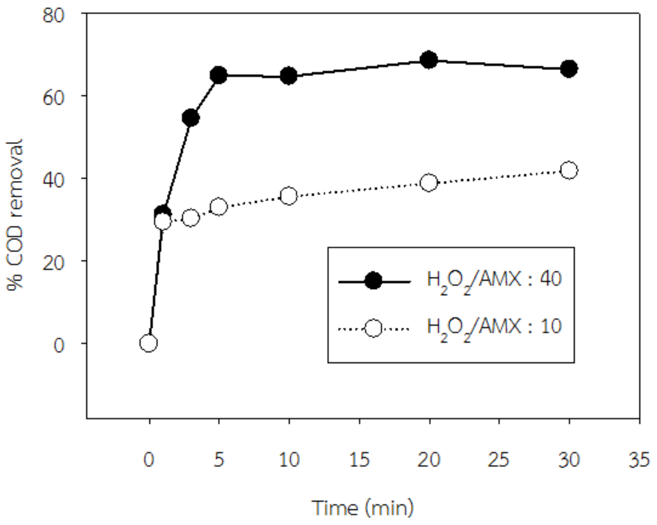


Figure 27 Influence of H2O2/AMX (MR) on COD removal as pH =2.5, H_2O_2/Fe^{2+} = 10 and current density = 0.55 $mAcm^{-2}$ by electro-Fenton process. RUN 4: H2O2/AMX (MR) 40 (●), RUN 21: H2O2/AMX (MR) 10 (O).

The molar ratio of H_2O_2/Fe^{2+} was investigated on process performance also. Evidently, high molar ratio of H_2O_2/Fe^{2+} promoted COD removal efficiency as illustrated in Figure 28 . More than 60 percent of COD removal was obtained by using the highest ratio of H_2O_2/Fe^{2+} (MR).

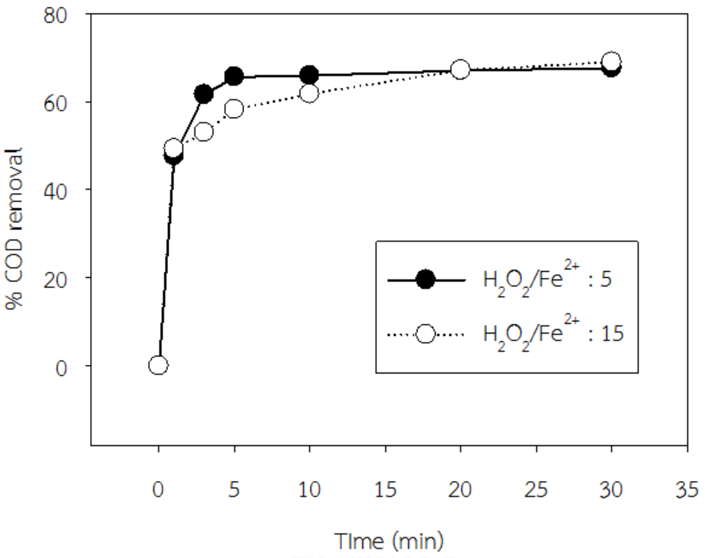


Figure 28 Influence of H_2O_2/Fe^{2+} MR) on COD removal as pH = 3, H_2O_2/AMX = 10 and current density = 0.55 mAcm^{-2}by electro-Fenton process. RUN 7: H_2O_2/Fe^{2+} 5 (●), RUN 20: H_2O_2/Fe^{2+} 15 (O).

The experimental results for using different H_2O_2/Fe^{2+}(MR) showed in Figure 22. RUN 7 that used 5 molar of H_2O_2/Fe^{2+}, much Fe^{2+} are supplied, exhibited the good performance during 5 minute operating time and then go steady. Differently, RUN 20 that used 15 molar of H_2O_2/Fe^{2+}, less amount of Fe^{2+}, showed dramatically extremely increased in 1 minute and then the percentage of COD removal gradually increased along the time. Especially, the COD removal of using 15 molar of H_2O_2/Fe^{2+} in 30 minute was higher than that in 5 molar of H_2O_2/Fe^{2+} and trended to continuously increase. This tendency was appeared as a result of amount of Fe^{2+} regeneration.

Finally, current density could impact to COD removal. The lowest of current density (0.1mA/cm^{-2}) exhibited the high COD removal. Then, more supplied current density continuously decreased COD removal efficiency that observed from experimental results as 1 mAcm^{-2} current density (Run 9) and 0.1 mAcm^{-2} current density (Run 13). Figure 29 displayed the different COD removal ability from using different current density. The tendency of COD removal using different current density was alike but in case of supplied lower current density expressed the better performance than the higher one did. In operating time current density provided the steady trend in both runs but met different efficiencies.

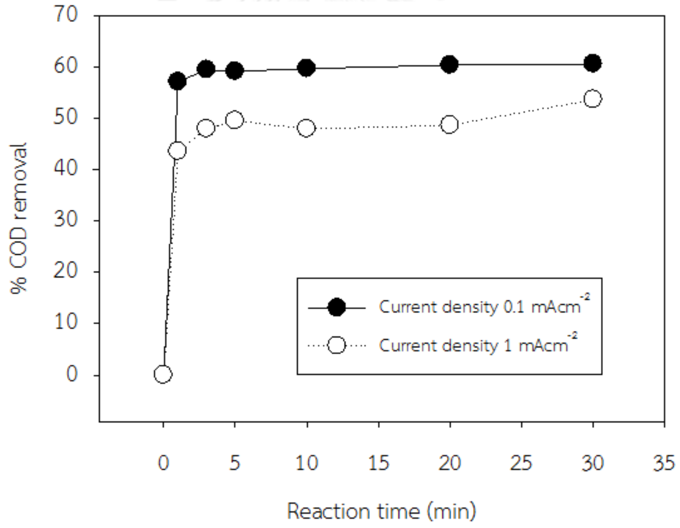


Figure 29 Influence of current density on COD removal as pH = 3, H_2O_2/AMX = 40 and H_2O_2/Fe^{2+} = 10by electro-Fenton process. RUN 13: current density 0.1 mAcm^{-2} (●), RUN 9: current density 1 mAcm^{-2} (O).

4.3.3.3 Interaction effect investigation for COD removal at 30 minute

Moreover, RSM can help to access the correlation of each factor. A contour graph helps to access process efficiency and contribute to identification of interaction between variables. Thus, a plotting of response and two variables was illustrated in a single contour plot. The relationship Surface plots between variables are shown in Figure 30-35.

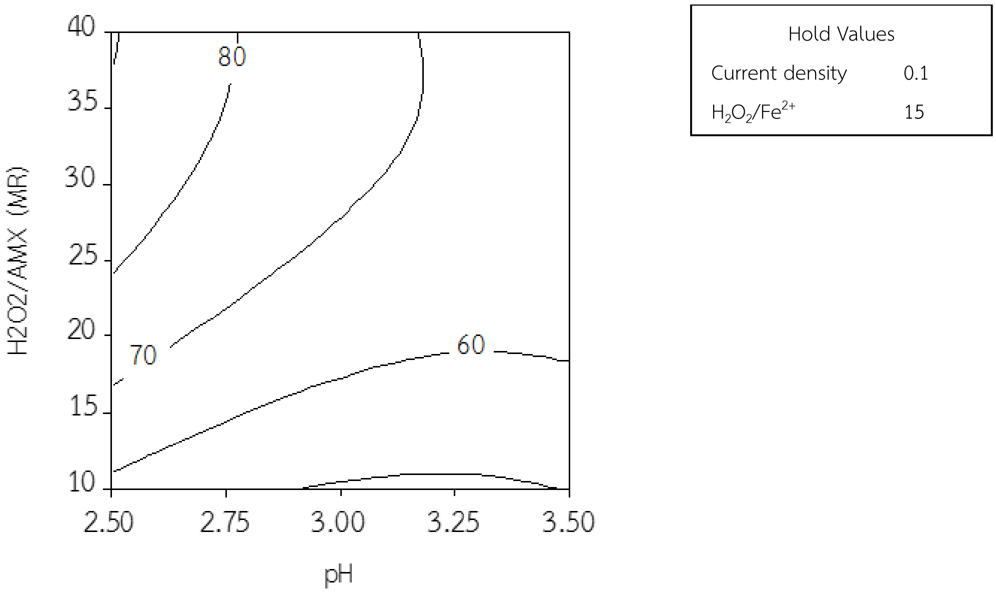


Figure 30 Relationship between H_2O_2/AMX (MR) and pH for COD removal in 30 minute using electro-Fenton process.

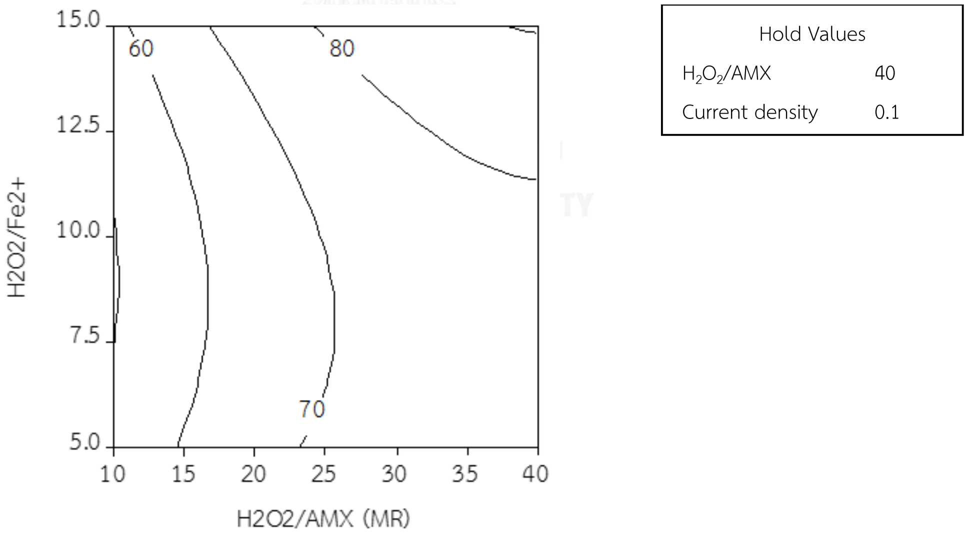


Figure 31 Relationship between H_2O_2/Fe^{2+} (MR) and H_2O_2//AMX (MR) for COD removal in 30 minute using electro-Fenton process.

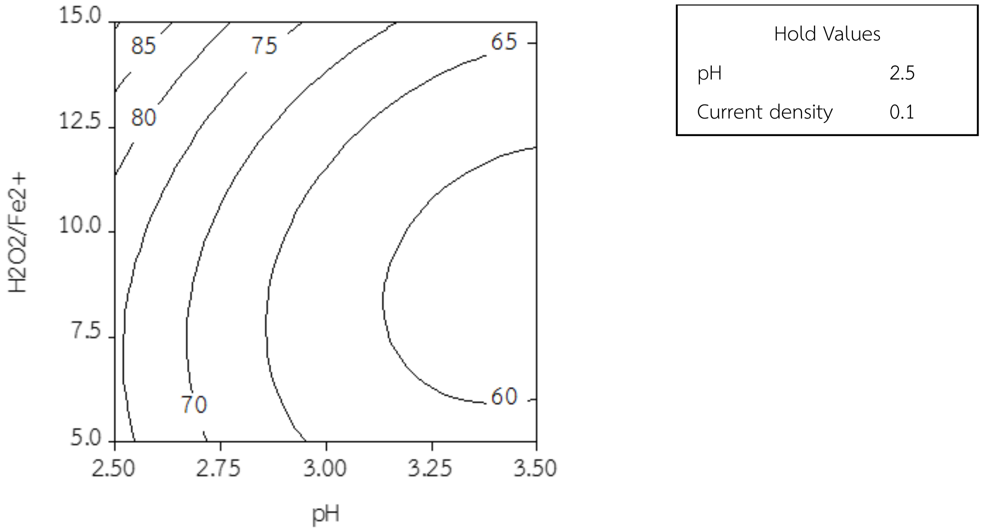


Figure 32 Relationship between H_2O_2/Fe^{2+} (MR) and pH for COD removal in 30 minute using electro-Fenton process.

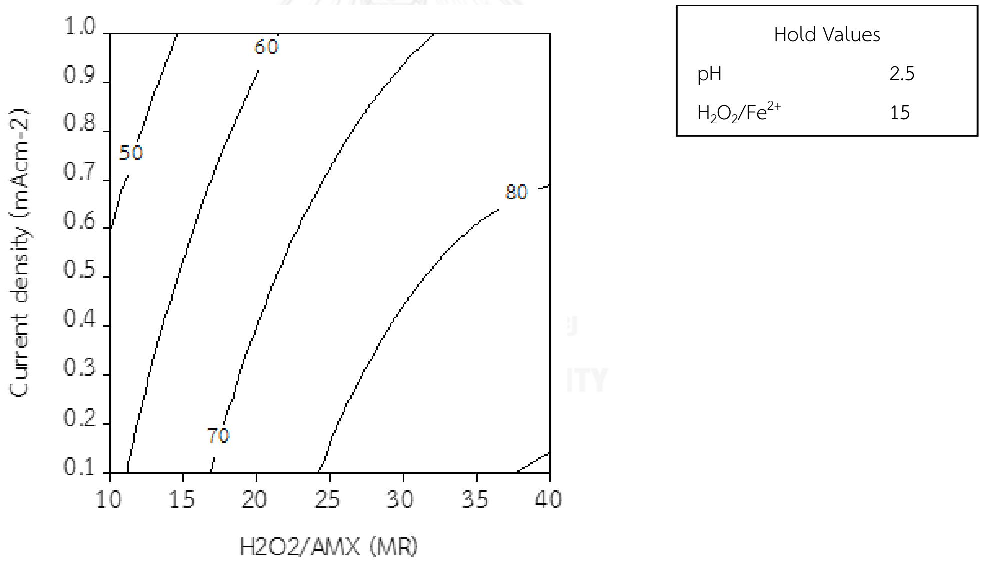


Figure 33 Relationship between current density and H_2O_2/AMX (MR) for COD removal in 30 minute using electro-Fenton process.

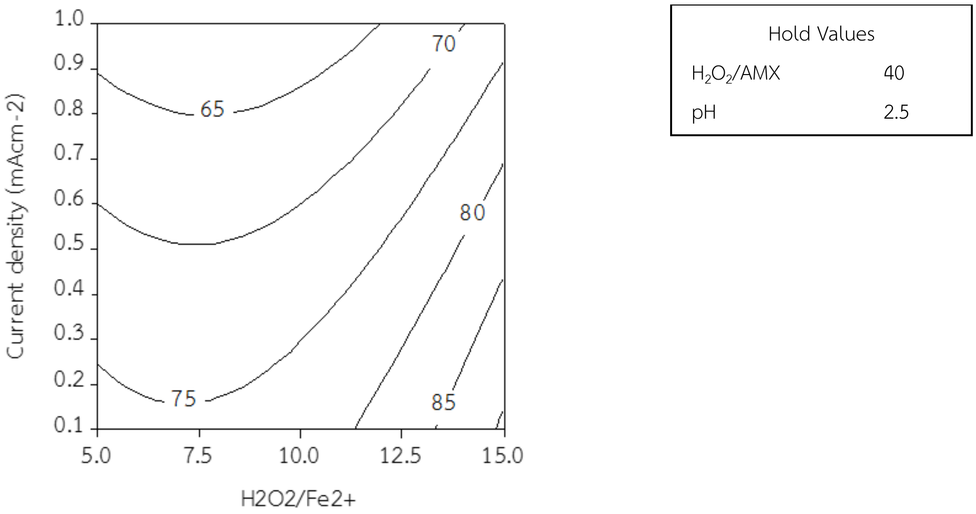


Figure 34 Relationship between current density and H_2O_2/Fe2+ (MR) for COD removal in 30 minute using electro-Fenton process.

