REMOVAL OF LIGNIN IN WASTEWATER FROM PULPING PROCESSES BY FENTON AND MODIFIED-FENTON PROCESSES

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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

การกำจัดลิกนินในน้ำเสียจากอุตสาหกรรมผลิตเยื่อกระดาษด้วยกระบวนการเฟนตันและเฟนตันแบบประยุกต์

นางสาววิภาดา วิศาลศิริรักษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

Thesis Title	REMOVAL OF LIGNIN IN WASTEWATER FROM PULPING PROCESSES BY FENTON AND MODIFIED-FENTON PROCESSES
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Field of Study	Environmental Management
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วิภาดา วิศาลศิริรักษ์ : การกำจัดลิกนินในน้ำเสียจากอุตสาหกรรมผลิตเยื่อกระดาษด้วยกระบวนการเฟนตันและเฟนตันแบบประยุกต์ (REMOVAL OF LIGNIN IN WASTEWATER FROM PULPING PROCESSES BY FENTON AND MODIFIED-FENTON PROCESSES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร.อรอนงค์ ลาภปริสุทธิ{, 128 หน้า.

ลิกนินเป็นสารประกอบอินทรีย์ที่พบในน้ำเสียอุตสาหกรรมผลิตเยื่อกระดาษ ซึ่งสารดังกล่าวก่อให้เกิดสีในน้ำเสียและยังเป็นพิษต่อสิ่งมีชีวิตในน้ำอีกด้วย ดังนั้นน้ำเสียจากโรงงานเยื่อกระดาษที่มีสารดังกล่าวปนเปื้อนจึงมีความจำเป็นที่ต้องถูกบำบัดก่อนปล่อยทิ้งสู่แหล่งน้ำธรรมชาติ ในงานวิจัยนี้ได้ทำการศึกษาการกำจัดลิกนินด้วยกระบวนการออกซิเดชันขั้นสูง โดยมุ่งเน้นศึกษากระบวนการเฟนตันแบบดั้งเดิมและเฟนตันแบบประยุกต์ในแง่ของสภาวะที่เหมาะสมสำหรับการดำเนินระบบเพื่อให้เกิดประสิทธิภาพมากที่สุด ตัวแปรที่ทำการศึกษาในครั้งนี้ได้แก่ อัตราส่วนความเข้มข้นระหว่างเฟอรัสไอออนและไฮโดรเจนเปอร์ออกไซด์ ค่าพีเอชเริ่มต้น ปริมาณสารทำปฏิกิริยาที่เหมาะสม สภาวะในการจ่ายสารทำปฏิกิริยาและความหนาแน่นของกระแสไฟฟ้า ผลการทดลองพบว่าสภาวะแบ่งจ่ายทั้งเหล็กและไฮโดรเจนเปอร์ออกไซด์ 12 ครั้งมีประสิทธิภาพในการย่อยสลายสี ลิกนิน และซีโอดีสูงสุดเนื่องจากลดการยับยั้งการเกิดอนุมูลไฮดรอกซิล โดยสามารถลดสีได้ 45% ลดปริมาณลิกนินได้ 39% และลดซีโอดีไปได้ 38% ที่สภาวะค่าอัตราส่วนระหว่างเฟอรัสไอออนและไฮโดรเจนเปอร์ออกไซด์ที่ 1:2.5 ค่าพีเอชเริ่มต้นที่ 3 และปริมาณเหล็กเฟอรัสที่ 400 มิลลิกรัมต่อลิตร นอกจากนี้เมื่อศึกษาปริมาณสลัดจ์ที่เกิดขึ้นพบว่าการแบ่งจ่ายทั้งเหล็กและไฮโดรเจนเปอร์ออกไซด์สามารถลดปริมาณสลัดจ์ไปได้ 20.7% เมื่อเปรียบเทียบกับการจ่ายแบบครั้งเดียวในช่วงเริ่มต้นปฏิกิริยา สำหรับสภาวะที่เหมาะสมของกระบวนการอิเล็กโตรเฟนตันสำหรับบำบัดลิกนิน คือ ค่าอัตราส่วนระหว่างเฟอรัสไอออนและไฮโดรเจนเปอร์ออกไซด์ที่ 1:1 และค่าความหนาแน่นกระแสไฟฟ้า 200 แอมแปร์ต่อตารางเมตรของขั้วไฟฟ้า อย่างไรก็ตามประสิทธิภาพในการย่อยสลายลิกนินในกระบวนการอิเล็กโตรเฟนตันน้อยกว่าการแบ่งจ่ายสารเคมีในกระบวนการเฟนตันเนื่องจากเหล็กเฟอริกไม่สามารถเปลี่ยนรูปกลับมาเป็นเหล็กเฟอรัสได้ ดังนั้นการบำบัดด้วยกระบวนการเฟนตันแบบแบ่งจ่ายสารเคมีถือว่ามีประสิทธิภาพดีในการบำบัดลิกนินจากน้ำเสียอุตสาหกรรมผลิตเยื่อกระดาษ

สาขาวิชา	การจัดการสิ่งแวดล้อม	ลายมือชื่อนิสิต	....
ปีการศึกษา	2557	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....

5687640020 : MAJOR ENVIRONMENTAL MANAGEMENT

KEYWORDS: PULP MILL WASTEWATER / LIGNIN / FENTON / MODIFIED-FENTON

WIPADA WISARNSIRIRAK: REMOVAL OF LIGNIN IN WASTEWATER FROM PULPING PROCESSES BY FENTON AND MODIFIED-FENTON PROCESSES. ADVISOR: DR.ON-ANONG LARPPARISUDTHI{, 128 pp.

Lignin is the organic compound in pulp mill wastewater that can cause high level of color and toxicity pollutant to living organisms. Therefore, pulp and paper industries needed to be treated prior to discharge into the environment. Advanced oxidation processes by Fenton and modified-Fenton were investigated in order to determine the process optimization and performance of reaction. The effect of operating parameter included ratio of Fe^{2+} and H_2O_2, initial pH, chemicals dosage, step feeding operation and current density were investigated to indicate the optimum operating conditions. Results showed that the performance of the process when using step feeding of both Fe^{2+} and H_2O_2 was found to be the highest oxidation efficiency on color, lignin and COD removal because this operation could reduce the scavenging effect on the reaction process. 45% of color removal, 39% of lignin removal and 38% of COD removal in term of oxidation efficiency were achieved in 1 hour under Fe^{2+} to H_2O_2 ratio of 1:2.5, initial pH of 3 and Fe^{2+} concentration of 400 mg/l. Moreover, this operation also reduce the sludge production of 20.7% at the same removal efficiency as initial feeding. For electro-Fenton process, optimum operating conditions were found to be Fe^{2+} to H_2O_2 ratio of 1:1 and current density of 200 A/m^2. However, removal efficiency in electro-Fenton was less than step feed operation in Fenton due to no Fe^{2+} regeneration. Thus, Fenton process with step feeding mode operation was effective for the treatment of pulp mill wastewater.

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

ACKNOWLEDGEMENTS

I would like to express my sincere to my thesis advisor, Dr. On-anong Larpparisudthi, for valuable suggestions, strong encouragement and extremely help in making this work. Moreover, I am grateful for her support and her motivation for me to achieve this thesis.

My gratitude is also extended to the chairmen Asst. Prof. Dr.Chantra Tongcumpou and Assoc. Prof. Dr.Patiparn Punyapalakul, Dr.Nonglak Boonrattanakij and Asst. Prof. Dr.Janjit Aeumjaturapat for serving as the thesis committee. They give me the valuable comments which enhance the quality of this work.

I would like to thank the SCG paper company for providing pulp mill effluent and their support on my research work.

I also would like to express my appreciation to all staff and colleagues at inter-department of environmental management and department of environmental engineering, Chulalongkorn University for financial assistances and laboratory supports.

Finally, a special thanks goes to my family for their love, understanding, encouragement and every support in my entire work. Without these assistance, my research has not been successfully accomplished.