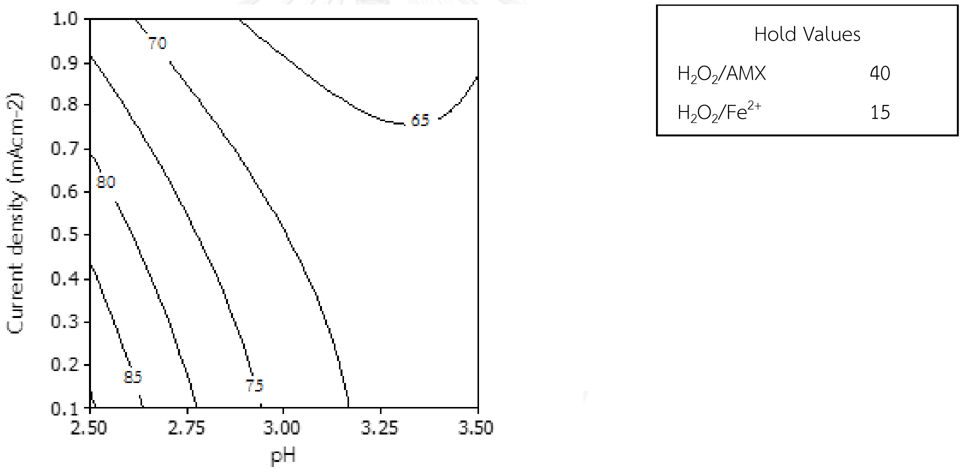


Figure 35 Relationship between current density and pH for COD removal in 30 minute using electro-Fenton process.

In electro-Fenton process, pH is one of important factor in controlling of $^\bullet$OH formation and dissolution of Fe^{2+} in solution. The pH in range of 2.5 – 3.5 was investigated in this study. As shown in Figure 30, more than 75% of COD removal was obtained below pH 3 holding the highest ratio of H_2O_2/AMX.

While using low ratio of H_2O_2/AMX at pH above 3 slight affected to COD removal efficiency in 30 minute of electro-Fenton process. Evidently, using high ratio of H_2O_2/AMX promoted high COD removal efficiency. The supplied high H_2O_2/AMX ratio implied that a lot of H_2O_2 was added than the lower ratio. More H_2O_2 concentration directly involved with $^{\bullet}$OH formation following the main reaction of Fenton's reaction 2.1.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad \text{Reaction 2.1}$$

Moreover, previous work reported that when pH increase the oxidation potential of $^{\bullet}$OH quite low than it did at normal pH (Höfl, Sigl, Specht, Wurdack, & Wabner, 1997). The other results for COD removal efficiency also decrease because of H_2O_2 decomposition. H_2O_2 is not stable and rapidly convert to molecular O_2 at high pH as Reaction 4.2 (Ramirez et al., 2007) and was destroyed by $^{\bullet}$OH scavenging effect as Reaction 4.3.

$$Reductant + H_2O_2 \rightarrow O_2 + products \qquad \text{Reaction 4.2}$$

$$H_2O_2 + \bullet OH \rightarrow H_2O + \bullet OH_2 \qquad \text{Reaction 4.3}$$

Moreover, Fe^{3+} that produce from Reaction 2.1 can be regenerated with electro-Fenton process at cathode as shown in Reaction 2.18 that previously mentioned (Ayodele, Lim, & Hameed, 2012).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} + OH^- \qquad \text{Reaction 2.18}$$

In addition, the result form RSM provided mathematic equation as mentioned in Table 10 The interaction between pH and H_2O_2/AMX (MR) showed negative effect on COD removal efficiency.

Anyway, when consider as the high ratio of H_2O_2/AMX, pH directly affected to form of iron that can be seen in Figure.30. The present of $Fe(OH)_3$ at High pH (pH>3) led to present the reaction of H_2O_2 with $Fe(OH)_3$ or Fe^{3+}catalyst following reaction 2.2 the mention above and reaction 4.2.3.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad \text{Reaction 2.2}$$

$$Fe(OH)_3 + H_2O_2 \rightarrow O_2 + H_2O \quad \text{Reaction 4.4}$$

Dissolved iron in form of $Fe(OH)_3$ and Fe^{3+} catalyst, which is the low effective catalyst according to low reaction rate. Low rate of both Fe^{3+} and $Fe(OH)_3$ react with H_2O_2 is 0.02 and 0.001 -0.01 $M^{-1}S^{-1}$, respectively. Low rate of these activities (0.001-0.01 $M^{-1}s^{-1}$) caused a low activity or no reaction between them and H_2O_2 (Neyen & Baeyens, 2003).

Beside electro-Fenton principle, appropriate ratio of Fenton's reagent is important as well. Although Fe^{2+} is well dissolved in low pH (2.5 - 2.8), too much of Fe^{2+} dissolved in solution did not express the highest efficiency. Observably, 15 molar ratio of H_2O_2/Fe^{2+} exhibited the highest COD removal efficiency. This because the influence of Fe^{2+} regeneration in electro-Fenton process.

The other ways to observe suitable ratio of H_2O_2/Fe^{2+} is displayed in Figure.31. As mention about the appropriate ratio, 15 MR of H_2O_2/Fe^{2+} provided the highest COD removal efficiency than 5 MR of H_2O_2/Fe^{2+} did. The changing in both side of 10 MR H_2O_2/Fe^{2+} enhanced COD removal. This increase may cause by many reasons. First reason, a lot of Fe^{2+} catalyst was used (5 MR H_2O_2/Fe^{2+}) led to more generation of $^{\bullet}OH$. Despite, increase in Fe^{2+} amount enhance COD removal, too much of Fe^{2+} may reduce efficiency. The second reason, although amount of Fe^{2+} is need to form $^{\bullet}OH$ in main reaction of Fenton, suitable ratio of H_2O_2/Fe^{2+} is need as well. As seen in Figure.31, using the highest molar ratio of H_2O_2/Fe^{2+} (15 MR), the lowest amount of Fe^{2+}, get more than 80% of COD removal.

The suitable ratio of amount of Fe^{2+} in solution may cause Fenton reaction effectively. In the present of excess Fe^{2+}, Fe^{2+} will act as scavengers as mention in reaction 2.3.

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-} \qquad \text{Reaction 2.3}$$

Not only suitable ratio of Fe^{2+} was necessary but H_2O_2/AMX also Suitable H_2O_2/AMX and H_2O_2/Fe^{2+} ratio promoted the best result for COD removal during 30 minute of operating time. The relationship between H_2O_2/AMX and H_2O_2/Fe^{2+} as displayed in Figure 32 that informed about critical ratio that affect to COD removal performance. The 40 mM of H_2O_2/AMX exhibited more than 80% COD removal than COD removal reduce along with decreased H_2O_2/AMX ratio. At H_2O_2/Fe^{2+} ratio equal to 10, the changing of both sides of H_2O_2/Fe^{2+} increased COD removal efficiency. Therefore, the molar ratio of H_2O_2/Fe^{2+} equal to 10 expressed the bad performance. The fact that these changing were impacted removal efficiency because of ferrous amount.

At high pH (pH>3), ferrous became iron hydroxide regarding their precipitation form. The converting of Fe^{2+} to iron hydroxide led to reduce amount of $^{\bullet}OH$ formation toward decrease COD removal. For these reason, the catalyst amount play important role as well. In the sufficient of H_2O_2, if inadequate Fe^{2+} caused low $^{\bullet}OH$ generation and the continuous reaction with organic substance would not satisfied. The suitable of Fe^{2+} concentration perform best result for COD removal and can be recovered at the end of reaction. In addition, if too much of Fe^{2+} and high current led to make yellow iron sludge attached electrodes and electrodes was destroyed because of high current density as displayed in Figure 33.

From this result, electrical current density was determined. Increased current density from 0.1 $mAcm^{-2}$ to 1 $mAcm^{-2}$ presented to have negative effect on COD removal as displayed in Figure.32, 34 and 35. Previous work reported increase current density trend to improve process efficiency (Methatham et al., 2013), However; excess current density are able to reduce their efficiency also.

This because if the high current density was supplied, O_2 would be discharged at anode Reaction 4.5 (Thirugnanasambandham et al.).

$$2H_2O \rightarrow 4H^+ + 2O_2 + 4e^- \qquad \text{Reaction 4.5}$$

Although, the increase in current density inhibited COD removal of electro-Fenton performance, the increase in both pH and current showed positive efficiency for COD removal. This fact is when supplied more current density into acidic solution, the evolution of hydrogen gas can be present following reaction 4.6 (Plakas, Karabelas, Sklari, & Zaspalis, 2013).

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{Reaction 4.6}$$

Therefore, applied high current density with more acid pH led to reducing of Fe^{2+} regeneration (Reaction 2.18), while this phenomenon not preferred presented in higher pH This phenomenon can be described why the increase in both pH and current density also promoted system capability.

Nonetheless, using high level of current density is not good because of H_2O_2 stability. The research of plakas suggest the high degree of electrical current (voltage larger than 1.3 V) destroyed H_2O_2 concentration with reaching time (Plakas et al., 2013).

In addition, the high voltage that cause by supplied current density led to form peroxodisulfate as in Reaction 4.7

$$2HSO_4^- \rightarrow S_2O_8^{2-} + H^+ + 2e^- \qquad \text{Reaction 4.7}$$

Then, the further reaction of peroxodisulfate with Fe^{2+} can form $Fe3^{+}$ with k= 23 $M^{-1}S^{-1}$(Sirés et al., 2007) as displayed in Reaction 4.8.

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$ Reaction 4.8

The generation of Fe^{3+} reduce ability of •OH generation and further decrease removal efficiency.

4.3.3.4 Optimization for COD removal in 30 minute by electro-Fenton process

Finally, all of variables were consider determining the appropriate value to be maximum condition in 30 minute of electro-Fenton process. Figure 29 displays the maximum value that was calculated from RSM. Finally, all of variables were consider determining the appropriate value to be maximum condition in 30 minute of electro-Fenton process. Figure 36 displays the maximum value that was calculated from predicted Equation 4.4.

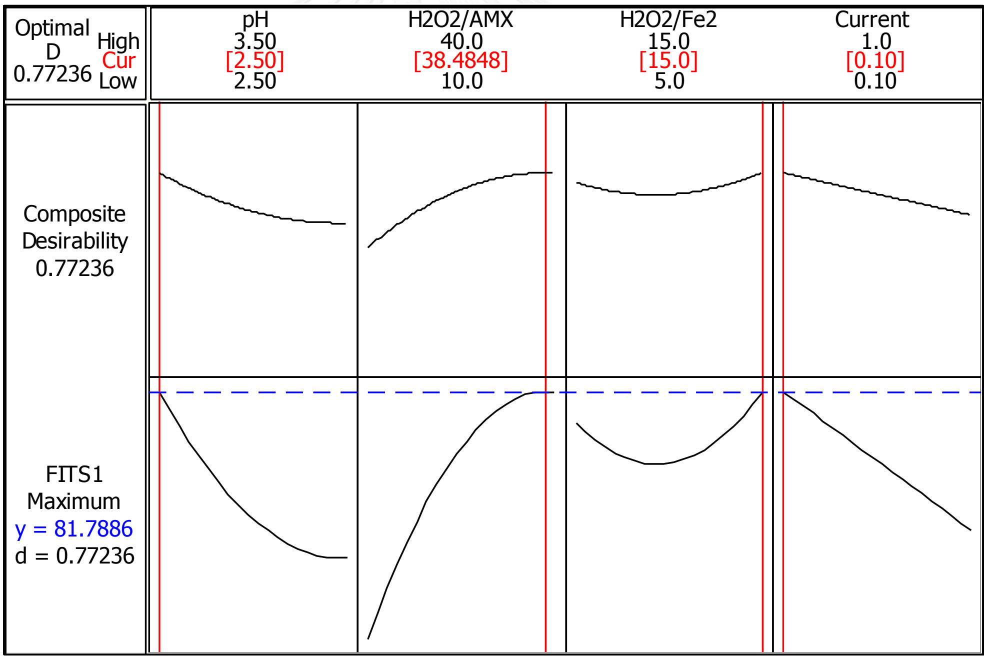


Figure 36 Maximum values in 30 minute of electro-Fenton process.

The information form RSM that clearly explained the impacts of several operating parameter was evaluated the quality of each factor. The experimental results indicated that the highest COD removal was at pH 2.5.

Similarly, these found in electro-Fenton process in initial stage. Hence, pH 2.5 was chosen as the maximum pH considering all of influent effects form the others variables and the best performance of effective Fenton's reagent.

The effect of H_2O_2/AMX (MR) concentration for COD removal on electro-Fenton process demonstrated increasing the H_2O_2/AMX ratio from 10 to 40 enhance COD removal efficiency. The maximum concentration ratio of H_2O_2/AMX (MR) was pointed as the maximum ratio in initial stage of electro-Fenton. In this study, the concentration of AMX was fixed as 0.3 mM while suitable H_2O_2 concentration was 12 mM that is a deal of H_2O_2 as 40 molar. This ratio was agreed with previous that demonstrated 40 was the effective ratio as high COD removal would obtain (Methatham et al., 2013)

That mention about the excess ratio that was ineffective to process performance. The suitable ration of H_2O_2 and Fe^{2+} catalyst resulted to continuously react of Fenton's reagent. Owing to the maximum H_2O_2 concentration was used (12 mM), amount of ferrous iron was expected at 15 molar ratio H_2O_2/Fe^{2+}. This appropriated ratio was changed to amount of Fe^{2+} equaling 0.8 mM. A mount of maximum Fe^{2+} that used in 30 minute of electro-Fenton process lower than it's in 5 minute. Unsurprisingly, The minimal concentration of Fe^{2+} are required because Fe^{2+} would produce from electro-regeneration from ferrous hydroxide sludge during 30 minute operating period. Reducing of ferrous amount agreed with previous work that reported COD, DOC and biodegradability of antibiotic wastewater containing Amoxicillin , Ampicillin and Cloxacillin decreased thanks to decreased ferrous ions dissolved in solution (Elmolla & Chaudhuri, 2009). This Fe^{2+} concentration in this study closed with its in previous work that they applied 1 mM of Fe^{2+} to remove COD on the degradation of 2,6-dimethylaniline using electro-Fenton process (Masomboon, 2008).

The last factor was evaluated to achieve high removal efficiency was electrical current density. The results indicated that low current density supplied supported high COD removal. A deal of 0.1 $mAcm^{-2}$ current density was selected to operate during 30 minute of electro-Fenton process. Moreover, the most effective COD removal was found as low current density supplied Because of energy saving reason, 0.1 $mAcm^{-2}$ was chosen to be a suitable current density in this section. In this study, the wanted current density for operate electro-Fenton on this study condition was less (0.1 $mAcm^{-2}$). According to there was a little difference on electro-Fenton compartment for example volume of reactor, area of electrode and distance between electrodes (Anotai, Sairiam, & Lu, 2011). Due to small surface area of electrodes that used in this study, low current density was more suitable and regenerated capacity of electrodes was less than the larger one. The result from calculated equation that showed in Table 10 represented positive effect of pH and current density. Finally, the obtained condition was further used in the next step.

Although, the effect of operating parameter of experimental result was described by using main and interaction plot, there was some detailed in experimental designed that can help to explain the result in deep.

Even though. 15 molar ration of H_2O_2/AMX show the appropriate result for high COF removal, there was different in amount Fenton reagent that was used in this same ratio.

Although, the effect of operating parameter of experimental result was described by using main and interaction plot, there was some detailed in experimental designed that can help to explain the result in deep.

Even though the same ration of H_2O_2/Fe^{2+} was used in experiment, using different molar of H_2O_2 also directly affected to COD removal efficiency as shown in Figure 37 - 39. When consider about H_2O_2 concentration, COD removal of the experiment using different molar ratio of H_2O_2/AMX reached to around 80, 75 and 50 % for the experiment that used 40, 25 and 10 MR of H_2O_2/AMX respectively.

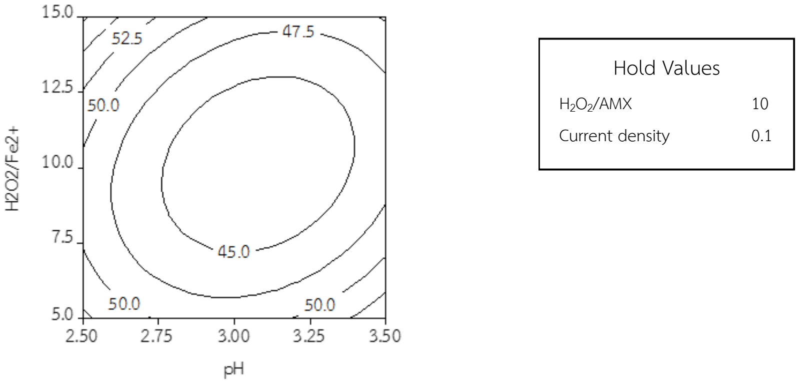


Figure 37 Interaction plot of pH versus H_2O_2/Fe^{2+} holding 10 H_2O_2/AMX (MR).

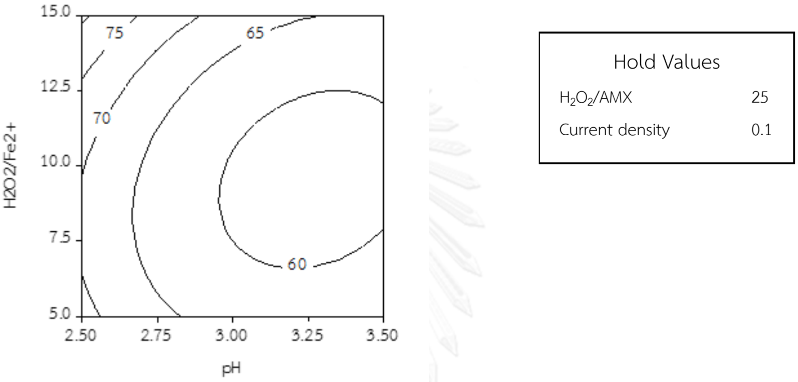


Figure 38 Interaction plot of pH versus H_2O_2/Fe^{2+} holding 25 H_2O_2/AMX (MR)

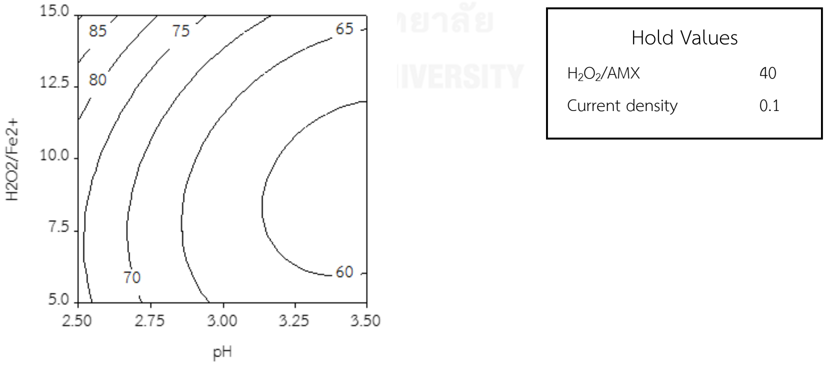


Figure 39 Interaction plot of pH versus H_2O_2/Fe^{2+} holding 40 H_2O_2/AMX (MR).

Using high molar ratio of H_2O_2/AMX implied that high amount of H_2O_2 was supplied, while using low molar ratio of H_2O_2/AMX implied that low amount of H_2O_2 was supplied. More H_2O_2 concentration directly affect to Fe^{2+}

ratio. According to the different molar ratio of H_2O_2/AMX, amount of Fe^{2+} in each experiment was not same. The various amount of Fenton's reagent was shown in table 5.

For example, using the same ratio of 10 H_2O_2/Fe^{2+} (MR) but different of H_2O_2/AMX was used (RUN 11 and 12). The amount of H_2O_2 12 and 3 mM was used with amount of Fe^{2+} 1.2 and 0.3, respectively. The higher COD removal presented in the experiment that used high amount of H_2O_2. 63.10% and 47.35% of COD removal was presented as show in picture 15. This result indicated using high ratio of H_2O_2/AMX was better.

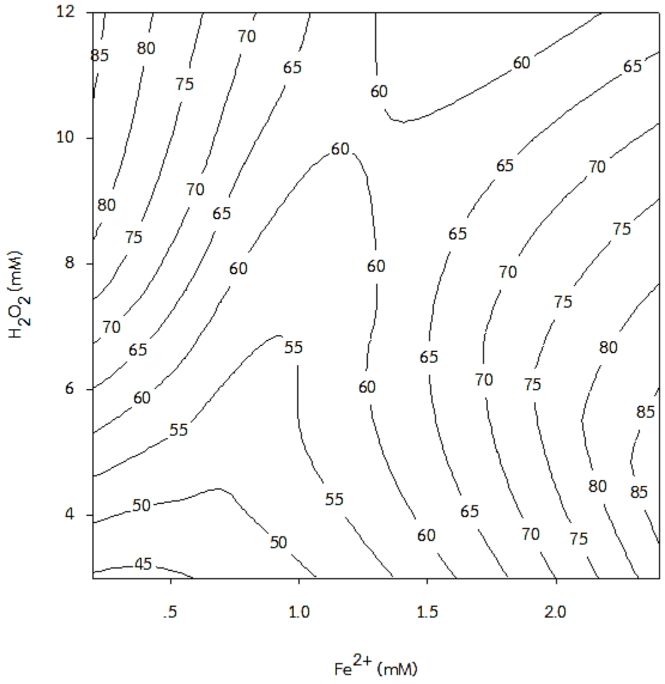


Figure 40 COD removal performance with using different amount of Fenton's reagent

From the contour plot of H_2O_2 and Fe^{2+} relationship as shown Figure 40, the high COD removal efficiency presented at two places. First place was presented in initial stage also that is the area that used low amount of H_2O_2 and high amount of Fe^{2+}. Using 5-8 mM of H_2O_2 and amount of Fe^{2+} was higher than 2.0 mM exhibited up to 80% of COD removal. While another place that also showed high COD removal efficiency is located at the area using high H_2O_2 and low amount of Fe^{2+}. Using a large deal of H_2O_2 (8 -12 mM) with low amount of Fe^{2+} (0.5 mM) expressed 80% of COD removal.

Observably, the present of high removal efficiency for 30 minute of operating time consisted of 2 main behaviors. Firstly, the efficiency came from added iron salt always show high efficiency when high Fe^{2+} (more than 2 mM) and 5-8 mM of H_2O_2 was supplied. Directly supply high amount of Fenton reagent promote •OH formation that can be improve COD removal. The second, high COD removal presented when supplied high H_2O_2 (8-12 mM) and low Fe^{2+} (1-5 mM). This caused by Fe^{2+} can be regenerated via electro chemically reaction during 30 minute of operating time. Thus, a few of Fe^{2+} was needed.

These can be explain the result that the COD removal efficiency of some experiment was much higher than the other using the same ratio of H_2O_2/Fe^{2+}.

From this experiment under the obtained maximum condition from BBD, The triplicates of maximum condition experiments were done. The approximate efficiency of electro-Fenton for COD removal was 68%, while the predicted value was 81.79%. This inaccuracy of calculation ca be occurred because there was the limitation of their predicted with coefficient relation of prediction (R^2 of prediction). The data of R-square in Table 11 was 77.81%. This value told us about how much of the accuracy from the prediction. When R-square prediction was considered with the experimental results, 65% was acceptable value in R-square predicted range (±18.15).

4.2.4 Maximum condition investigation

The maximum condition that selected in this study was chose by the experimental results that based on RSM. The maximum condition from second part used as selected condition. Further process, 0.3 mM AMX was operated under pH 2.5, 40 molar ratio of H_2O_2/AMX, 15 molar ratio of $H_2O_2/Fe^{2+}$and 0.1 mAcm^{-2} of current density. The selected maximum condition was chose regarding the principle of electro-Fenton that focused on Fe^{2+} generation. Moreover, the COD removal performance of 30 minute of operating time still high than 5 minute.

As the results of previous steps, maximum condition was installed. Figure 30 that displayed a new set of experiments that carried out in maximum condition. During operating time 30 minute, AMD degradation in term of COD removal was expressed as 68 percent.

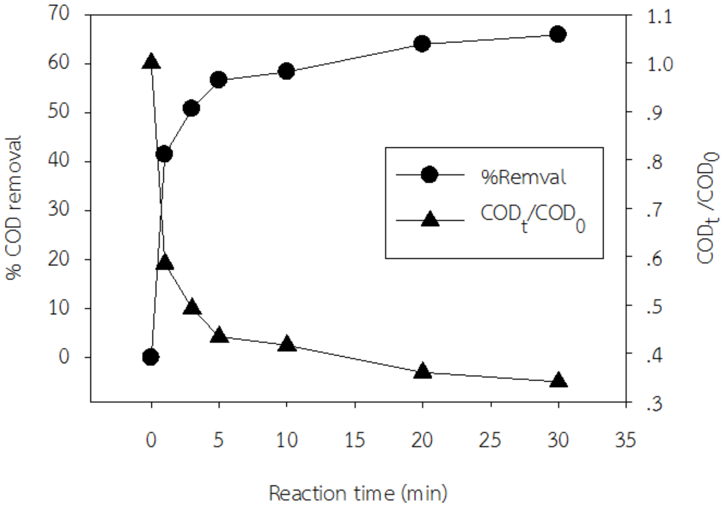


Figure 41 COD removal operating by maximum condition: pH 2.5, H_2O_2/AMX (MR) 40, H_2O_2/Fe^{2+} 15 and current density 0.1 mAcm^{-2}.

The results indicated that initial AMX concentration was 68 percent removed in term of COD. 56.55 percent of COD rapidly removed in first 5 minute and then just 9.3 percent of COD slowly increased up to 30 minute of operating time. This can explained that AMX degradation in term of COD was removed by $^{\bullet}$OH following Reaction 2.1. Fenton's reagent was consumed for generate $^{\bullet}$OH. Evidently, the changing in a mounts of Fenton's reagent is showed in Figure 30.

H_2O_2 remaining as shown in Figure 42, H_2O_2 was quickly consumed in first minute, the experimental result showed 7.77 mM of H_2O_2 was remained in 1 minute. The rapid decrease of H_2O_2 in 1 minute was caused by consumed H_2O_2 to form $^{\bullet}$OH. Then, continuously decreased to 4.96 mM of H_2O_2 was remained at 30 minute. On this stage of electro-Fenton, H_2O_2 trended to decrease along the time. There were many reasons for H_2O_2 decrease. Main reason that mentioned before that H_2O_2 and Fe^{2+} is responsible for form $^\bullet OH$. The combination of H_2O_2 and Fe^{2+} can produce $^\bullet OH$, OH^- and Fe^{3+}. Fe^{3+} is product from Reaction 2.1 that can react with H_2O_2 as a result of H_2O_2 depletion. Furthermore, the scavenging effect of H_2O_2 that react with •OH presented following Reaction 2.6 or produce oxygen radical following Reaction 4.9

$$\bullet OH + H_2O_2 \rightarrow O_2^{\bullet -} + H^+ + H_2O \qquad \text{Reaction 4.9}$$

Finally, event there is nothing reacts with H_2O_2, H_2O_2 concentration still decrease. This because H_2O_2 can decompose itself shows in Reaction 4.10 (Galbacs & Csanyi, 1983).

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad \text{Reaction 4.10}$$

In this study, the minimal ratio of H_2O_2 calculated by stoichiometric equation that balanced amount of required H_2O_2 and 0.3 mM AMX as shown in Reaction 4.11

$$C_{16}H_{19}N_3O_5S + 39\,OH \qquad \text{Reaction 4.11}$$
$$\rightarrow 16CO_2 + H_2O + 3NH_3 + 45H^+$$

As a result of calculation, 40 mole of H_2O_2 is required to produce sufficient •OH for degrade 1 mole of AMX. Because $^\bullet OH$ can be produced by

Equation 2.1 with ratio 1:1:0.1 for $^{\bullet}OH$, H_2O_2 and Fe^{2+}, respectively. Therefore, 12 mM of 0.3 mM H_2O_2 was expected to achieve this goal.

However, if using the amount of required H_2O_2 followed stoichiometric equation, the process efficiency would be improved by supplied more H_2O_2. Because of the other reaction that can be present in electro-Fenton process caused lose in amount of $^{\bullet}OH$ toward lose in degradation efficiency. The results indicated that using 40 H_2O_2/AMX (MR) was sufficient of degrade AMX solution but too much amount of H_2O_2 than its calculated form stoichiometric was better.

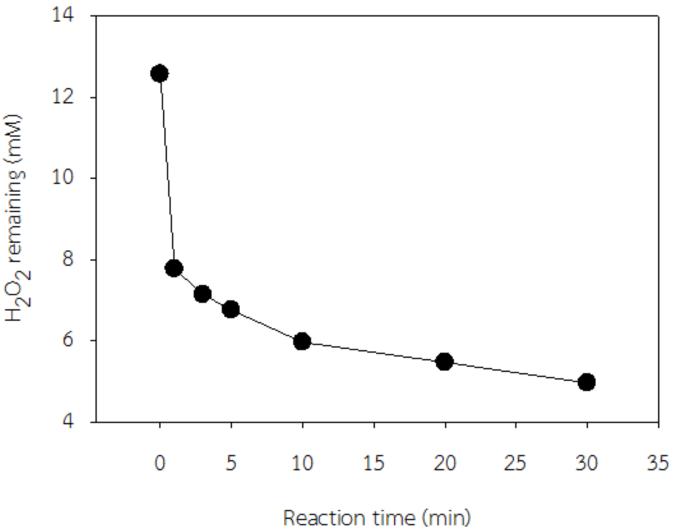


Figure 42 H_2O_2 remaining during operating of maximum condition.

In addition the other of Fenton's reagent was investigated. Ferrous remaining as shown in Figure 43 can described that amount of Fe^{2+} dramatically decreased in first minute to 0.2 mM and continuously decreased to 0.11 mM in 5 minute of operating time. After 5 minute, slight decrease of Fe^{+2} to 0.06 mM was present. However, the decrease tendency of Fe^{2+} during 5 – 30 minute did not same as H_2O_2 did. This because Fe^{2+} did not decompose itself like H_2O_2 did. Moreover, Fe^{2+} can regenerate following Reaction 2.18 as previously mentioned.

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$ Reaction 2.18

However, amount of remaining Fe^{2+}not only increased by electro regeneration but also reduced by many reaction such as it is act like the scavenging effects of •OH, it react with oxygen radical (O_2•¯), product from the excess of H_2O_2, superoxide ions (HO_2•), product form the reaction of Fe^{3+} and H_2O_2, (Reaction 2.4).

$$Fe^{2+} + O_2^{\bullet -} \rightarrow Fe^{3+} + O_2^{-}$$ Reaction 2.4

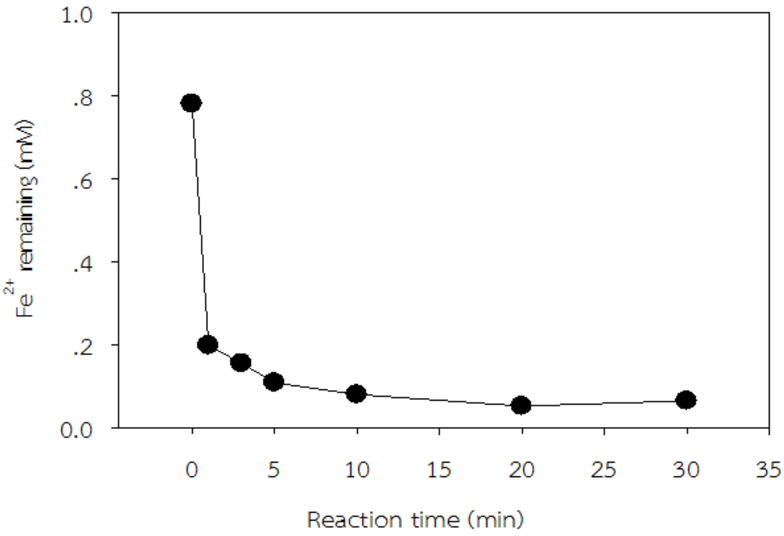


Figure 43 Fe^{2+} remaining during operating of maximum condition.