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CHARPTER 1

INTRODUCTION

1.1 Background of the research

Pulp industries have rapidly grown to supply both domestic demand and export for many years as a result of the economic growth. As a result, pulp mill has been considered as one of major polluting industries that produces a variety of pollutants and releases them into the environment. In Thailand, there are more than 90 plants of pulp and paper mill resulting in large amounts of wastewater are generated, about 29-40 m^3 of wastewater for each ton of pulp produced (Thongkrua, 2010). The most pollutants in pulp mill effluent include organic in nature, chlorinated phenolic compounds, lignin and its derivatives. Lignin is the main component responsible for color in pulping wastewater. Lignin composes of phenolic groups such as P-coumaryl alcohol unit, Coniferyl alcohol unit and Synapyl alcohol unit linked together at several different locations. It uses to hold the cell together and gives the wood structure more strength. About 21-29% of wood is lignin which ends up as waste (Rao, 1987; Simon, 2004). The structure of lignin is very complex and these elements are arranged differently therefore conventional wastewater treatment processes are not capable to particularly separate nor remove. Pulp mill effluent which has strong color and contain high lignin, inhibits the growth of aquatic lifess by reducing the penetration of sunlight, and resulting in a reduction of photosynthetic processes. The color organic compounds also have tended to form a ring structure with metals to become toxic to aquatic organisms. Consequently, it is necessary that the colored wastewater should be treated before discharge into the environment.

Nowadays, advanced oxidation processes (AOPs) are commonly used for the lignin and color removal. Fenton processes which one of AOPs are the combination of Fe^{2+} and H_2O_2 in acidic solution to generate OH• to break down the contaminants into harmless compounds. Electro-Fenton processes which are one type of modified-Fenton processes are the combination of Fenton’s reagent and electrochemical reactions. In these processes, the electrical current induces the generation of Fe^{2+} by oxidation of iron electrode or the generation of H_2O_2 by reduction of oxygen or the regeneration of Fe^{3+} to Fe^{2+} resulting in OH· production to attack pollutants. COD removal efficiency in tissue wastewater using electro-Fenton processes was about 80%, after 60 minutes (Un, Topal, Oduncu, & Ogutveren, 2014).

In this study, the removal of color and lignin in pulp mill wastewater by Fenton and modified-Fenton processes were investigated as a function of initial pH, ratio of Fe^{2+} and H_2O_2, Fenton’s reagent dose, current density and step feeding mode in order to determine the optimum treatment conditions and studied the performance of reaction.

Removal efficiency of process is studied in term of COD reduction, lignin degradation and color removal.

1.2 Objectives of investigation

1.2.1 To determine the optimum operating conditions of the lignin and color removal by Fenton and modified-Fenton processes.

1.2.2 To investigate the lignin and color removal by Fenton and modified-Fenton processes.

1.3 Hypotheses

1.3.1 Fenton and modified-Fenton processes could be effective for removal of color and lignin in pulp mill wastewater.

1.3.2 The color and lignin removal efficiency in Fenton and modified-Fenton processes depends on initial pH, ratio of Fe^{2+} and H_2O_2, Fenton’s reagent dose, current density and step feeding.

1.4 Scope of investigation

1.4.1 All experiments carried out in laboratory scale with batch-mode operation at laboratory of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Thailand.

1.4.2 All experiments were conducted at room temperature.

1.4.3 Synthetic wastewater was used. Real wastewater sample was received from SCG paper company, Banpong Pulp Mill, Ratchaburi, Thailand.

1.4.4 Operating parameters in Fenton process depended on initial pH, ratio of Fe^{2+} and H_2O_2, chemicals dosage and current density for electro-Fenton process.

1.4.5 Original and step feedings were compared in term of color, lignin and COD removal efficiency.

1.5 Expected benefits

1.5.1 Hydroxyl radicals can effectively drgrade lignin so that the color and COD in treated wastewater would be in the acceptable range.

1.5.2 Fenton and modified-Fenton processes would be effectively applied for the other types of wastewater.

CHARPTER 2

THEORIES AND LITERATURE REVIEWS

2.1 Pulping processes (Lavigne, 1979; UNEP, 1996)

2.1.1 Wood preparation

The bark of logs can be removed by going through a debarker. After that, the logs are cut by multi-knife chipper into suitable sized pieces, and then they are screened to remove the overlarge chips.

2.1.2 Pulp disintegration

Lignin could be separated from the cellulose in these processes.

2.1.2.1 Mechanical pulping process

The fibers are physically separated from each other by grinder. An objective of these processes is to maintain lignin in order to achieve in high yield with acceptable properties and brightness. The yield of paper per unit volume of wood typically results in high, up to 95% (Tunay, Erdeml, Kabdasli, & Olmez, 2008). However, mechanically produced pulp provides low grade pulp and highly colored.

2.1.2.2 Chemical pulping process

It involves the use of chemicals mixed with raw materials to digest chips and gives more flexible of fibers, resulting in high strength of properties. Nevertheless, the yield of pulp is about 40-50% of the original wood material. There are 2 types of chemical pulping which are alkaline and sulfite processes.

2.1.2.2.1 Alkaline processes

(1) Soda process

A process uses an alkaline solution (only NaOH) as the cooking chemical mixed with chips for digestion. It gives pulp with lower strength than other chemical pulping and can be used for easy pulped materials.

(2) Kraft process

This process uses the alkaline solution consisting of NaOH and Na_2S as cooking liquor to digest the woods. Na_2S acts as buffer which allows digestion to be possible at lower pH, therefore, it reduces the damage to fibers and increases pulp strength. Major advantage of this process is to apply to all types of wood and produced a variety of pulp used.

2.1.2.2.2 Sulfite process

A process uses acidic mixture of sulfurous (H_2SO_3) and bisulfite ion (HSO_3^-) as cooking chemical to digest the lignin bonds in wood fibers. They account for less than 10% of the total chemical pulp production because this process permits the production of many different types.

2.1.2.3 Semi-chemical pulping process

A process is the combination of chemical and mechanical processes to digest pulp fibers. Wood chips are softened in a digester with chemicals and then the pulps are completed by mechanical methods. Pulp yield ranges from 55-90%, depending on the process used. Nonetheless, residue lignin in pulps is also high (EPA, 2002).

2.1.3 Washing

After the wood becomes to pulp, the pulp is washed to remove some cooking chemicals, dissolved lignin and dissolved organic compounds from wood chips by going through a series of washer and screens.

2.1.4 Bleaching

After washing process, the pulps have bleached to increase their brightness by adding some chemicals to the pulps. The commonly bleaching chemicals used are element chlorine (Cl), chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), and sodium hypochlorite (NaClO) that can transform lignin into an alkali-soluble form. After bleaching process is completed, the pulp go through the paper-making processes.

2.2 Pulp mill wastewater

Pulp and paper mill wastewater is currently concerned because large amounts of wastewater are produced, about 29-40 m^3/ton of pulp (Pollution Control, 2001). The major sources of pollutants occur at pulping and bleaching stages. Moreover, the characteristic of wastewater generated depends on wood materials, process treatment technology and the amount of wastewater to be used in each process. Table 2.1 shows commonly component of pulp mill wastewater.

Table 2. 1 The component of pulp mill wastewater (Alén, Rytkönen, & McKeough, 1995)

Components	Content (% by solid weight)
Organic compounds	
- Lignin	25-45%
- Aliphatic carboxylic acids	25-35%
- Other compounds	3-5%
Inorganic compounds	
- Sodium	17-20%
- Sulfur	3-5%

2.3 Treatment technologies of pulp and paper mill wastewater

2.3.1 Physical treatment

2.3.1.1 Adsorption

Adsorption technology is effective application in wastewater treatment. Performance depends on type of adsorbent and characteristic of wastewater to be treated. Shawwa et.al. (2001) reported that using activated coke as adsorbent can remove 90% of color, COD, DOC and AOX in bleaching wastewater.