The confirmation of Fe^{2+} regeneration for ensures that Fe^{2+} can regenerate via Reaction 2.18. To ensure this regeneration, thus amount of Fe^{2+} remaining in Fenton and extended electro-Fenton was investigated as displayed in Figure 44.

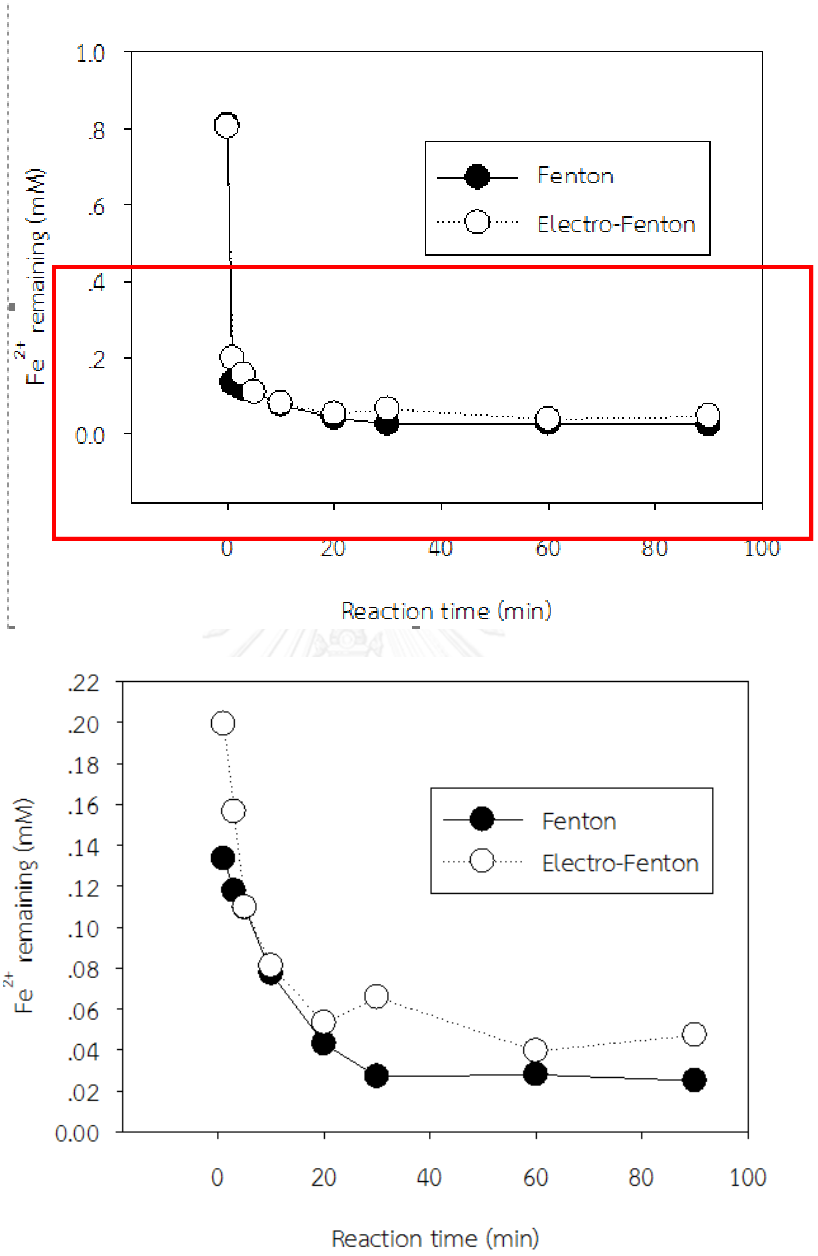


Figure 44 Fe^{2+} profile under operating maximum condition (b) extened of Fe^{2+} profile under operating maximum condition

4.2.5 Investigation of treated wastewater

After finished experiment, the treated water was evaluated for make sure the treated water can be degrade by biology.

The study of Sarria investigate AOS value of wastewater contained biorecalcitrant compounds. They observed many parameter of treated water for develop combined photochemical and biological treatment to ensure that the treated water did not destroy biological process. The observed parameter included aliphatic, aromatic, BOD, COD, DOC and AOS. They found that the tendency of BOD_5/COD and AOS were alike. Thus, this can be support the capacity of AOS that can indicate biological ability (Sarria et al., 2002). As shown in Figure 45. AOS value of treated water during experimental period trended to increase along the time. This tendency was alike BOD_5/COD tendency that BOD_5/COD did.

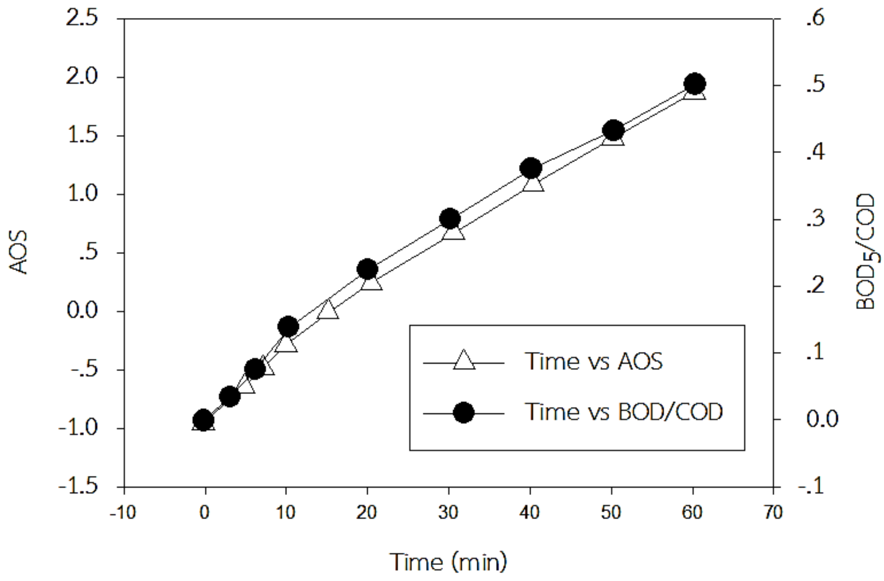


Figure 45 AOS and BOD5/COD value of treated water through photochemical treatment.

Moreover, other research studied on the degradation of antibiotic (Amoxicillin, Ampicillin and Cloxacillin) using photo-Fenton process indicated AOS value of the treated water that treated by photo-Fenton increased. They also indicated that the high AOS means there was highly biodegradable ability of treated water and less toxic. (Emolla and chuburi, 209)

Therefore, AOS was chosen to be one indicator in this study. The measurement of DOC and COD is important factors for evaluated the average oxidation state (AOS). The treated solution was evaluate average oxidation stage (AOS) following

$$AOS = 4\frac{(DOC - COD)}{DOC}$$ Equation 4.5

AOS is average oxidation state

DOC is organic carbon remaining in a sample after filtering the sample in moles of C L^{-1} (MR)

COD is chemical oxygen demand in moles of O_2 L^{-1} (MR)

Figure 46 displayed tendency of COD and DOC from maximum condition. Both COD and DOC trend to decrease with the same trend, nonetheless the great tendency presented in DOC decrease. A great number of slopes and continuous decrease of DOC presented, while COD quite presented little slopes.

The average oxidation state of treated wastewater after applied electro-Fenton process is shown in Figure 47.

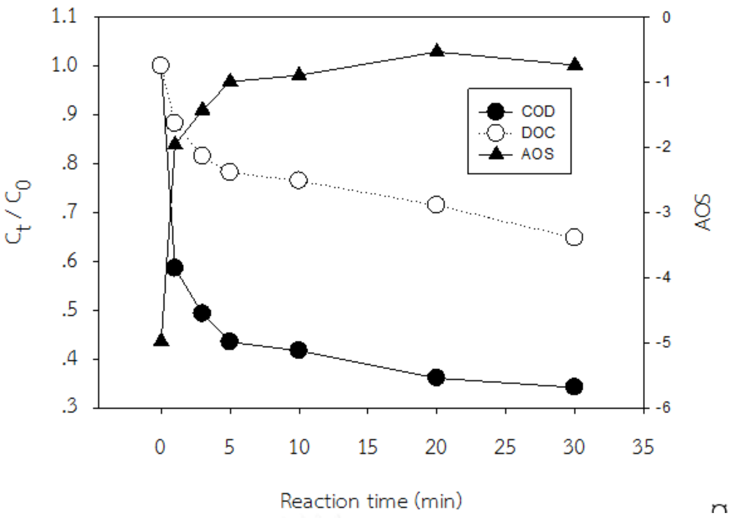


Figure 46 AMX degradation in term of COD (o) and DOC using the left hand side axis. The AOS evolution (▲) using the right hand side axis.

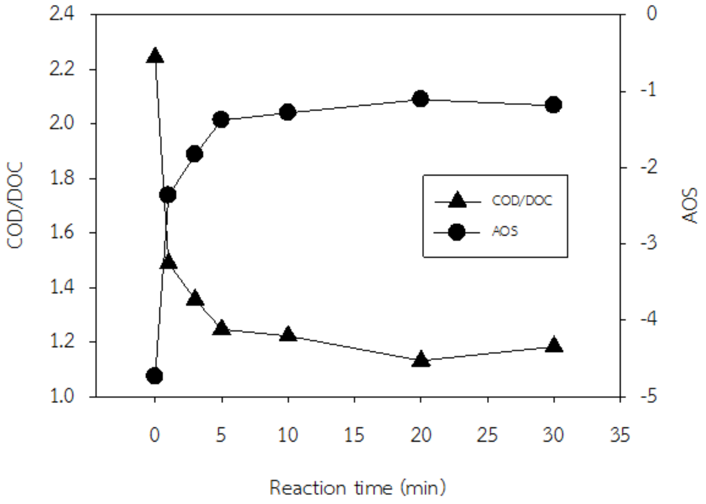


Figure 47 AMX degradation in term of COD/DOC using the left hand side axis. The AOS evolution (▲) using the right hand side axis.

During electro-Fenton operating period, AOS of the treated water increase along the time, especially in first minute of reaction time. The increase of AOS was suggested that intermediates contained solution reduce theirs refractory however; this AOS should slightly concern because the recommended AOS value is 1 (Hernández-Shek, Agudelo Henao, Mendoza Marín, & Torres Castañeda, 2012). Various AOS values are taken +4 for CO_2 that represent the most oxidizing state of carbon while and -4 for CH_4 that represent the most reduced state of carbon. AOS indicate oxidation in complex solution that consists of formal substance and their by-products. Moreover, AOS value can indicate that the solution become easily degrade by biological methods less toxic of by-product and intermediate. If there are more oxidized of intermediate; it means the sample has more bio-degradable ability under aerobic condition. Beside the increase of COD/DOC indicate that organic contented remaining in the solution of electro-Fenton process was on an average in a higher oxidation state than the lower one (Sarria et al., 2002).

Under the maximum condition for degrade 0.3 mMof AMX, It can be seen that electro-Fenton process expressed high performance than Fenton reaction.

Even though, AMX easily hydrolyze and degrade in both acid and base condition, β-Lactam ring is easily opened by β-Lactamase enzyme (Lamm, Gozlan, Rotstein, & Avisar, 2009). The destroying of 4 membered of β-Lactam ring to form AMX-penicillioic acid, which consists of free carboxylic acid. Next, AMX-penicillioic acid form AMX-Diketopiperazine2’5’, six1membered ring intermediate.

4.2.6 Kinetic investigation

The results show that maximum COD removal is obtained in 30 minutes by electro-Fenton process, kinetic is investigated. As mentioned previously, COD removal could be divided into 2 parts. The first step (initial stage) was a major section to removal efficiency. Initial step was considered base on Fenton reaction that used Fe^{2+} from outside. The initial rate was evaluated by using experimental results and applying the graphical method for differentiation formulas of first-order equation.

There were many mechanism involved with organic matter degradation in electro-Fenton process, however; the remained substance or the produced substance did not consider because COD was representative overall substance in process.

The reaction rate is the changing in amount of concentration over a time interval. According to law of reaction rate, the concentration of reactant is consumed to from a product. In batch mode, the rate can be described by the differential equation that express in term of first order equation.

The reaction rate is the changing in amount of concentration over a time interval. According to law of reaction rate, the concentration of reactant is consumed to from a product. In batch mode, the rate can be described by the differential equation that express in term of firs-order kinetic.

$$r_A = \frac{dC_A}{dt} \qquad \text{Equation 4.6}$$

Even though, the first-order and pseudo-first order model is commonly practice to explain kinetic, the phenomena of electro-Fenton that mainly produce Fe^{2+} cannot clearly describes the rate of reaction (Gozmen et al 2003). There are some limitations in precious data that not exist in linear regression of first-order and second-order model as well Wang and Lemley .

The kinetic depending on the differential equation of first-order equation Equation4.6, the reaction rate can be performed as Equation4.7.

$$r = -\frac{dCOD}{dt} = kCOD \qquad \text{Equation 4.7}$$

Where COD is COD concentration at beginning and at the given time t, k is the apparent first-order rate constant for AMX degradation in term of COD by electro-Fenton process.

The rate equation was arranged to easy form as shown in equation below.

$$\frac{-dCOD}{COD} = kdt$$

$$\int -\frac{dCOD}{COD} = \int kdt$$

$$-\int_{COD_0}^{COD} \frac{dCOD}{COD} = k\int_{t0}^{t} dt$$

$$-\ln COD|\begin{matrix} COD \\ COD_0 \end{matrix} = kt$$

$$\ln \frac{COD_0}{COD} = kt \qquad \text{Equation 4.8}$$

From arrangement of rate equation, the kinetic constant will be obtained from the plotting between ln (COD_0/COD) versus time with linear regression as seen in Equation 4.8.

Then, the data were plotted by using the Equation 4.8 as shown in Figure 48.

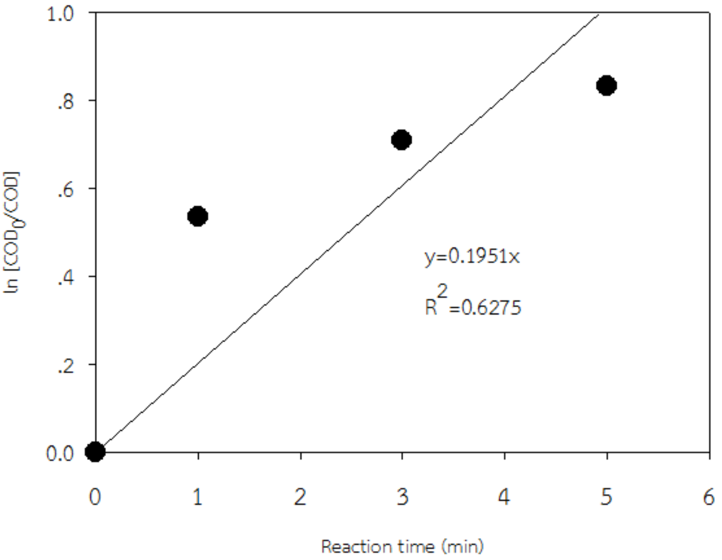


Figure 48 Plotting of ln COD_0/COD versus time of experimental data

From Figure35, the plotting between $\ln COD_0/COD$ did not go along with one strength line. Therefore, 1st order kinetic did not support with the experimental results.

After that, second order equation was applied to describe this reaction.

$$Rate = -\frac{d[COD]}{dt} \qquad \text{Equation 4.6}$$

$$= k[COD][COD]$$

$$= k[COD]^2$$

Where k is a second order rate constant (M^{-1} $time^{-1}$)

The rate equation was arranged to easy form as shown in equation below.

$$-\frac{d[COD]}{dt} = k[COD]^2$$

$$\int \frac{d[COD]}{[COD]^2} = \int -kdt$$

$$\int \frac{1}{[COD]^2} d[COD] = -k \int dt$$

$$\left.\frac{-1}{[COD]}\right| \begin{matrix} t \\ t_0 \end{matrix} = -kt|\begin{matrix} t \\ 0 \end{matrix}$$

$$\frac{-1}{[COD]_t} - \frac{-1}{[COD]_0} = -k(t-0)$$

$$\frac{1}{[COD]_t} - \frac{1}{[COD]_0} = kt$$

$$\frac{1}{[COD]_t} = kt + \frac{1}{[COD]_0} \qquad \text{Equation 4.8}$$

The plotting between $\frac{1}{[A]_t}$ versus time with linear regression as seen in Equation 4.8.

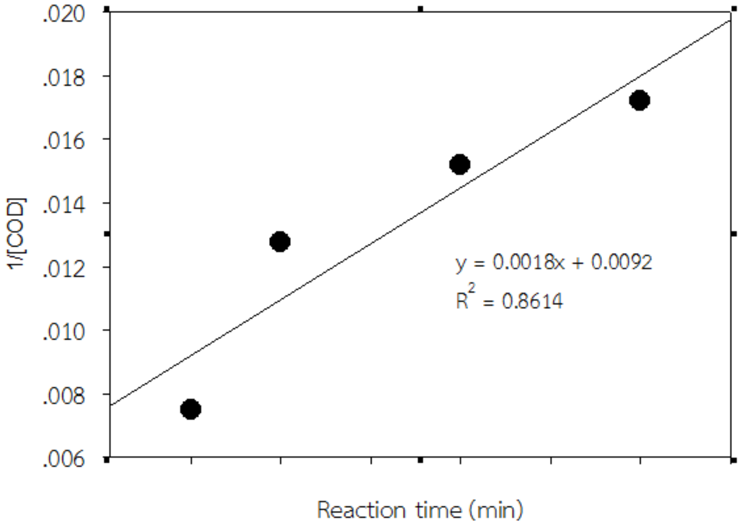


Figure 49 Plotting of 1/[COD] versus time of experimental data

From the result of plotting graph between 1/[COD] versus reaction time, slope of linear regression represented the value of rate constant following second order reaction with R^2 was 0.86 .

As shown in Figure 49 , the oxidation kinetics of AMX degradation in term of COD removal in 1 L synthetic solution under maximum condition in 0-1 minute also fitted with second-order kinetics (R^2 =0.86). The obtained values give us for constant value for COD removal in 5 minute. During 0-5 minute of operating time, kinetic strongly depend on the concentration of COD. The kinetic for AMX degradation in term of COD removal for electro-Fenton was described by pseudo-second order kinetic with k and order as 0.0018 min^{-1} and order was 2.

The rate constant for COD removal was not describing reaction well because of R^2 value. Accordingly, the new way to determine kinetic was determined but the new determination of kinetic order still based on range this three ranges.

According to rate equation, the new arrangement to find out order of rate reaction displayed in Equation 4.9 and 4.10.

$$-\frac{dCOD}{dt} = kCOD^{\alpha}$$ Equation 4.9.

$$\ln\left(-\frac{dCOD}{dt}\right) = \ln k + \alpha \ln COD$$ Equation 4.10

Consequently, the value of ln (-dCOD/dt) versus ln COD were taken into graph.

Constant value (k) and order of reaction (α) can be found from Y-axis intercept value and coefficient value of X-axis.

To determine kinetic, first of all, the relationship between ΔCOD/Δt and average time and were taken into graph for find out the average COD concentration at interval time. Then, the simple way to explain the reaction rate in the experiment is reasonable to applied graphical method with respect COD concentration because we did not know the changing concentrating along the time. If the experimental equation did not fit with the primitive of a differential equation, the approximate method would be applied. The method correlates with using the average point of time interval to carry out average value to make new equation. Graphical method provided the value of changing COD concentration by the time. After that, the obtained values were rearranged form as show in Equation 4.10

The constant at lnCOD (α) term was represented order of rate reaction, while ln k was represented kinetic constant. The rate equation for AMX degradation by electro-Fenton process showed in Figure 50.

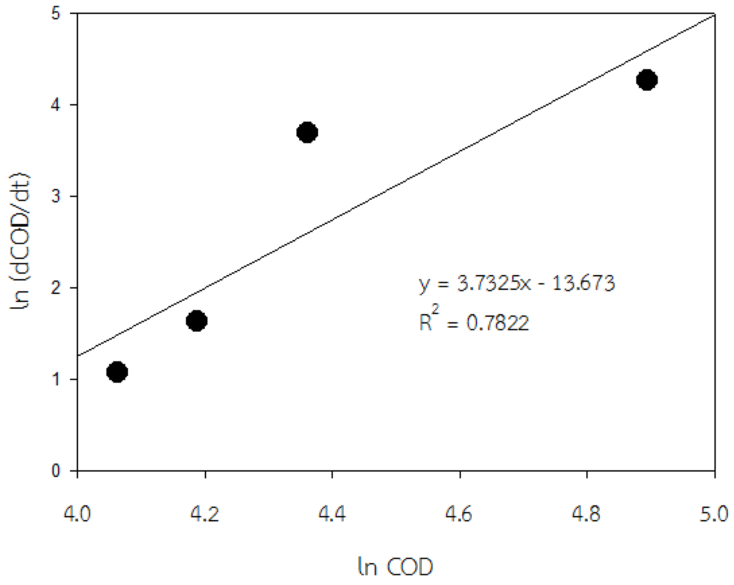


Figure 50 Plotting of ln (dCOD/dt) versus ln COD of experimental data.

Nonetheless, the first-order model was applied to evaluate kinetic in term of TOC of electro-Fenton process, the representative kinetic constant of overall reaction was separated to two groups Brill1998. The divided kinetic was agreed with Deshpande (2012) that study a kinetic electrochemical method of high-strength pharmaceuticals wastewater (Deshpande, Ramakant, & Satyanarayan, 2012). They divided their COD kinetic into two stages for easily and preciously describe their behaviors.

As shown in Figure 50 showed the oxidation kinetics of AMX degradation in term of COD removal in 1 L synthetic solution under optimal condition in 0-5 minute. During 0-5 minute of operating time, kinetic strongly depend on the concentration of COD. The kinetic for AMX degradation in term of COD removal for electro-Fenton was described by pseudo-first order kinetic with k and order was 1.16×10^{-6} min^{-1} (ln k = -13.67) and 3.7, respectively.

The summary of all kinetic for COD removal of AMX degradation during 5 minute of operating time as displayed in Table 12.

Table 12 Summary of all kinetic for COD removal

Order	.k (min^{-1})	R^2
1st order	0.1951	0.6275
2nd order	0.0018	0.8614
3.7th order	6.28×10^{-7}	0.782

From experimental result, first order did not describe kinetic of COD removal well. According to high value of R^2, the order of reaction equaled to 2nd and k equaled to 0.0018 min^{-1} described reaction well than the others.

Therefore, second order represented to order of reaction rate for COD removal with constant (k) was $6.28 \times 10^{-7} min^{-1}$.

In addition, other research described rate constant of pharmaceutical in term of COD removal. The first-order model was applied to evaluate kinetic in term of TOC of electro-Fenton process, the representative kinetic constant of overall reaction was separated to two groups Brill1998. The divided kinetic was agreed with Deshpande (2012) that study a kinetic electrochemical method of high-strength pharmaceuticals wastewater (Deshpande, Ramakant, & Satyanarayan, 2012). They divided their COD kinetic into two stages for easily and preciously describe their behaviors.

These apparent rate constant values were smaller than previous published results with similar pharmaceutical compound. This agree with work of Yahya who reported the kinetic for antibiotic degradation (Yahya et al., 2014). Fast rate of AMX degradation in term of COD described as the attribution of $^{\bullet}OH$ was assumed as main mechanism for this degradation likewise Fenton's oxidation. The high effective of $^{\bullet}OH$ quickly react with organic substance caused rapid decrease in COD removal.

Therefore, the rate constant in this range should be faster. Much research defined first order reaction to be the representative rate equation of initial stage. The kinetic study of antimicrobial agent using electro-Fenton suggested the fast reaction rate because $^{\bullet}$OH.

Beside reaction of electro-Fenton reaction of Fe^{2+} regeneration, there are three main reaction involved with (Neyen & Baeyens, 2003). First is the regeneration of Fe^{2+} from Fe^{3+} on cathode.

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad \text{Reaction 2.18}$$

Second reaction is the formation of $^{\bullet}$OH that is main reaction of Fenton reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^{-} \qquad \text{Reaction 4.12}$$

The last involved reaction is the degradation of organic substance.

$$\bullet OH + RH \rightarrow product \qquad \text{Reaction 2.9}$$

In addition, these side reactions can be occur in solution.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \qquad \text{Reaction 2.2}$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-} \qquad \text{Reaction 2.3}$$

$$H_2O_2 + product \rightarrow products \qquad \text{Reaction 4.13}$$

$$\bullet OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad \text{Reaction 4.14}$$

Many of mechanism can be effects to the changing of COD in electro-Fenton process (Neyen & Baeyens, 2003).

The constant pseudo-first order kinetic of antibiotic using competitive method by electro-Fenton was 2.02×10^{9} - 1.01 10^{10} M^{-1} s^{-1} (Panizza et al., 2014). Other research on kinetic investigation reported 1.4× 10^{-3} s^{-1} was pseudo first-order kinetic for oxidation of ibuprofen by hydroxyl radicals under electro-Fenton process.

The kinetic of COD should lower than kinetic of chemical because COD represent the over organic contained in solution. The formation of AMX degradation in initial stage still exists in solution, they did not mineralize to CO_2 and H_2O_2 agreed with a deal of remained TOC. Nonetheless, another order of rate constant was reported as well. The kinetic constant in term of COD of three antibiotic aqueous solution containing amoxicillin, ampicillin and cloxacillin was investigated by Elmolla and Chaudhuri. Their obtained 0.029 and 0.0144 min^{-1} was rate decay constant for AMX under photo-Fenton (H_2O_2/Fe^{2+}= 1.5:0.75) and Fenton (H_2O_2/Fe^{2+}= 3:0.3), respectively.

Another rate constant also report, the study of Basavaraja and mahamood 2012 reported the pseudo second order rate constant of Diclofenae antti-inflammatory at concentration 31.43×10^{-3} and 157.17 ×10^{-3} mM was 206.95 and 75.55 $M^{-1}S^{-1}$, respectively (Basavaraju & Hahamood, 2012).

4.2.7 Investigation of CA addition

Additional experiment was performing by adding CA in form of potassium clavulanate into the solution for observes the changing on process performance. The comparison of this changing was considered as initial concentration of antibiotic combination. The approximately COD concentration was fitted as well as the COD concentration did in previous step. Amount of potassium clavulanate was added in to the solution depending on commercial ratio of AMX and CA that attributed in market.

The results from this investigation are shown in Figure 51 COD was reduce much more and rapidly during first minute of operating time.

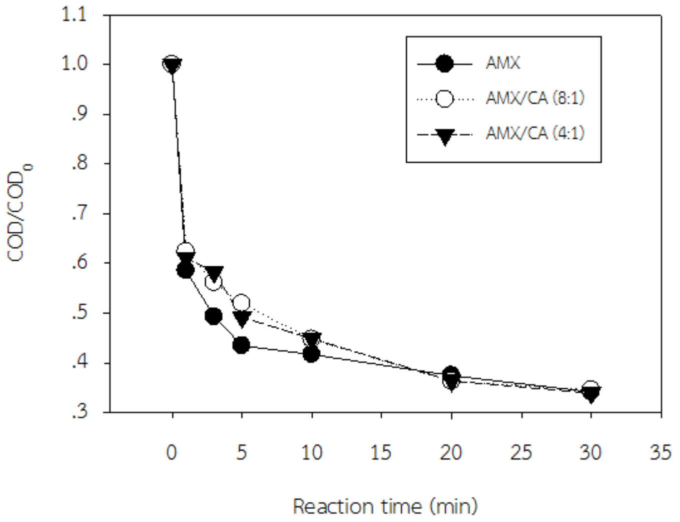


Figure 51 COD changing during elecctro-Fenton precess with different CA concentration (•) only AMX, (O) AMX/CA (8:1), (▼) AMX/CA(4:1).

The tangencies of all experiment chancing concentration were alike. Beside the controlled concentration of these three experiments, whether changing in amount of AMX and CA was do not effects the process performance. The concentration compared with initial concentration (COD/COD_0) dramatically decrease in first minute and trend to decrease long the time. The final concentration compared with initial concentration (COD/COD_0) of each experiment was 0.34, 0.35 and 0.34 for the AMX, AMX/CA (1:8) and AMX/CA (1:4), respectively.

Even if, there were little different in percentage of COD removal during 1 – 10 minute first of reaction time, these variance can be explained by time interval concentration per initial concentration ratio.

Moreover, the treated effluent that added CA was investigated AOS as well. The comparison AOS of treated water using different processes including Fenton, electro-Fenton and non-process was shown in Figure 52. The different AOS of different process were obtained. The highest AOS was presented in electro-Fenton that contained AMX/CA 4:1. As focusing on COD concentration of antibiotic solution as fitted as 125 mgL^{-1}, AMX/CA (4:1) exhibited high value of both DOC/COD and AOS value as 0.87 and 0.34. This implied that adding CA improved biodegradable ability of solution.

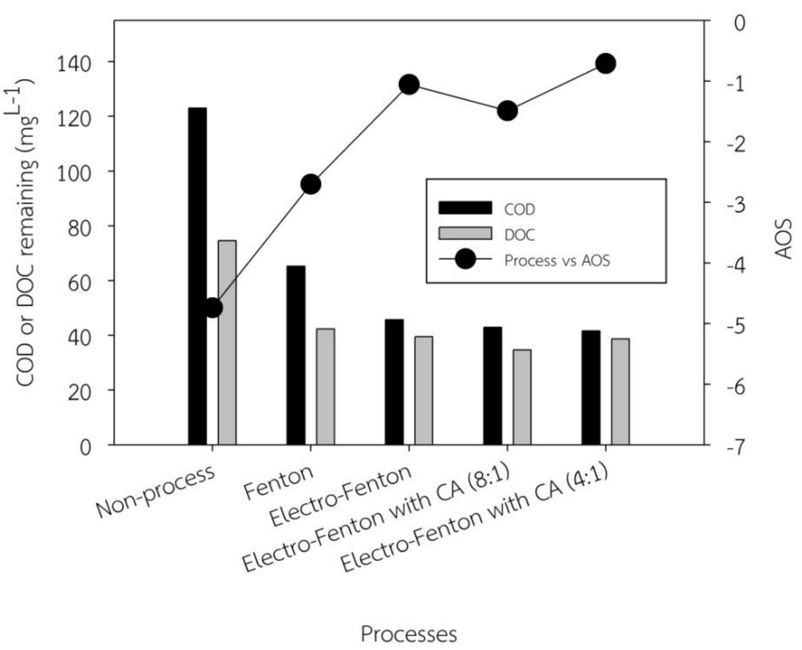


Figure 52 COD, DOC and AOS values for Fenton, electro-Fenton, electro-Fenton adding CA (AMX:CA, 8:1) and (AMX:CA, 4:1).

CHAPTER IV

CONCLUSION

5.1 Conclusion

The following conclusions were obtained from this study

Under the same condition, electro-Fenton process can remove AMX and its oxidation products that represented in form of COD removal much and more fast and effectively than traditional Fenton and electrolysis did due to the capacity of Fe^{2+} regeneration with sufficient H_2O_2 of electro-Fenton which enhanced the formation of $^{\bullet}OH$.

BBD was effective instruments, helping the determination of significant variables and the prediction of the maximum conditions to optimize the process performance.