2.3.1.2 Ion exchange

The pollutants go through the ion-exchange resin until the available exchange sites are saturated. However, this method has not been widely used for color removal because these perform poorly in the presence of other additive in wastewater. Moreover, high operating cost and different characterization of wastewater are the limitation of this process (Laazlo, 1995).

2.3.2 Chemical treatment

2.3.2.1 Coagulation

Coagulation is commonly used by adding chemicals to wastewater to produce the floc forming that settle down by gravity. Metal salt of iron and aluminum are widely used as coagulant to reduce the color in pulp mill wastewater. According to the Almemark and Ekengren (1989) study, they found that alum coagulation can remove 80% of color in pulp mill effluent.

2.3.3 Biological treatment

Some colorants and organic matters provide a nutrient for microorganism and are converted into biomass and water. Kumar et al. (2014) reported that the microorganism namely *Paecilomyces* sp. can be significantly remove in 80% of color, 81% of lignin, 76% of AOX and 74% of phenol after 7 days of treatment. Table 2.2 shows advantages and limitations of pulp and paper mill wastewater treatment technologies.

Each type of process has some common advantages and disadvantages. The effectiveness of such methods is highly varied by the wastewater characterization. However, of the most interest in this study are Fenton and electro-Fenton methods.

Table 2. 2 Technologies to treat pulp and paper mill wastewater (Anjaneyulu, 2005)

Treatment technologies	Advantages	Limitations
1. Physical treatment		
- Adsorption	-High removal efficiency	-High cost regeneration process
- Ion exchange	-Regeneration with low loss of adsorbents	-Specific application
2. Chemical treatment		
- Coagulation	-High removal efficiency	-Sludge production
3. Biological treatment	-Biogas is produced under anaerobic condition	-Longer retention time -Specific removal

2.4 Lignin

2.4.1 Properties and structure of lignin

In nature, cellulose, hemicelluloses and lignin are the major components of wood as shown in Table 2.3. Each of these components contributes to fiber properties that impact to product properties. Lignin is brown color chemical and tasteless compound. It acts as the glue to hold the celluloses together to control the liquid transportation in the living plant.

Table 2. 3 Major chemical components in softwood and hardwood (Tengcharoen, 2003)

Constituent	Percentage of lignin (%)	
	Softwood	Hardwood
Cellulose	45	43
Hemicelluloses	5-20	15-30
Lignin	24-32	17-25

In lignin structure, phenylpropane monomers (C_9) or phenolic units namely P-coumaryl, Conifeyl and Synapyl alcohol are the major components in lignin structure. The structure of phenylpropane monomers presents in Figure 2.1. A linkage can occur at different locations on each phenolic unit that causes many different linkage types to be possible. The most commonly linkages are shown in Figure 2.2. Table 2.4 presents the amount of linkage in softwood and hardwood lignin. Moreover, lignin contains many functional groups that affect to reactivity. It mostly contains methoxyl groups as presented in Table 2.5.

Table 2. 4 Percentage of linkage in softwood and hardwood lignin (Runge, 2005)

Linkage types	Dimer structure	Percentage of total linkage	
		Softwood lignin	Hardwood lignin
β-0-4	Phenylpropane β-aryl	50	60
α-0-4	ether	2-8	7
β-5	Phenylpropane α-aryl	9-12	6
5-5	ether	10-11	5
4-0-5	Phenylcoumaran	4	7
β-1	Biphenyl	7	7
β-β	Diayl ether	2	3
	β-β-linked structures		
	1,2-diarylpropane		

Table 2. 5 Functional groups in softwood lignin (Technology)

Functional groups	Functional groups content per 100 C_9 units
Carbonyl	10-15
Benzyl alcohol	15-20
Phenolic hydroxyl	15-30
Methoxyl	92-96

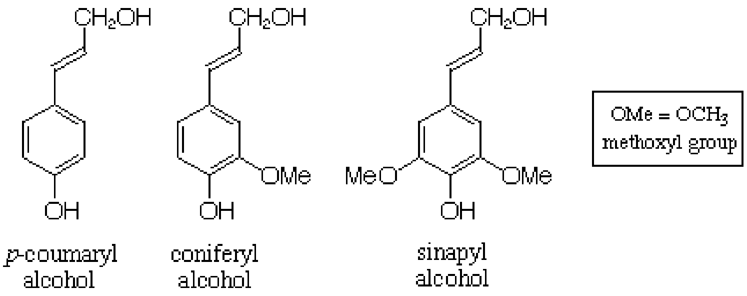


Figure 2. 1 Three phenylpropane monomers in lignin molecule (Chotinantasaeth, 2007)

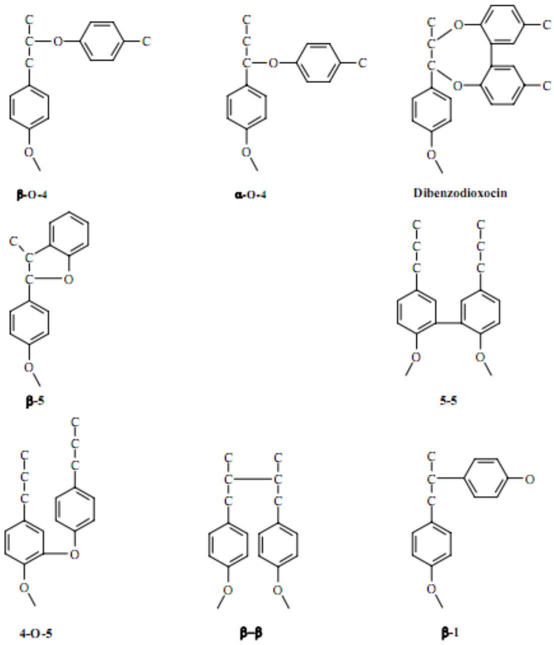


Figure 2. 2 Commonly linkage of lignin (Runge, 2005)

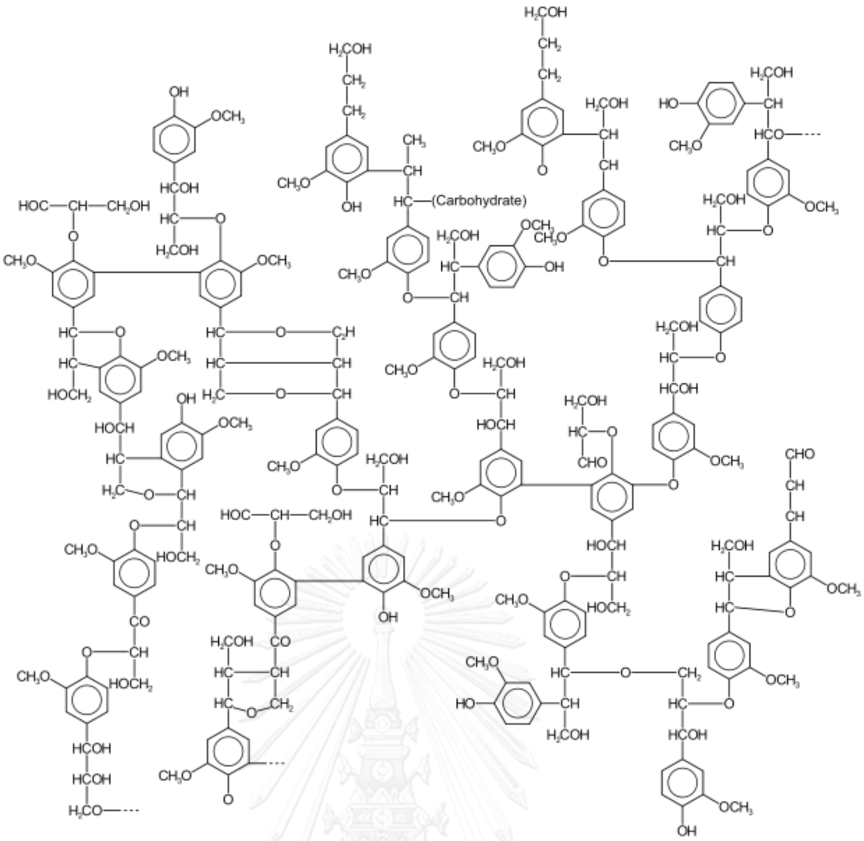


Figure 2. 3 Hypothetical structure of softwood lignin (Hammel & Cullen, 2008)

Lignin is very complex compound due to various linkages between the phenylpropane units and functional groups. Figure 2.3 shows the general softwood lignin structure.

2.4.2 Types of lignin

Lignin can be categorized into P-Hydroxyphenyl lignin, Guaiacyl lignin and Syringyl lignin. P-Hydroxyphenyl lignin contained principally of P-coumaryl alcohol is found in grasses and agricultural crops. Guaiacyl lignin, found in softwood and hardwood, composes of coniferyl monomer while Syringyl lignin, generally found in hardwood, contains sinapyl alcohol. The ratio of guaiacyl to sinapyl lignin is varied from 4:1-1:2 among different hardwood (R.A, 1983). Moreover, there are many types of lignin that can be divided by source and pulping process such as wheat straw lignin, sulfite lignin and kraft lignin.

2.4.3 Use of lignin

The commonly use of lignin can be mixed in concrete mixture to give more strength. In addition, it can be used for the production of plasterboard to reduce the water required. The reduction in amount of water makes lower temperatures to dry the plasterboard for saving energy. Other application of lignin are additive for the composite color, pesticides, emulsifier, wetting agents and surfactants for oil recovery.

2.4.4 Effect of lignin on the environment

Color in pulp mill effluent is one of environmental concerns. Although color is not concerned as major problems, it has been realized that the colored wastewater can affect on the visual pollution and inhibit the growth of aquatic lifes by reducing the penetration of sunlight, to reduce the photosyntetic. In addition, Rao and Dutta (1987) found that lignocellulose can be precipitated at the bottom leading to the decreasing of dissolved oxygen in water. Moreover, lignin can be absorbed on slowly biodegradable compounds to cause the biological effects according to the following studies

Dekker et al. (2002) found that lignin affect on the growth of fungal namely *Botryosphaeris* sp. In addition, Yakovleva et al. (2004) reported that lignin wastewater produces a genetic hazard to both of mollusks and corn. Moreover, Pessala et al. (2004) reported that half maximal effective concentration (EC_{50}) is about 34 mg/l for lignin in bleaching wastewater and 11 mg/l of EC_{50} for commercial alkali lignin.

2.5 Fenton process

Fenton reaction is the combination of Fe^{2+} and H_2O_2 under acidic solution to generate OH• and is considered as one of the most effective and economical oxidation method. However, it has a major drawback as given in Table 2.6.

Table 2. 6 Major advantages and disadvantages of Fenton process

Advantages	Disadvantages
1. High removal efficiency 2. Cost effective 3. Simple and operate easily 4. No energy required	1. Disposal cost is normally expensive. 2. Ferrous ions are used rapidly than they can be generated in decreasing of oxidation rate.

2.5.1 Fenton mechanism

In Fenton reaction, H_2O_2 is decomposed by Fe^{2+} to generate OH· under acidic solution as shown in the equation 2.1 (Tudthiam, 2012)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \quad : \quad k_1 = 70\ M^{-1}S^{-1} \qquad (2.1)$$
$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \quad : \quad k_2 = 0.001\text{-}0.01\ M^{-1}S^{-1} \qquad (2.2)$$

$$FeOOH^{2+} \rightarrow HO_2\cdot + Fe^{2+} \qquad (2.3)$$

Fe^{3+} can return to Fe^{2+} by another molecule of H_2O_2. However, this reaction occurs slowly comparing to reaction in equation 2.1, therefore, Fe^{3+} is mainly found in the system. In some cases, Fe^{3+} might be used instead of Fe^{2+} as a source of iron so called as a Fenton-like reaction as shown in equation 2.2-2.3. Under an excess of Fe^{2+}, the $OH\cdot$ generated can further react with Fe^{2+} to produce Fe^{3+} as shown in equation 2.4. As seen in equation 2.10, H_2O_2 can act as $OH\cdot$ scavenger to reduce the process efficiency. Fenton reaction is very complex reaction and side reactions are given in equation 2.4-2.11 (Tudthiam, 2012)

$$Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^- \quad : \quad k_3 = 4.3x10^6\ M^{-1}S^{-1} \qquad (2.4)$$

$$H_2O_2 \rightarrow HO_2^{\cdot} + H^+ \quad : \quad k_4 = 1.59x10^{-12}\ M^{-1}S^{-1} \qquad (2.5)$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + O_2^{\cdot} \quad : \quad k_5 = 1.2x10^6\ M^{-1}S^{-1} \qquad (2.6)$$

$$Fe^{2+} + O_2^{\cdot} \rightarrow Fe^{3+} + O_2 \quad : \quad k_6 = 1x10^7\ M^{-1}S^{-1} \qquad (2.7)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad : \quad k_8 = 1.2x10^6\ M^{-1}S^{-1} \qquad (2.8)$$

$$OH\cdot + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad : \quad k_9 = 2.7x10^7\ M^{-1}S^{-1} \qquad (2.9)$$

$$H_2O + H_2O \rightarrow H_2O_2 + O_2 \quad : \quad k_{10} = 8.3x10^5\ M^{-1}S^{-1} \qquad (2.10)$$

$$OH\cdot + OH\cdot \rightarrow H_2O_2 \quad : \quad k_{11} = 5.3x10^9\ M^{-1}S^{-1} \qquad (2.11)$$

After that, the hydroxyl radicals react with the contaminent (RH) by the abstraction of hydrogen to generate organic radicals (R·) and then they go to react with oxygen and H_2O_2 suddenly as summarize in equation 2.12-2.14 (Methatham, 2011).

$$R\cdot + O_2 \rightarrow ROO\cdot \qquad (2.12)$$

$$2R\cdot + O_2 \rightarrow 2RO\cdot \qquad (2.13)$$

$$R\cdot + H_2O_2 \rightarrow ROH + OH^- \qquad (2.14)$$

Because ROO· and RO· are not steady, they go to combine with ferrous ions and photons to produce ROH and ROOH which can be further oxidized and convert the intermediates to end products as given in equation 2.15-2.18 (Porananont, 2006).

$$ROO\cdot + Fe^{2+} \rightarrow ROO\text{-}Fe \qquad (2.15)$$

$$ROO\text{-}Fe + H^+ \rightarrow R\text{-}OOH + Fe^{3+} \qquad (2.16)$$

$$RO\cdot + Fe^{2+} \rightarrow RO\text{-}Fe \qquad (2.17)$$

$$RO\text{-}Fe + H^+ \rightarrow R\text{-}OH + Fe^{3+} \qquad (2.18)$$

2.5.2 Effect of process conditions (Simon, 2004)

2.5.2.1 pH

Fenton process is generally operated in acidic conditions. Optimum pH ranges 2-4 and it is the most efficient at pH of 2.8 (Plgnatello, 1992). If the pH is too high, iron species can begin to precipitate as $Fe(OH)_3$ thus the amount of catalyst will be decreased. In addition, H_2O_2 can be decomposed to oxygen and water at the higher pH. On the other hand, lower pH can be also promoted H_2O_2 convert to oxonium ion by combined one proton, leading to the decreasing rate in Fenton reaction as shown in equation 2.19.

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{2.19}$$

2.5.2.2 Temperature

Temperature between 20-30°C is the optimum range because of higher process efficiency in term of reaction rate in this range. Generally, rate of Fenton reaction increases with increasing temperature. However, as temperature rises above 40-50°C, the efficiency of process will be decreased due to the degradation of hydrogen peroxide into oxygen and water.