Under the studied conditions, 15 molar ratio H_2O_2/AMX was found to be the most significant variables on AMX degradation in term of COD removal. COD removal improved with increase amount of H_2O_2, while acid pH exhibited the best performance on AMX degradation than the others.

The maximum conditions for electro-Fenton in this study range using BBD were 2.5, 40 MR, 15 MR, 0.1 $mAcm^{-2}$ for pH, H_2O_2/AMX, H_2O_2/Fe^{2+} and electrical current density, respectively. Under these condition, 65% of COD would be remove.

The empirical equation for COD removals in 30 minute in this study range was established. The independent variables could be written as displayed in equation as

$$\begin{aligned} COD\ removal_{OVer\ all} \\ &= 56.545 - 1.829A + 8.854B + 1.525C \\ &- 3.333D + 4.321A^2 - 6.656B^2 + 5.403C^2 \\ &- 3.167AB + 3.407AD \end{aligned}$$

Where A is pH, B is molar ratio of H_2O_2/AMX, C is molar ratio of H_2O_2/Fe^{2+} , D is Current density ($mAcm^{-2}$)

CA was no effects to COD removal efficiency by using 30 minute electro-Fenton.

5.2 Suggestion

According to the properties of AMX that easily degrade in acid condition promote Fenton and electro-Fenton processes but the measurement of AMX should be considered with use in low level.

For more accuracy of COD measurement, analyze it immediately cannot practice but as soon as possible can be done if eliminate H_2O_2 by using Sodium sulfide anhydrous.

REFERENCES

Adriaenssens, N., Coenen, S., Versporten, A., Muller, A., Minalu, G., Faes, C., . . . Goossens, H. (2011). European Surveillance of Antimicrobial Consumption (ESAC): outpatient macrolide, lincosamide and streptogramin (MLS) use in Europe (1997-2009). *J Antimicrob Chemother, 66 Suppl 6*, vi37-45. doi: 10.1093/jac/dkr456

Andreozzi, R., Canterino, M., Marotta, R., & Paxeus, N. (2005). Antibiotic removal from wastewaters: The ozonation of amoxicillin. *Journal of Hazardous Materials, 122*(3), 243-250. doi: http://dx.doi.org/10.1016/j.jhazmat.2005.03.004

Andreozzi, R., Caprio, V., Ciniglia, C., de Champdoré, M., Lo Giudice, R., Marotta, R., & Zuccato, E. (2004). Antibiotics in the Environment: Occurrence in Italian STPs, Fate, and Preliminary Assessment on Algal Toxicity of Amoxicillin. *Environmental Science & Technology, 38*(24), 6832-6838. doi: 10.1021/es049509a

Anotai, J., Sairiam, S., & Lu, M. C. (2011). Enhancing Treatment Efficiency of Wastewater Containing Aniline by Electro-Fenton Process. *Sustain. Environ. Res, 21*(3), 141-147.

Anotai, J., Singhadech, S., Su, C.-C., & Lu, M.-C. (2011). Comparison of o-toluidine degradation by Fenton, electro-Fenton and photoelectro-Fenton processes. *Journal of Hazardous Materials, 196*, 395-401.

Anotai, J., Su, C.-C., Tsai, Y.-C., & Lu, M.-C. (2010). Effect of hydrogen peroxide on aniline oxidation by electro-Fenton and fluidized-bed Fenton processes. *Journal of Hazardous Materials, 183*(1–3), 888-893. doi: http://dx.doi.org/10.1016/j.jhazmat.2010.07.112

APHA. (1992). *Standard Methods for the Examination Chemistry*. Washington D.D.: American Public Health Association.

Arslan-Alaton, I., & Dogruel, S. (2004). Pre-treatment of penicillin formulation effluent by advanced oxidation processes. *Journal of Hazardous Materials, 112*(1–2), 105-113. doi: http://dx.doi.org/10.1016/j.jhazmat.2004.04.009

Ayodele, O. B., Lim, J. K., & Hameed, B. H. (2012). Pillared montmorillonite supported ferric oxalate as heterogeneous photo-Fenton catalyst for degradation of amoxicillin. *Applied Catalysis A: General, 413–414*(0), 301-309. doi: http://dx.doi.org/10.1016/j.apcata.2011.11.023

Barreiro, J. C., Capelato, M. D., Martin-Neto, L., & Bruun Hansen, H. C. (2007). Oxidative decomposition of atrazine by a Fenton-like reaction in a H2O2/ferrihydrite system. *Water Research, 41*(1), 55-62. doi: http://dx.doi.org/10.1016/j.watres.2006.09.016

Basavaraju, M., & Hahamood. (2012). Degradation Kinetics of Diclofenae in Water by Fenton's Oxidation. *Journal of Sustainable Energy & Environment, 3*, 173-176.

Brillas, E., Sirés, I., & Oturan, M. A. (2009). Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. *Chemical Reviews, 109*(12), 6570-6631. doi: 10.1021/cr900136g

Castiglioni, S., Bagnati, R., Calamari, D., Fanelli, R., & Zuccato, E. (2005). A multiresidue analytical method using solid-phase extraction and high-pressure liquid chromatography tandem mass spectrometry to measure pharmaceuticals of different therapeutic classes in urban wastewaters. *Journal of Chromatography A, 1092*(2), 206-215. doi: http://dx.doi.org/10.1016/j.chroma.2005.07.012

Dahdouh, N. E. L. (2013). *Evaluation of eco toxicity of amoxicillin and erythromycin on fish and mosquito in lan condition* (Master), AL Azhar University.

Daneshvar, N., Aber, S., Vatanpour, V., & Rasoulifard, M. H. (2008). Electro-Fenton treatment of dye solution containing Orange II: Influence of operational parameters. *Journal of Electroanalytical Chemistry, 615*(2), 165-174. doi: http://dx.doi.org/10.1016/j.jelechem.2007.12.005

Deshpande, A., Ramakant, & Satyanarayan, S. (2012). Treatment of Pharmaceutical Wastewater by Electrochemical Method: Optimization of Operating Parameters by Response Surface Methodology. *Journal of Hazardous, Toxic, and Radioactive Waste, 16*(4), 316-326. doi: doi:10.1061/(ASCE)HZ.2153-5515.0000133

Dinov, I. (2002). Statistics onlinecoputational resource (SOCR). from http://www.socr.ucla.edu/applets.dir/f_table.html

Elmolla, E. S., & Chaudhuri, M. (2009). Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the photo-Fenton process. *Journal of Hazardous Materials, 172*(2–3), 1476-1481. doi: http://dx.doi.org/10.1016/j.jhazmat.2009.08.015

Elmolla, E. S., & Chaudhuri, M. (2010). Comparison of different advanced oxidation processes for treatment of antibiotic aqueous solution. *Desalination, 256*(1-3), 43-47.

Fent, K., Weston, A. A., & Caminada, D. (2006). Ecotoxicology of human pharmaceuticals. *Aquatic Toxicology, 76*(2), 122-159. doi: http://dx.doi.org/10.1016/j.aquatox.2005.09.009

Fick, J., Söderström, H., Lindberg, R. H., Phan, C., Tysklind, M., & Larsson, D. G. J. (2009). Contamination of surface, ground, and drinking water from pharmaceutical production. *Environmental Toxicology and Chemistry, 28*(12), 2522-2527. doi: 10.1897/09-073.1

Galbacs, Z. M., & Csanyi, L. J. (1983). Alkali-induced decomposition of hydrogen peroxide. *Journal of the Chemical Society, Dalton Transactions*(11), 2353-2357. doi: 10.1039/DT9830002353

Ghoneim, M. M., El-Desoky, H. S., & Zidan, N. M. (2011). Electro-Fenton oxidation of Sunset Yellow FCF azo-dye in aqueous solutions. *Desalination, 274*(1–3), 22-30. doi: http://dx.doi.org/10.1016/j.desal.2011.01.062

Glaze, W. H., Kang, J.-W., & Chapin, D. H. (1987). The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. *Ozone: Science & Engineering, 9*(4), 335-352. doi: 10.1080/01919518708552148

Güven, G., Perendeci, A., & Tanyolaç, A. (2008). Electrochemical treatment of deproteinated whey wastewater and optimization of treatment conditions with response surface methodology. *Journal of Hazardous Materials, 157*(1), 69-78. doi: http://dx.doi.org/10.1016/j.jhazmat.2007.12.082

Haag, W. R., & Yao, C. C. D. (1992). Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environmental Science & Technology, 26*(5), 1005-1013.

Haller, M. Y., Müller, S. R., McArdell, C. S., Alder, A. C., & Suter, M. J. F. (2002). Quantification of veterinary antibiotics (sulfonamides and trimethoprim) in animal manure by liquid chromatography–mass spectrometry. *Journal of Chromatography A, 952*(1–2), 111-120. doi: http://dx.doi.org/10.1016/S0021-9673(02)00083-3

Halling-Sørensen, B., Nors Nielsen, S., Lanzky, P. F., Ingerslev, F., Holten Lützhøft, H. C., & Jørgensen, S. E. (1998). Occurrence, fate and effects of pharmaceutical substances in the environment- A review. *Chemosphere, 36*(2), 357–393.

Hermosilla, D., Cortijo, M., & Huang, C. P. (2009). Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes. *Science of The Total Environment, 407*(11), 3473-3481. doi: http://dx.doi.org/10.1016/j.scitotenv.2009.02.009

Hernández-Shek, M. A., Agudelo Henao, A. C., Mendoza Marín, C., & Torres Castañeda, H. (2012). Solar photo-Fenton optimisation in treating carbofuran-contaminated water. *2012, 32*(1). doi: 71-76

Hernando, M. D., Mezcua, M., Fernández-Alba, A. R., & Barceló, D. (2006). Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta, 69*(2), 334-342.

Höfl, C., Sigl, G., Specht, O., Wurdack, I., & Wabner, D. (1997). Oxidative degradation of aox and cod by different advanced oxidation processes: A comparative study with two samples of a pharmaceutical wastewater. *Water Science and Technology, 35*(4), 257-264. doi: http://dx.doi.org/10.1016/S0273-1223(97)00033-4

Homem, V., Alves, A., & Santos, L. (2010). Amoxicillin degradation at ppb levels by Fenton's oxidation using design of experiments. *Science of The Total Environment, 408*(24), 6272-6280. doi: http://dx.doi.org/10.1016/j.scitotenv.2010.08.058

Homem, V., Alves, A., & Santos, L. (2013). Microwave-assisted Fenton's oxidation of amoxicillin. *Chemical Engineering Journal, 220*(0), 35-44. doi: http://dx.doi.org/10.1016/j.cej.2013.01.047

Homem, V., & Santos, L. (2011). Degradation and removal methods of antibiotics from aqueous matrices – A review. *Journal of Environmental Management, 92*(10), 2304-2347. doi: http://dx.doi.org/10.1016/j.jenvman.2011.05.023

HPSC. (2014). European Antimicrobial Resistance Surveillance System (EARSS). from http://www.hpsc.ie/A-Z/MicrobiologyAntimicrobialResistance/EuropeanAntimicrobialResistanceSurveillanceSystemEARSS/

Idrees Ala Khail, M. (2009). *Analysis of amoxicillin in counterfeit antibiotics from the Subcontinent and the Middle East.* (Ms), Coventry University.

Isarain-Chávez, E., Arias, C., Cabot, P. L., Centellas, F., Rodríguez, R. M., Garrido, J. A., & Brillas, E. (2010). Mineralization of the drug β-blocker atenolol by electro-Fenton and photoelectro-Fenton using an air-diffusion cathode for H2O2 electrogeneration combined with a carbon-felt cathode for Fe2+ regeneration. *Applied Catalysis B: Environmental, 96*(3–4), 361-369. doi: http://dx.doi.org/10.1016/j.apcatb.2010.02.033

Kavitha, V., & Palanivelu, K. (2004). The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere, 55*(9), 1235-1243. doi: http://dx.doi.org/10.1016/j.chemosphere.2003.12.022

Kristiansson, E., Fick, J., Janzon, A., Grabic, R., Rutgersson, C., Weijdegård, B., . . . Larsson, D. G. J. (2011). Pyrosequencing of Antibiotic-Contaminated River Sediments Reveals High Levels of Resistance and Gene Transfer Elements. *PLoS ONE, 6*(2), e17038. doi: 10.1371/journal.pone.0017038

Kümmerer, K. (2009). Antibiotics in the aquatic environment – A review – Part I. *Chemosphere, 75*(4), 417-434. doi: http://dx.doi.org/10.1016/j.chemosphere.2008.11.086

Kümmerer, K. (2011). Antibiotics in the Aquatic Environment *Antimicrobial Resistance in the Environment* (pp. 325-335): John Wiley & Sons, Inc.

Lamm, A., Gozlan, I., Rotstein, A., & Avisar, D. (2009). Detection of amoxicillin-diketopiperazine-2′, 5′ in wastewater samples. *Journal of Environmental Science and Health, Part A, 44*(14), 1512-1517. doi: 10.1080/10934520903263306

Lee, Y. B., Kim, D. J., Ahn, C. H., & Scholtz, E. C. (2010). Pharmaceutical formulation of clavulanic acid: Google Patents.

Masomboon, N. (2008). *Degradation of 2-6-dimethylaniline and aniline by Fenton thechnogies.* (Master), Chulalonfkorn University.

Mavronikola, C., Demetriou, M., Hapeshi, E., Partassides, D., Michael, C., Mantzavinos, D., & Kassinos, D. (2009). Mineralisation of the antibiotic amoxicillin in pure and surface waters by artificial UVA- and sunlight-induced Fenton oxidation. *Journal of Chemical Technology & Biotechnology, 84*(8), 1211-1217. doi: 10.1002/jctb.2159

McEvory, G. K. (2001). AHFS Drug Information *AHFS Drug Information*, 383-389.

Methatham, T., Lu, M.-C., & Ratanatamskul, C. (2013). Effect of operating parameters on triclosan degradation by Fenton’s reagents combined with an electrochemical system. *Desalination and Water Treatment, 52*(4-6), 920-928. doi: 10.1080/19443994.2013.827308

Neyen, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation techinque. *J. Hazardous Materials, 98*, 33-50.

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

Panizza, M., Dirany, A., Sirés, I., Haidar, M., Oturan, N., & Oturan, M. (2014). Complete mineralization of the antibiotic amoxicillin by electro-Fenton with a BDD anode. *Journal of applied electrochemistry, 44*(12), 1327-1335. doi: 10.1007/s10800-014-0740-9

Pereira, J. H. O. S., Reis, A. C., Nunes, O. C., Borges, M. T., Vilar, V. J. P., & Boaventura, R. A. R. (2013). Assessment of solar driven TiO2-assisted photocatalysis efficiency on amoxicillin degradation. *Environmental Science and Pollution Research, 21*(2), 1292-1303.

Plakas, K. V., Karabelas, A. J., Sklari, S. D., & Zaspalis, V. T. (2013). Toward the Development of a Novel Electro-Fenton System for Eliminating Toxic Organic Substances from Water. Part 1. In Situ Generation of Hydrogen Peroxide. *Industrial & Engineering Chemistry Research, 52*(39), 13948-13956. doi: 10.1021/ie400613k

Pubchem. (2014). Compound summary for CID 33613. Retrieved 20/10/2014, 2014, from http://pubchem.ncbi.nlm.nih.gov//compound/33613?from=summary#section=Top

Putra, E. K., Pranowo, R., Sunarso, J., Indraswati, N., & Ismadji, S. (2009). Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics. *Water Research, 43*(9), 2419-2430. doi: http://dx.doi.org/10.1016/j.watres.2009.02.039

Qiang, Z., Chang, J.-H., & Huang, C.-P. (2003). Electrochemical regeneration of Fe2+ in Fenton oxidation processes. *Water Research, 37*(6), 1308-1319. doi: http://dx.doi.org/10.1016/S0043-1354(02)00461-X

Ramirez, J. H., Costa, C. A., Madeira, L. M., Mata, G., Vicente, M. A., Rojas-Cervantes, M. L., . . . Martín-Aranda, R. M. (2007). Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay. *Applied Catalysis B: Environmental, 71*(1–2), 44-56. doi: http://dx.doi.org/10.1016/j.apcatb.2006.08.012

Sairiam, S. (2008). *Enhancing treatment efficiency of wastewater containing aniine by electro-Fenton process.* (Master), Chulalongkorn.