2.5.2.3 Ratio of Fe^{2+} and H_2O_2

The removal efficiency tends to increase with increasing H_2O_2 and Fe^{2+} concentration. Nevertheless, H_2O_2 and Fe^{2+} are not only reacted to produce hydroxyl radicals, but are also scavengers of hydroxyl radicals on process efficiency as shown in equation 2.4 and 2.10. Therefore, the ratio of Fe^{2+} to H_2O_2 affect the rates of $OH\cdot$ production and scavenging. It is an important to determine optimum ratio of Fe^{2+} and H_2O_2. Typically, the optimum ratio of Fe^{2+} and H_2O_2 ranges between 1:2-1:25 (wt/wt).

2.5.2.4 Inorganic anion concentration

Degradation rate of Fenton processes decreases due to the presence of anions that can be scavenger of $OH\cdot$. Anions, such as bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), phosphate (PO_4^{3-}) and chlorine (Cl^-), can reduce the process efficiency in direct proportion to their concentration as shown in equation 2.20-2.23. From the study, Pighatello (1992) observed the degradation of 2,4-dichlorophenoxy acetic acid (2,4-D) by Fenton-like reaction. He found that SO_4^{2-} or Cl^- has more potential the inhibition of 2,4-D removal than NO_3^- or ClO_4^-.

$$OH\cdot + HCO_3^- \rightarrow \cdot CO_3^{2-} + H_2O \tag{2.20}$$

$$OH\cdot + CO_3^{2-} \rightarrow \cdot CO_3^{2-} + OH^- \tag{2.21}$$

$$OH\cdot + PO_4^{3-} \rightarrow \cdot HPO_4^{2-} + OH^- \tag{2.22}$$

$$OH\cdot + Cl^- \rightarrow \cdot Cl + OH^- \tag{2.23}$$

2.6 Electro-Fenton processes

Electro-Fenton method is one of effective technology for the treatment of wastewater because it is high to solve the environmental problems. Compared to the conventional Fenton processes, the electro-Fenton has an advantages for allowing better control, Fe^{3+} can be continuously converted to Fe^{2+} at cathode electrode leaded to higher process efficiency and electricity as a clean energy source is used in process, thus it cannot produce the secondary contaminants. However, this method provided in high an operational costs due to the electricity.

2.6.1 Types and mechanisms of electro-Fenton process (Methatham, 2011)

2.6.1.1 Cathodic Fenton Process (EF-H_2O_2)

H_2O_2 can be produced at cathode electrode by reduction of oxygen while Fe^{2+} is externally added into solution. This type needs to provide O_2 continuously according to the equation 2.24.

At cathode side: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (2.24)
At anode side: $0.5O_2 + H_2O \rightarrow 2OH\cdot$ (2.25)

2.6.1.2 Anodic Fenton Process (EF-FeOX)

In this method, H_2O_2 is externally added into the reactor while a iron anode is used as to produce the Fe^{2+} in solution. Thus, Fe^{2+} can be regenerated at cathode as given in equation 2.26.

At cathode side: $Fe^{3+} + e- \rightarrow Fe^{2+}$ (2.26)
$H_2O + e- \rightarrow 0.5H_2 + OH^-$ (2.27)
At anode side: $Fe \rightarrow Fe^{2+} + 2e^-$ (2.28)
$H_2O \rightarrow 2H^+ + 0.5O_2 + 2e^-$ (2.29)

2.6.1.3 Fenton Sludge Recycling System (FSR)

H_2O_2 and Fe^{2+} are externally provided into system. One advantage of this method is to reduce iron sludge by the generation of Fe^{2+} from Fe^{3+} reduction at cathode side. In this case, Fe^{3+} can be converted to Fe^{2+} more effectively and at faster rate, thus, it provided in higher OH· production and the pollutants degradation rate.

At cathode side: $Fe^{3+} + e- \rightarrow Fe^{2+}$ (2.30)
$H_2O + e- \rightarrow 0.5H_2 + OH^-$ (2.31)
At anode side: $Fe^{2+} \rightarrow Fe^{3+} + 2e^-$ (2.32)
$H_2O \rightarrow 2H^+ + 0.5O_2 + 2e^-$ (2.33)

In this work, iron electrode is used as Fe^{2+} source while H_2O_2 is externally applied into the solution. After H_2O_2 is reacted with Fe^{2+} to generated OH·, most mechanisms are similar to a conventional Fenton.

2.6.2 Effect of electro-Fenton processes conditions (C.-c. Jiang & Zhang, 2007)

It is well known that initial pH, ratio of Fe^{2+} and H_2O_2, anion and temperature affect process efficiency of both Fenton and electro-Fenton reaction. In addition, current density and distance between electrodes also affect on treatment efficiency of electro-Fenton method.

2.6.2.1 Current density

A current density has a great effect on the production of Fe^{2+}. Higher current density leads to increase the OH· production, which are highly reactive for the degradation. However, degradation rate in electro-Fenton processes is lower at higher current density due to the scavenging effect of Fe^{2+}. There are some study reported that current density in electro-Fenton should be no more than 10 A/m^2, while another reported that the greater limit value of current density should be 6.4 A/m^2.

2.6.2.2 Distance between electrodes

Electrode distance is another factor that affects to the removal of pollutants. For the shorter distance, short circuit between anode and cathode can be occurred and regeneration of Fe^{2+} could be easily oxidized to ferric ions at the anode side. For the longer distance, more energy is consumed because cell resistance would increase with a greater distances. Thus, it is important to use the optimum electrode distance for giving the better of performance.

2.6.2.3 Supporting electrolyte

Normally, sodium sulphate is used as the supporting electrolyte to increase the conductivity in solution, thus it helps to increase oxidation efficiency. Electrolyte is necessary in solution with enough conductivity. Zhou et al. (2007) reported that higher Na_2SO_4 concentration lead to higher current density and then H_2O_2 is more produced resulting increasing of process efficiency. However, it is not efficient way to enhance the process efficiency by adding excessive support electrolyte due to the consumption of OH· by high SO_4^{2-} concentration as in equation 2.34 and also leads to extra cost.

$$OH\cdot + SO_4^{2-} \rightarrow OH^- + SO_4^- \qquad (2.34)$$

2.7 Literature reviews

2.7.1 Lignin

Thongkrua (2010) employed the photocatalytic method to report the intermediate or by products of lignin removal in pulp and paper mill wastewater. The results showed that some lignin derivatives from residual lignin degradation were 2-methylbenzaldehyde, 2,4-dimethylbenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde (vanillin) which had toxicity less than the parent compound.

Pan et al. (2012) used electrochemical oxidation combined with photocatalytic method for remediation of lignin wastewater. In this study, the effect of applied current, initial lignin concentration and temperature were investigated. Moreover, they determined the secondary products of lignin degradation by HPLC and FTIR. According to the finding, the decomposition of lignin proceeded rapidly at 100 mA of oxidation current and 60°C of temperature. Concentration of lignin did not affect to this system. Under these optimum conditions, the activation energy was 16.04 kJ/mol and 64.6% of COD removal. Finally, they found that vanillin and vanillic acid were intermediate products form lignin oxidation.

2.7.2 Fenton process

Torrades et al. (2011) studied the treatment of black liquor effluent from pulp and paper industry by Fenton process based on central composite experimental statistical design. They found that the optimum concentration were 4.655 mM of Fe^{2+} and 44.1 mM of H_2O_2 for removing organic compounds in black liquor under pH of 3 and at room temperature (298K). The molar ratio of H_2O_2 to Fe^{2+} was 9.5. Under these conditions, COD reduction, aromatic content reduction (UV_{254}) and lignin removal (UV_{280}) were obtained as 94.8%, 80.9% and 85.6%, respectively within 90 minutes. Moreover, they suggested that Fenton processes were possible to combine with a subsequent biological treatment.

Araujo et al. (2002) observed the effect of H_2O_2 concentration on Fenton’s reagent in kraft black liquor. From the result, it was shown that the main products were formed in higher molecular weight at low concentration of H_2O_2 of 5-15 mM. At the end of treatment, 6.8-44.8% of lignin content was removed. On the other hand, lignin can be converted into lower molecular compounds at high dosage of H_2O_2 of 60 mM, with 90-100% of lignin and color removal efficiency. In addition of H_2O_2 alone causes the fragmentation of lignin molecules under acidic mixture and room temperature.

Catalkay et al. (2007) conducted a study of remediation of toxic chemicals in pulp mill effluent in term of color, TOC, AOX removal by Fenton method. Operating parameters which are initial pH, Fe^{2+} dosage and H_2O_2 concentration were studied. Wastewater used in all experiments was from biological treatment plant with initial COD and BOD of 400 mg/l and 240 mg/l, respectively. The results showed that the concentration of 2.5 mM of Fe^{2+}, 20 mM of H_2O_2 and initial pH of 5 were effective and enhance the process. The removal efficiency of TOC, color and AOX were 88%, 85% and 89%, respectively.

Munoz et al. (2014) studied on sawmill wastewater treatment by Fenton oxidation. They carried out an experiment to determine proper operating conditions such as temperature, Fe^{2+} concentration, H_2O_2 dose and H_2O_2 feeding in term of COD and TOC reduction. Furthermore, they investigated by-products after reactions were completed. From the experimental results, they found that oxidation rate of reaction increased with the increase of temperature, 60% of COD reduction was achieved at 120˚C. In addition, 25 mg/l of Fe^{2+} concentration and stoichiometric dose of H_2O_2 were effective for degrading desired compounds in the sawmill effluent. Moreover, providing the H_2O_2 in multiple additions avoided competitive scavenging reaction allowing the better oxidation process. For identifying the formation of by-products, the main by-products were organic acids such as acetic, oxalic and formic and traces of 4-hydroxy-2-butanone. For estimated operation costs, it is relatively low.

2.7.3 Modified-Fenton process

Mahmud et al. (2011) studied the effect of feeding of H_2O_2 to Fe^{2+} ratio to minimize the sludge production and maximize COD removal in landfill leachate. For single step feeding, it was shown that the highest removal of COD and color were found 68% and 87%, respectively with sludge production of 75% at optimum pH of 5 and optimum H_2O_2 to Fe^{2+} molar ratio of 1.3, while the COD and color removal efficiency with a three-step feeding of reagents were 11% and 7% higher respectively, and with 17% less sludge production than single feeding.

Martins et al. (2010) investigated the effect of H_2O_2 feeding mode on the treatment of phenolic wastewater by Fenton process. In experiment, H_2O_2 was added into the reactor by three different ways; initial feeding, 6-times feeding and 12-times feeding. They found that TOC removal was 55.7% when the total amount of H_2O_2 was added at the beginning of experiments. When H_2O_2 was divided into 6 injections, TOC removal was 61.4% and up to 67% for 12 additions. This was due to the scavenging effect of H_2O_2 due to the excess reagent.

Zhang et al. (2007) investigated the removal of landfill leachate by electro-Fenton method in batch reactor. Many parameters include distance between electrodes, electrical current, ratio of Fe^{2+} and H_2O_2 and H_2O_2 feeding were studied to observe the optimum conditions in term of COD degradation. Cathode and anode electrodes of 59.5 cm^2 working area were made from Ti/RuO_2-IrO_2. Appropriated amount of irons and H_2O_2 were supplied into the reaction. Ferrous ions could be regenerated by the reduction of ferric ions at the cathode side. For the effect of distance between electrodes, they found that the optimum distance are from 1.3 to 2.1 cm. In addition, they reported that the current of 2.5A was the most effective for removal of landfill leachate in this process. Moreover, they showed that the molar ratio of H_2O_2 and Fe^{2+} of 12 and continuous addition of H_2O_2 were provided in higher COD reduction. Under these optimum conditions, COD removal was obtained as more than 80%.

Umran et al.(2014) studied the treatment of tissue paper wastewater by electro-Fenton. The cylindrical iron was used as cathode while the turbine impeller with 8 flat blades was used as an anode electrode. They found that the efficiency in term of COD removal of 80 % was obtained after 60 minutes at the optimum current density of 20 mA/cm^2.

Jiang and Mao (2012a) observed the treatment of phenol-containing wastewater by improved electro-Fenton process. A porous cathode, instead of a plate cathode, is used to increase the regeneration of ferric ions to ferrous ions. As a result, 0.75A of current leads to the providing in higher ferrous ions generation efficiency in the electrolytic system. Moreover, they reported when H_2O_2 was added by a one step at the first of experiments, COD removal was 84.1%, being much higher than that of continuous H_2O_2 feeding mode. However, the COD removal efficiency does not increase further in the duration of experiment. On the contrary, continuous feeding of H_2O_2 keeps an increasing the efficiency of COD removal and finally exceeds that of the single step feeding way.

Babuponnusami and Muthukumar (2010) compared the performance of Fenton and electro-Fenton on phenol remediation. According to the finding, cathode and anode electrodes totally immerses into solution containing 1000 mg/l of Na_2SO_4 to increase the conductivity. Two electrodes with 25 cm^2 of working area were made up of stainless steel. Base on the results, it can be concluded that Fe^{2+} concentration, H_2O_2 concentration, current density, electrode distance, initial pH and initial phenol dosage affected phenol degradation. Under the optimum Fe^{2+} concentration of 4 mg/l, H_2O_2 dosage of 500 mg/l, initial pH of 3, electrode distance of 5 cm and current density of 12 mA/cm^2, phenol removal efficiency by electro-Fenton was higher than Fenton process and also required less time for mineralization. Moreover, rate constant of both processes are shown in Table 2.7.

Table 2. 7 Rate constant of Fenton and electro-Fenton processes

Name of processes	Rate constant, k (min^{-1})	Reports value, k (min^{-1})
Fenton	0.0067	0.0059
Electro-Fenton	0.0286	0.0280

From the previous literature review, the study of the color removal from pulp mill wastewater by Fenton and electro-Fenton are not widely investigated. Thus, it is interesting to observe the optimum operating conditions to be applied for real wastewater. Torrades et al. (2011) studied the effect of Fe^{2+} to H_2O_2 ratio and initial pH on color removal by Fenton process and found that the molar ratio of 1:9.5 and pH of 3 were provided in higher color removal, while Catalkay et al. (2007) reported that the optimum ratio was 1:25. Moreover, Umran et al. (2014) observed the effect of current density on COD removal by electro-Fenton process and found that the current density of 20 mA/cm^2 was the most effectiveness for degradation of tissue paper wastewater. However, step feeding mode and the combination of Fenton’s reagent and electrochemical system have not been investigated for color removal in pulp mill wastewater. Therefore, this study is aimed to determine the effect of operating parameters and understand the modified-Fenton reaction.

CHARPTER 3

METHODOLOGY

This work studied the optimum operating condition to remove lignin and color from pulp mill wastewater by Fenton and modified-Fenton processes. The experiments can be categorized into the following 4 categories:

(1) Real wastewater characterization

(2) Control experiment

Control experiments were performed to study the effect of Fe^{2+} and H_2O_2 on color, lignin and COD removal.

(3) Fenton process

The operating conditions were investigated in the function of Fe^{2+} to H_2O_2 ratio, initial pH and Fenton's reagent. This part is aimed to study and understand the effect of operating conditions on color, lignin and color removal.

(4) Modified-Fenton process

Development of operation feeding and combination of Fenton's reagent and electrochemical system was performed to reduce the scavenging effect and enhance the process efficiency.

3.1 Chemicals and equipments

3.1.1 Chemicals

All chemical substances used in this study are analytical grade.