Sarria, V., Parra, S., Adler, N., Péringer, P., Benitez, N., & Pulgarin, C. (2002). Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds. *Catalysis Today, 76*(2–4), 301-315. doi: http://dx.doi.org/10.1016/S0920-5861(02)00228-6

Saudagar, P. S., Survase, S. A., & Singhal, R. S. (2008). Clavulanic acid: A review. *Biotechnology Advances, 26*(4), 335-351. doi: http://dx.doi.org/10.1016/j.biotechadv.2008.03.002

Schreiber, F., & Szewzyk, U. (2008). Environmentally relevant concentrations of pharmaceuticals influence the initial adhesion of bacteria. *Aquatic Toxicology, 87*(4), 227-233. doi: http://dx.doi.org/10.1016/j.aquatox.2008.02.002

Schwab, B. W., Hayes, E. P., Fiori, J. M., Mastrocco, F. J., Roden, N. M., Cragin, D., . . . Anderson, P. D. (2005). Human pharmaceuticals in US surface waters: A human health risk assessment. *Regulatory Toxicology and Pharmacology, 42*(3), 296-312. doi: http://dx.doi.org/10.1016/j.yrtph.2005.05.005

Sirés, I., Oturan, N., & Oturan, M. A. (2010). Electrochemical degradation of β-blockers. Studies on single and multicomponent synthetic aqueous solutions. *Water Research, 44*(10), 3109-3120. doi: http://dx.doi.org/10.1016/j.watres.2010.03.005

Sirés, I., Oturan, N., Oturan, M. A., Rodríguez, R. M., Garrido, J. A., & Brillas, E. (2007). Electro-Fenton degradation of antimicrobials triclosan and triclocarban. *Electrochimica Acta, 52*(17), 5493-5503. doi: http://dx.doi.org/10.1016/j.electacta.2007.03.011

Sun, J.-H., Sun, S.-P., Fan, M.-H., Guo, H.-Q., Lee, Y.-F., & Sun, R.-X. (2008). Oxidative decomposition of p-nitroaniline in water by solar photo-Fenton advanced oxidation process. *Journal of Hazardous Materials, 153*(1–2), 187-193. doi: http://dx.doi.org/10.1016/j.jhazmat.2007.08.037

Thirugnanasambandham, K., Kandasamy, S., Sivakumar, V., kumar, R. K., & Mohanavelu, R. Modeling of by-product recovery and performance evaluation of Electro-Fenton treatment technique to treat poultry wastewater. *Journal of the Taiwan Institute of Chemical Engineers*(0). doi: http://dx.doi.org/10.1016/j.jtice.2014.09.004

Trovó, A. G., Pupo Nogueira, R. F., Agüera, A., Fernandez-Alba, A. R., & Malato, S. (2011). Degradation of the antibiotic amoxicillin by photo-Fenton process – Chemical and toxicological assessment. *Water Research, 45*(3), 1394-1402. doi: http://dx.doi.org/10.1016/j.watres.2010.10.029

USEPA. (2012). Toxic Contaminants in the Chesapeake Bay Technical Report from http://www.noticeandcomment.com/Toxic-Contaminants-in-the-Chesapeake-Bay-Technical-Report-fn-67519.aspx

Yahya, M. S., Oturan, N., El Kacemi, K., El Karbane, M., Aravindakumar, C. T., & Oturan, M. A. (2014). Oxidative degradation study on antimicrobial agent ciprofloxacin by electro-fenton process: Kinetics and oxidation products. *Chemosphere, 117*(0), 447-454. doi: http://dx.doi.org/10.1016/j.chemosphere.2014.08.016

APPENDIX A

Appendix A1: 1,10-phenanthroline standard method for ferrous concentration determination (APHA, 1992)

Principle

The standard method to determined amount of ferrous ion in water at the present time has no interfere from color, turbidity, phosphate or heavy metal. The method base on the reaction between 1,10-phenanthroline and ferrous to form an reddish orange color complex iron at pH 3.2-3.3. This method can measure iron concentration as low as 10 $\mu g mL^{-1}$

Reagent

1. Hydrochloric acid (HCl) stock solution: 20 ml of concentration hydrochloric acid is diluted to 1,000 mL with water.
2. Ammonium acetate buffer solution: 500 g of $NH_4C_2H_3O_2$ is dissolved in 300 mL of water. Full fill to 2,000 mL with 1,400 mL of concentration glacial acetic acid.
3. Phenanthroline solution : 5 g of 1,10-phenanthrolinehydrochloride ($C_{12}H_8N_2$ HCL+H_2O) are dissolved in 1,000 mL of water.
4. Stock Ferrous ion solution : 20 ml of H_2SO_4 is added to 50 ml water and 2.5 g of ferrous sulfate ($FeSO_4 \bullet 7H_2O$) is added. Full fill to 1,000 mL with water. The concentration of stock solution is 500 mgL^{-1} as Fe^{2+}.

Laboratory Equipment

1. UV- visible spectrophotometer, Wavelength 510 nm was used for analyze ferrous ion
2. 50 ml Erlenmeyer flask
3. Medicine dropper

Procedure

1. 25 ml of HCl is added to 50 mL volumetric flask. Then, 10 mL of phenanthroline solution and 5 mL of ammonium acetate solution are added with vigorous stirring.
2. 1 mL of flited sample is added. Then, full fill water to make volume to 50 mL. After that waiting for 10 min for color development, this step be careful the sample should not expose the sunlight.
3. Measured sample by using UV- visible spectrophotometer with wavelength at 510 nm.

Calibration curve

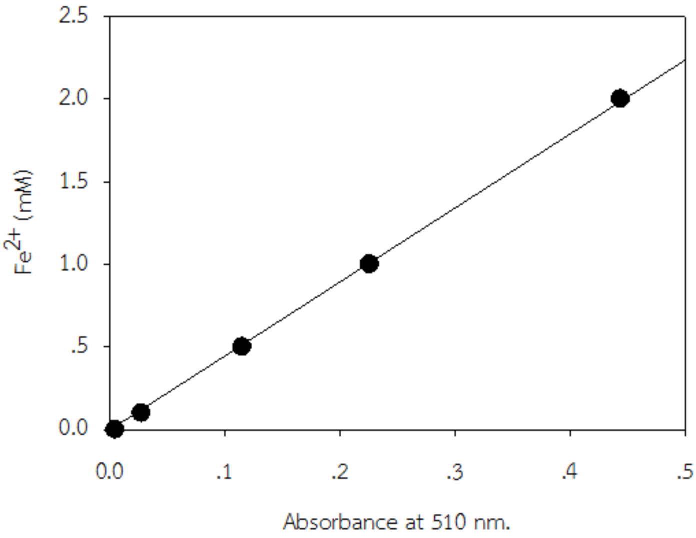
The concentration of standard solution of ferrous was analyzed by using UV-visible spectrophotometer with wavelength at 510 nm. Calibration curve was plotted between Ferrous concentration and absorbance at 510 nm.

1. 25 ml of HCl is added to 50 mL volumetric flask. Then, 10 mL of phenanthroline solution and 5 mL of ammonium acetate solution are added with vigorous stirring.
2. 1 ml of 0, 0.05, 0.5, 1 and 1.5 mgL-1 as Fe^{2+} is pipetted, respectively. Then, full fill water to make volume to 50 mL. After that waiting for 10 min for color development, this step must be careful the sample should not expose the sunlight.
3. Measured sample by using UV- visible spectrophotometer with wavelength at 510 nm.

Calculation

$y = 4.5534x - 0.0248$

Where x is absorbance at 510 nm and Y is Fe^{2+} concentration (mM)



Appendix A2 : Analysis of hydrogen peroxide

Principle

This method measure color intensities of hydrogen peroxide which are react with potassium titanium (IV) oxalate reagent under acid condition. The formations of pertitanic acid complex as TiO_2 in solution appear yellow color.

Reagent

Potassium titanium (IV) oxalate solution: 27.2 mL of concentrated sulfuric acid (H2SO4) dilute with 300 mL dionized water. Then 35.4 f of potassium titanium (IV) oxalate ($K_2TiO(C_2O_4)2{\cdot}2H_2O$) are added to the solution and make volume up to 1 L with dionized water.

Apparatus

UV- visible spectrophotometer, Wavelength 400 nm was used for analyze ferrous ion

25 mL Erlenmeyer flask

Medicine dropper

Procedure

Add 5 mL of potassium titanium (IV) oxalate solution to volumetric flask.

Transfer 1mL of sample to 25 ml Erlenmeyer flask.

Add 25 mL with dionized water and mix. Next, wait 15 min for developed color.

Measured sample by using UV- visible spectrophotometer with wavelength at 400 nm

Calibration curve

Add 5 ml of potassium titanium (IV) oxalate solution to volumetric flask.

Transfer 1mL of 0, 0.1, 1, 5,10 and 20mM of H_2O_2 to 25 ml volumetric flask.

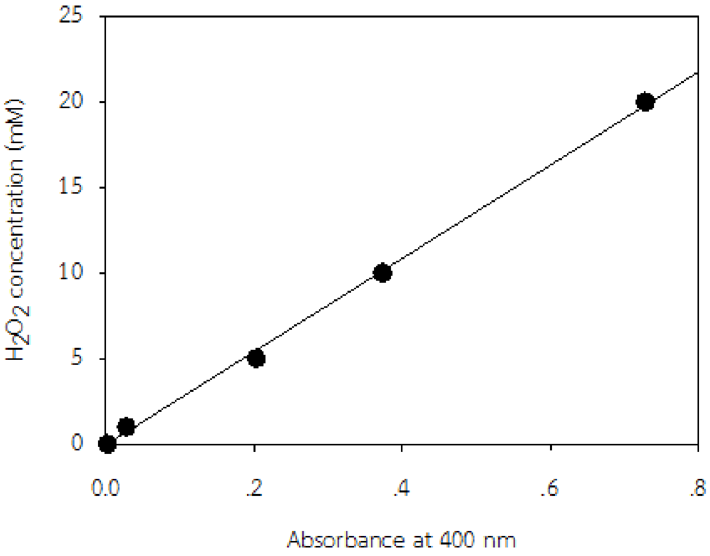
Add 25 mL with dionized water and mix. Next, wait 15 min for developed color.

Measured sample by using UV- visible spectrophotometer with wavelength at 400 nm.

Calculation

$Y = 27.497x - 0.1494$

Where x is absorbance at 400 nm and Y is H_2O_2 concentration (mM)



APPENDIX B

Appendix B: Experimental Apparatus

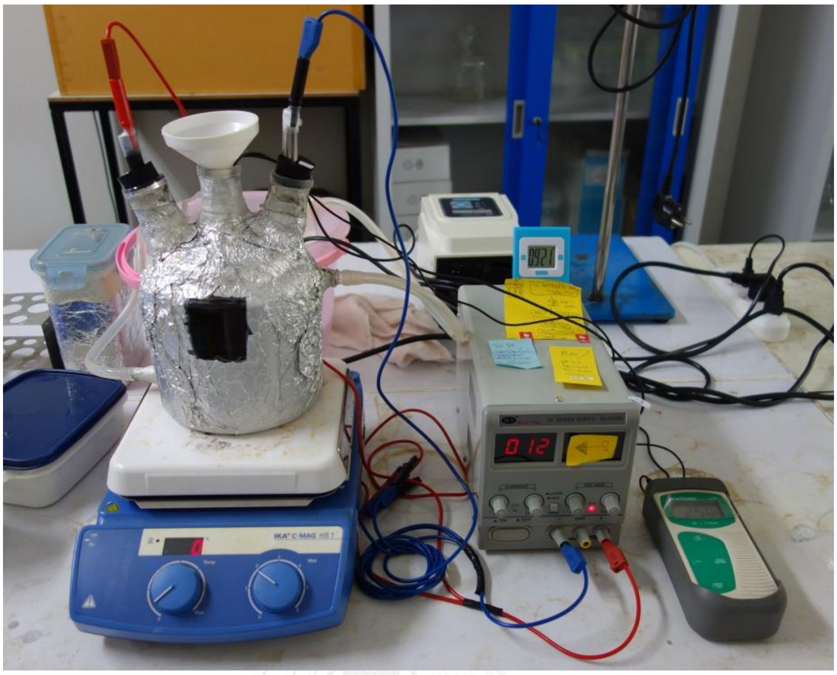


Figure B1. Electro-Fenton reactor setup

Figure B2. Electrodes of electro-Fenton reactor (left: anode, right: cathode)

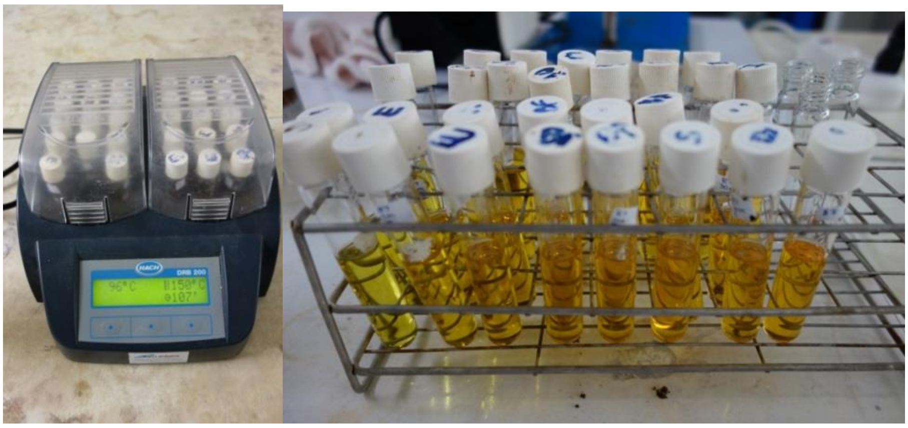


Figure B3. COD analysis

Figure B4. Total Organic Carbon (TOC) analyzer instrument

Figure B5. UV spectrometer

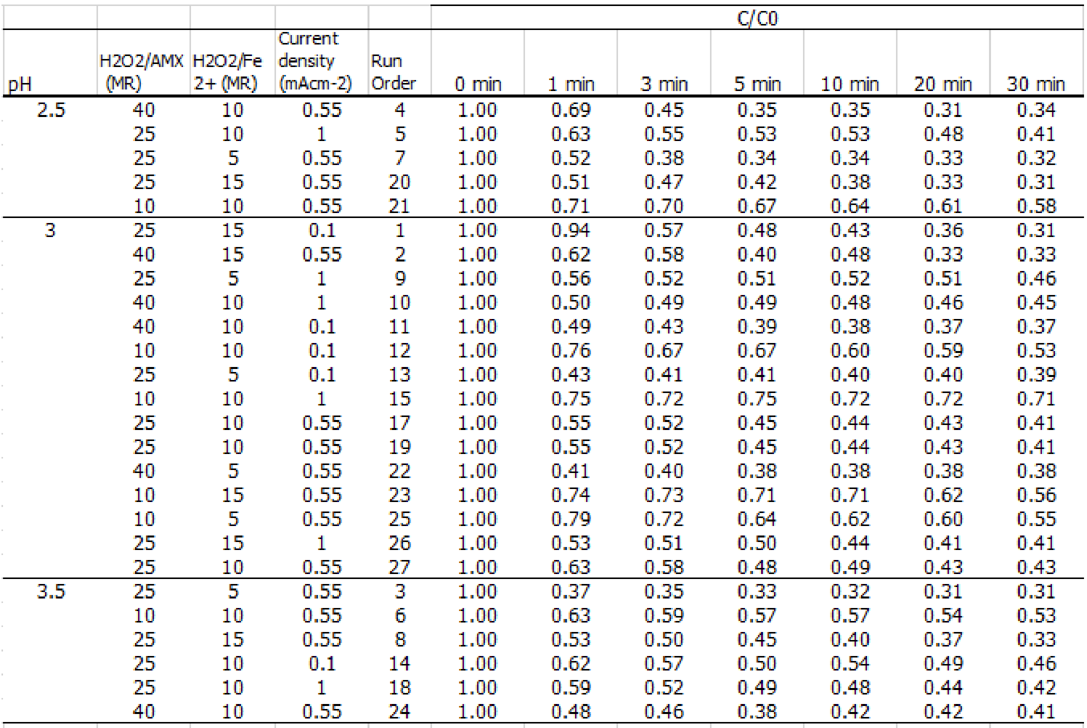
Figure B6. pH meter

APPENDIX C

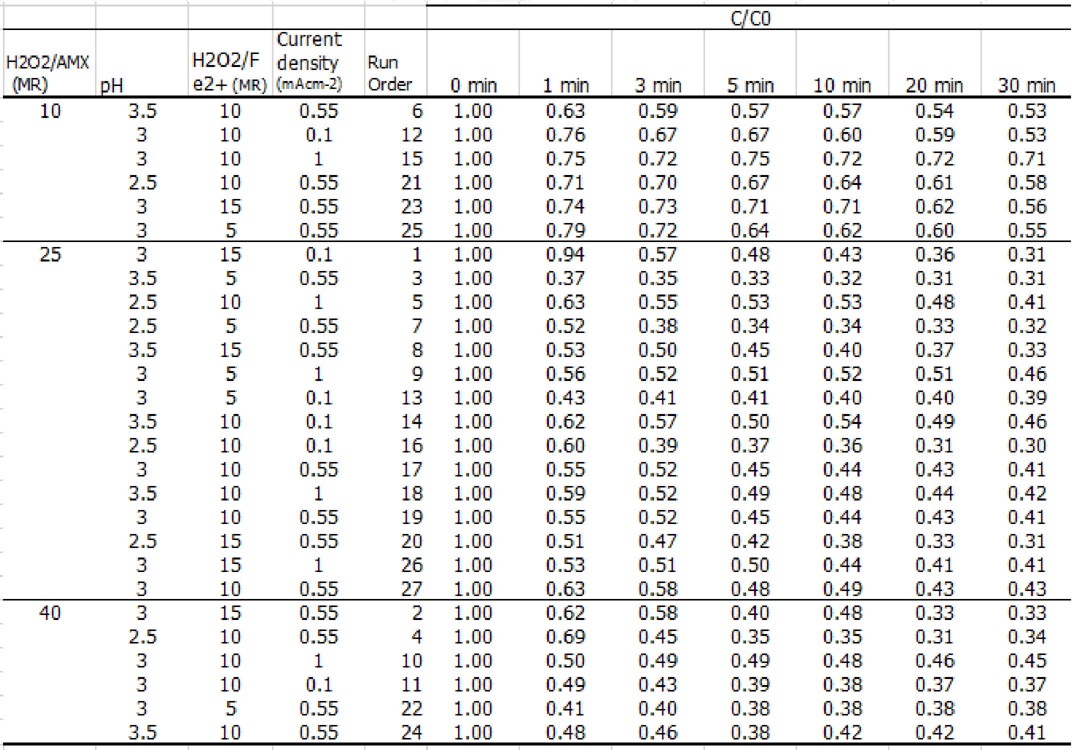
Table C.1 Experimental data of COD by volatilization, electrolysis, electrolysis with H_2O_2, electrolysis with Fe^{2+}, Fenton reaction in controlled experiment

Time (min)	C/C_0				
	Volatilization	Electrolysis	Electrolysis + H_2O_2	Electrolysis + Fe^{2+}	Fenton reaction
0	1.00	1.00	1.00	1.00	1.00
1	1.00	0.98	0.80	0.94	0.59
3	0.99	0.98	0.82	0.89	0.59
5	0.99	0.97	0.82	0.88	0.57
10	0.99	0.97	0.82	0.88	0.53
20	0.99	0.97	0.82	0.88	0.57
30	0.98	0.96	0.82	0.88	0.53

Table C.2 Experimental data of COD/COD$_0$ by electro-Fenton process.



					C/C0						
pH	H2O2/AMX (MR)	H2O2/Fe 2+ (MR)	Current density (mAcm-2)	Run Order	0 min	1 min	3 min	5 min	10 min	20 min	30 min
2.5	40	10	0.55	4	1.00	0.69	0.45	0.35	0.35	0.31	0.34
	25	10	1	5	1.00	0.63	0.55	0.53	0.53	0.48	0.41
	25	5	0.55	7	1.00	0.52	0.38	0.34	0.34	0.33	0.32
	25	15	0.55	20	1.00	0.51	0.47	0.42	0.38	0.33	0.31
	10	10	0.55	21	1.00	0.71	0.70	0.67	0.64	0.61	0.58
3	25	15	0.1	1	1.00	0.94	0.57	0.48	0.43	0.36	0.31
	40	15	0.55	2	1.00	0.62	0.58	0.40	0.48	0.33	0.33
	25	5	1	9	1.00	0.56	0.52	0.51	0.52	0.51	0.46
	40	10	1	10	1.00	0.50	0.49	0.49	0.48	0.46	0.45
	40	10	0.1	11	1.00	0.49	0.43	0.39	0.38	0.37	0.37
	10	10	0.1	12	1.00	0.76	0.67	0.67	0.60	0.59	0.53
	25	5	0.1	13	1.00	0.43	0.41	0.41	0.40	0.40	0.39
	10	10	1	15	1.00	0.75	0.72	0.75	0.72	0.72	0.71
	25	10	0.55	17	1.00	0.55	0.52	0.45	0.44	0.43	0.41
	25	10	0.55	19	1.00	0.55	0.52	0.45	0.44	0.43	0.41
	40	5	0.55	22	1.00	0.41	0.40	0.38	0.38	0.38	0.38
	10	15	0.55	23	1.00	0.74	0.73	0.71	0.71	0.62	0.56
	10	5	0.55	25	1.00	0.79	0.72	0.64	0.62	0.60	0.55
	25	15	1	26	1.00	0.53	0.51	0.50	0.44	0.41	0.41
	25	10	0.55	27	1.00	0.63	0.58	0.48	0.49	0.43	0.43
3.5	25	5	0.55	3	1.00	0.37	0.35	0.33	0.32	0.31	0.31
	10	10	0.55	6	1.00	0.63	0.59	0.57	0.57	0.54	0.53
	25	15	0.55	8	1.00	0.53	0.50	0.45	0.40	0.37	0.33
	25	10	0.1	14	1.00	0.62	0.57	0.50	0.54	0.49	0.46
	25	10	1	18	1.00	0.59	0.52	0.49	0.48	0.44	0.42
	40	10	0.55	24	1.00	0.48	0.46	0.38	0.42	0.42	0.41



					C/C0						
H2O2/AMX (MR)	pH	H2O2/Fe2+ (MR)	Current density (mAcm-2)	Run Order	0 min	1 min	3 min	5 min	10 min	20 min	30 min
10	3.5	10	0.55	6	1.00	0.63	0.59	0.57	0.57	0.54	0.53
	3	10	0.1	12	1.00	0.76	0.67	0.67	0.60	0.59	0.53
	3	10	1	15	1.00	0.75	0.72	0.75	0.72	0.72	0.71
	2.5	10	0.55	21	1.00	0.71	0.70	0.67	0.64	0.61	0.58
	3	15	0.55	23	1.00	0.74	0.73	0.71	0.71	0.62	0.56
	3	5	0.55	25	1.00	0.79	0.72	0.64	0.62	0.60	0.55
25	3	15	0.1	1	1.00	0.94	0.57	0.48	0.43	0.36	0.31
	3.5	5	0.55	3	1.00	0.37	0.35	0.33	0.32	0.31	0.31
	2.5	10	1	5	1.00	0.63	0.55	0.53	0.53	0.48	0.41
	2.5	5	0.55	7	1.00	0.52	0.38	0.34	0.34	0.33	0.32
	3.5	15	0.55	8	1.00	0.53	0.50	0.45	0.40	0.37	0.33
	3	5	1	9	1.00	0.56	0.52	0.51	0.52	0.51	0.46
	3	5	0.1	13	1.00	0.43	0.41	0.41	0.40	0.40	0.39
	3.5	10	0.1	14	1.00	0.62	0.57	0.50	0.54	0.49	0.46
	2.5	10	0.1	16	1.00	0.60	0.39	0.37	0.36	0.31	0.30
	3	10	0.55	17	1.00	0.55	0.52	0.45	0.44	0.43	0.41
	3.5	10	1	18	1.00	0.59	0.52	0.49	0.48	0.44	0.42
	3	10	0.55	19	1.00	0.55	0.52	0.45	0.44	0.43	0.41
	2.5	15	0.55	20	1.00	0.51	0.47	0.42	0.38	0.33	0.31
	3	15	1	26	1.00	0.53	0.51	0.50	0.44	0.41	0.41
	3	10	0.55	27	1.00	0.63	0.58	0.48	0.49	0.43	0.43
40	3	15	0.55	2	1.00	0.62	0.58	0.40	0.48	0.33	0.33
	2.5	10	0.55	4	1.00	0.69	0.45	0.35	0.35	0.31	0.34
	3	10	1	10	1.00	0.50	0.49	0.49	0.48	0.46	0.45
	3	10	0.1	11	1.00	0.49	0.43	0.39	0.38	0.37	0.37
	3	5	0.55	22	1.00	0.41	0.40	0.38	0.38	0.38	0.38
	3.5	10	0.55	24	1.00	0.48	0.46	0.38	0.42	0.42	0.41

					C/C0						
H2O2/Fe2 + (MR)	pH	H2O2/AMX (MR)	Current density (mAcm-2)	Run Order	0 min	1 min	3 min	5 min	10 min	20 min	30 min
5	3.5	25	0.55	3	1.00	0.37	0.35	0.33	0.32	0.31	0.31
	2.5	25	0.55	7	1.00	0.52	0.38	0.34	0.34	0.33	0.32
	3	25	1	9	1.00	0.56	0.52	0.51	0.52	0.51	0.46
	3	25	0.1	13	1.00	0.43	0.41	0.41	0.40	0.40	0.39
	3	40	0.55	22	1.00	0.41	0.40	0.38	0.38	0.38	0.38
	3	10	0.55	25	1.00	0.79	0.72	0.64	0.62	0.60	0.55
10	2.5	40	0.55	4	1.00	0.69	0.45	0.35	0.35	0.31	0.34
	2.5	25	1	5	1.00	0.63	0.55	0.53	0.53	0.48	0.41
	3.5	10	0.55	6	1.00	0.63	0.59	0.57	0.57	0.54	0.53
	3	40	1	10	1.00	0.50	0.49	0.49	0.48	0.46	0.45
	3	40	0.1	11	1.00	0.49	0.43	0.39	0.38	0.37	0.37
	3	10	0.1	12	1.00	0.76	0.67	0.67	0.60	0.59	0.53
	3.5	25	0.1	14	1.00	0.62	0.57	0.50	0.54	0.49	0.46
	3	10	1	15	1.00	0.75	0.72	0.75	0.72	0.72	0.71
	2.5	25	0.1	16	1.00	0.60	0.39	0.37	0.36	0.31	0.30
	3	25	0.55	17	1.00	0.55	0.52	0.45	0.44	0.43	0.41
	3.5	25	1	18	1.00	0.59	0.52	0.49	0.48	0.44	0.42
	3	25	0.55	19	1.00	0.55	0.52	0.45	0.44	0.43	0.41
	2.5	10	0.55	21	1.00	0.71	0.70	0.67	0.64	0.61	0.58
	3.5	40	0.55	24	1.00	0.48	0.46	0.38	0.42	0.42	0.41
	3	25	0.55	27	1.00	0.63	0.58	0.48	0.49	0.43	0.43
15	3	25	0.1	1	1.00	0.94	0.57	0.48	0.43	0.36	0.31
	3	40	0.55	2	1.00	0.62	0.58	0.40	0.48	0.33	0.33
	3.5	25	0.55	8	1.00	0.53	0.50	0.45	0.40	0.37	0.33
	2.5	25	0.55	20	1.00	0.51	0.47	0.42	0.38	0.33	0.31
	3	10	0.55	23	1.00	0.74	0.73	0.71	0.71	0.62	0.56
	3	25	1	26	1.00	0.53	0.51	0.50	0.44	0.41	0.41

					C/C0						
Current density (mAcm-2)	pH	H2O2/AMX (MR)	H2O2/Fe2 + (MR)	Run Order	0 min	1 min	3 min	5 min	10 min	20 min	30 min
0.1	3	25	15	1	1.00	0.94	0.57	0.48	0.43	0.36	0.31
	3	40	10	11	1.00	0.49	0.43	0.39	0.38	0.37	0.37
	3	10	10	12	1.00	0.76	0.67	0.67	0.60	0.59	0.53
	3	25	5	13	1.00	0.43	0.41	0.41	0.40	0.40	0.39
	3.5	25	10	14	1.00	0.62	0.57	0.50	0.54	0.49	0.46
0.55	3	40	15	2	1.00	0.62	0.58	0.40	0.48	0.33	0.33
	3.5	25	5	3	1.00	0.37	0.35	0.33	0.32	0.31	0.31
	2.5	40	10	4	1.00	0.69	0.45	0.35	0.35	0.31	0.34
	3.5	10	10	6	1.00	0.63	0.59	0.57	0.57	0.54	0.53
	2.5	25	5	7	1.00	0.52	0.38	0.34	0.34	0.33	0.32
	3.5	25	15	8	1.00	0.53	0.50	0.45	0.40	0.37	0.33
	3	25	10	17	1.00	0.55	0.52	0.45	0.44	0.43	0.41
	3	25	10	19	1.00	0.55	0.52	0.45	0.44	0.43	0.41
	2.5	25	15	20	1.00	0.51	0.47	0.42	0.38	0.33	0.31
	2.5	10	10	21	1.00	0.71	0.70	0.67	0.64	0.61	0.58
	3	40	5	22	1.00	0.41	0.40	0.38	0.38	0.38	0.38
	3	10	15	23	1.00	0.74	0.73	0.71	0.71	0.62	0.56
	3.5	40	10	24	1.00	0.48	0.46	0.38	0.42	0.42	0.41
	3	10	5	25	1.00	0.79	0.72	0.64	0.62	0.60	0.55
	3	25	10	27	1.00	0.63	0.58	0.48	0.49	0.43	0.43
1	2.5	25	10	5	1.00	0.63	0.55	0.53	0.53	0.48	0.41
	3	25	5	9	1.00	0.56	0.52	0.51	0.52	0.51	0.46
	3	40	10	10	1.00	0.50	0.49	0.49	0.48	0.46	0.45
	3	10	10	15	1.00	0.75	0.72	0.75	0.72	0.72	0.71
	3.5	25	10	18	1.00	0.59	0.52	0.49	0.48	0.44	0.42
	3	25	15	26	1.00	0.53	0.51	0.50	0.44	0.41	0.41

Table C.3 Experimental data of COD/COD$_0$ by electro-Fenton process in electro-Fenton

Time (min)	Opt		
	COD (mgL^{-1})	DOC (mgL^{-1})	AOS
0.00	133.74	64.61	-4.74
1.00	78.33	52.61	-2.37
3.00	65.89	48.61	-1.83
5.00	58.10	46.61	-1.38
10.00	49.00	45.61	-1.28
20.00	50.08	42.61	-1.11
30.00	45.67	38.61	-1.19

VITA

Miss Paranee Boonchuay was born on July 16, 1989 in Surathani province. She graduated Bachelor’s degree of Environmental Engineering from Khon Kaen University. After that she continued study in Master’s degree of science in Environment management, Chulalongkorn University

Some part of this thesis has been published in proceeding of The 4 th TIChE international conference, Furama hotel, Chiang mai, Thanliand on 18-19 December, 2014.