3.1.1.1 pH adjustment

- Sulfuric acid (H_2SO_4), Qrec
- Sodium hydroxide (NaOH), Ajax

3.1.1.2 Lignin measurement

- Alkali lignin, Aldrich

3.1.1.3 Fenton's reagent

- Ferrous sulphate hepta-hydrated ($FeSO_4$), Ajex
- Hydrogen peroxide (30%, H_2O_2), Ajex

3.1.1.4 Chemical for stopping the reaction

- Sodium hydroxide (NaOH), Ajex
- Manganese dioxide (MnO_2), Ajex

3.1.1.5 COD measurement

- Silver sulphate ($AgSO_4$), Qrec
- Mercury sulphate ($HgSO_4$), Qrec
- Sulfuric acid (H_2SO_4), Qrec
- Ferrous ammonium sulphate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), Ajax
- Potassium dichromate ($K_2Cr_2O_7$), Ajax
- Ferroin indicator solution

3.1.1.6 Iron measurement

- Hydrochloric acid (37%,HCl), Qrec
- Ammonium acetate ($NH_4C_2H_3O_2$), Carlo
- Hydroxylamine ($NH_2OH \cdot HCl$), Ajax
- 1,10-Phenanthroline ($C_{12}H_6N_2 \cdot H_2O$), Ajax
- Ferrous ammonium sulphate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), Ajax
- Glacial acetic acid (CH_3COOH), Qrec

3.1.1.7 Color measurement

- Potassium hexachlroplatinate (K_2PtCl_6), Qrec
- Cobaltous chloride ($CoCl_2 \cdot 6H_2O$), Ajax

3.1.2 Equipments

(1) pH meter : Seven easy, METTER TOLEDO

(2) UV-VIS spectrophotometer : Genesys 10 UV scanning, single cell holder, Thermo Fisher Scientific, USA

(3) Magnetic stirrer : SHPM-10, Fine Tech Korea and magnetic bar

(4) Fenton and electro-Fenton reactors (beaker)

(5) Steel electrode

(6) DC power supply : GPR-6060D, GW Instek

(7) Clock timer

(8) Hot air oven : ED/FD, Binder

(9) Cylinder : 250, 1000 ml

(10) Micropipet : 1, 5, 10 ml : Proline Plis, Biotech

(11) Volumetric flask : 50, 100, 500 ,1000 ml

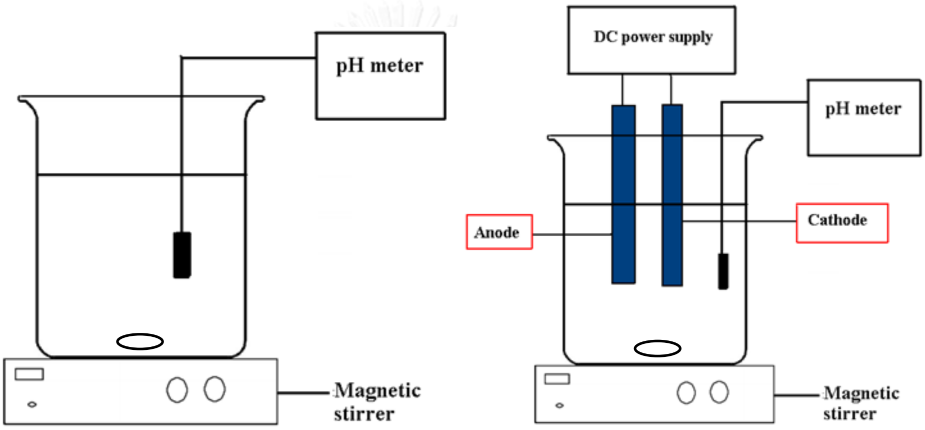
(12) Test Tubes : 25x150mm Tetrafluorethylene (TFE) lid

(13) Weighting machine : 4-digital balance : Ohaus

(14) Beaker : 50, 100, 250, 1000 ml

3.1.3 Fenton and electro-Fenton reactors

All experiments were carried out in batch-mode operation using a beaker of 1 L capacity and a magnetic stirrer to mixing the chemicals as shown in Figure 3.1. For electro-Fenton, anode and cathode electrode were made from steel with a size of 50 cm^2 working area and a direct-current source providing electrical current between electrodes.



(a) (b)

Figure 3. 1 (a) Fenton reactor (b) Electro-Fenton reactor

3.1.4 Synthetic wastewater

Lignin synthetic wastewater was prepared by dissolving alkali lignin in water supply. Initial concentration of lignin used in experiment was the same as that of the wastewater from SCG Paper Company, Banpong pulp mill, Ratchaburi, Thailand. Real wastewater has an initial COD of 2800-3100 mg/l, initial pH of 7.5-8.5, color concentration of 7,200-7,400 pt-co unit color and initial lignin concentration of 900-1100 mg/l. The detail of analytical method for synthetic and real wastewater based on standard method as mentioned in Appendix A.

3.2 Procedures of control experiments

3.2.1 The effect of ferrous

This experiment was carried out to determine the impact of Fe^{2+} on chemical reaction and coagulation which occurs after neutralization. The flow chart of experimental procedure is given in Figure 3.2.

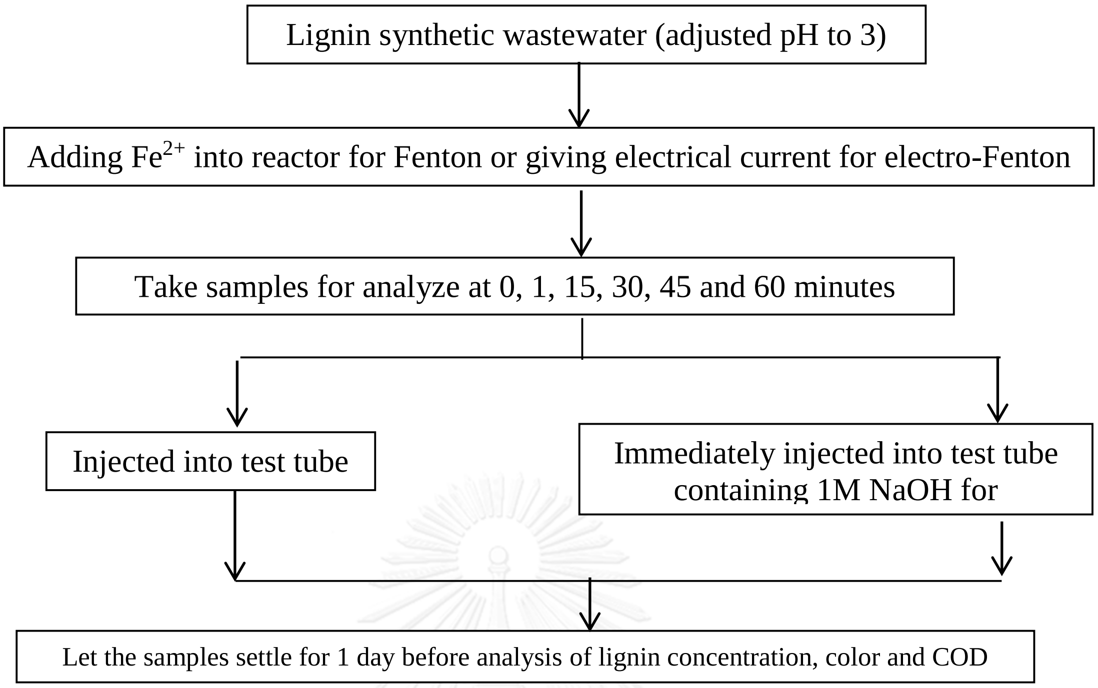


Figure 3. 2 Flow chart of ferrous control experiment

3.2.2 The effect of H_2O_2

H_2O_2 control experiment was conducted to determine the effect of direct oxidation by H_2O_2. Desired H_2O_2 was added into synthetic wastewater of pH 3. The experiment procedures for H_2O_2 control is shown in Figure 3.3.

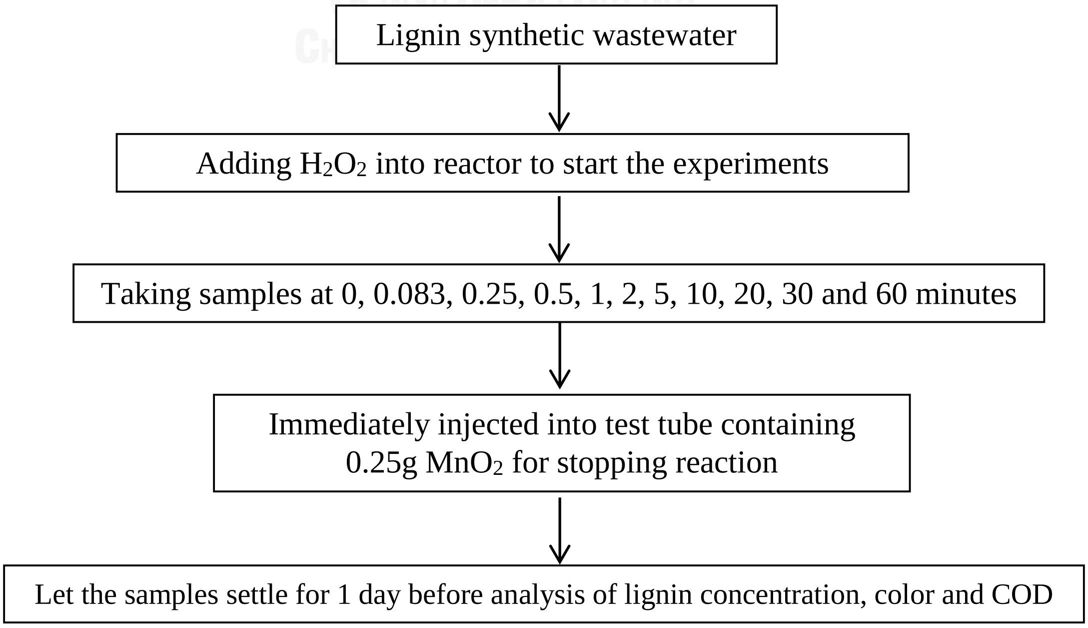


Figure 3. 3 Experimental procedure of H_2O_2 control

3.3 Fenton experiments

3.3.1 Fenton experiment procedures

Synthetic wastewater was prepared at the same concentration as that of the black liquor sample from SCG Paper Company by dissolving 0.91g alkali lignin in 1L of water supply and then 1M of H_2SO_4 was added into system for the adjustment to desired initial pH. After that, a suitable amount of Fe^{2+} was applied into reactor and the particles completely dissolved by magnetic mixer. Later, the desired H_2O_2 was supplied into solution to start the experiments. Samples were taken using a glass syringe at 0, 0.083, 0.25, 0.5, 1, 2, 5, 10, 20, 30 and 60 minutes and immediately mixed with 1M of NaOH and 0.25g of MnO_2 to stop the reaction. After that, the samples were left to settle for one day and analyzed for lignin concentration, color, COD and Fe concentration. The experimental steps are summarized in Figure 3.4.

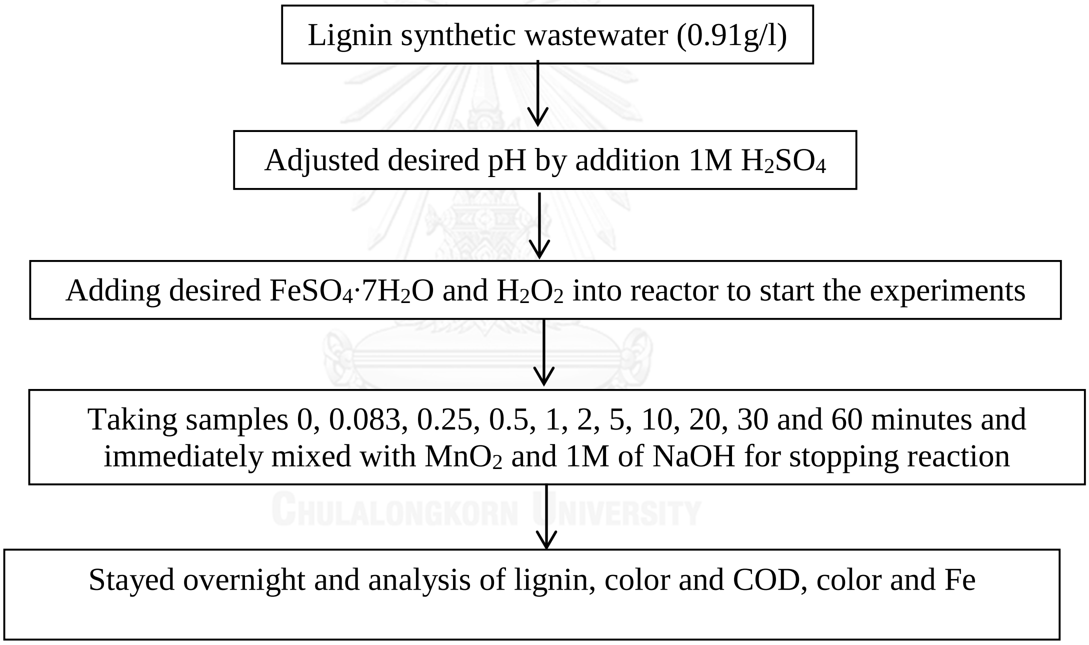


Figure 3. 4 Fenton experiment procedures

3.3.2 Fenton experiment scenario

The studied operating parameters in Fenton experiment are shown in Table 3.1

Lignin concentration (g/l)	Operating parameters
0.91	1. Fe^{2+} to H_2O_2 ratio 2. initial pH 3. Fenton’s dosage

Table 3. 1 Studied operating parameters

3.3.2.1 Effect of Fe^{2+}*:* H_2O_2 *ratio* (scenario A)

An objective is to observe the optimum Fe^{2+} to H_2O_2 ratio. The experiments were conducted under the condition as shown in Table 3.2.

Table 3. 2 Detail of scenario A

Lignin concentration (g/l)	pH	Fe^{2+} (mg/l)	H_2O_2 (mg/l)	Fe^{2+} to H_2O_2 ratio
0.91	3	400	240	1:0.6
			400	1:1
			1,000	1:2.5
			2,000	1:5
			4,000	1:10
			6,000	1:15
			8,000	1:20

3.3.2.2 Effect of initial pH (scenario B)

To investigate the impact of pH on lignin and color degradation is the goal of this part. The experiments were carried out at optimum Fe^{2+}:H_2O_2 ratio obtained from previous section and varied pH from 2 to 3 and 4 as shown in Table 3.3.

Table 3. 3 Detail of scenario B

Lignin (g/l)	pH	Fe^{2+} (mg/l)	H_2O_2 (mg/l)	Fe^{2+} to H_2O_2 ratio
0.91	2	400	From scenario A	From scenario A
	3			
	4			

3.3.2.3 Effect of Fenton's reagent dose (scenario C)

This experiment aim to verify the effect of Fenton's reagent dose on color and lignin removal using optimum Fe^{2+}:H_2O_2 and optimum pH obtained from previous section. However, the concentration of Fe^{2+} and H_2O_2 are varied as given in Table 3.4.

Table 3. 4 Detail of scenario C

Lignin concentration (g/l)	pH	Fe^{2+} (mg/l)	H_2O_2 (mg/l)	Fe^{2+}:H_2O_2
0.91	From scenario B	300	750	From scenario A
		400	1,000	
		500	1,250	

3.4 Modified-Fenton experiments

3.4.1 Modified-Fenton procedures

In step-feeding experiment, the most procedures are similar to conventional Fenton. H_2O_2 and ferrous ions was added into the solution in the function of 6-times feeding and 12-times feeding. Moreover, the step feed of H_2O_2 was conducted to enhance the process efficiency.

In electro-Fenton experiments, anode and cathode electrodes were made from steel and DC power supply was additionally installed in the reactor to provide electrical current between electrodes. Space between electrodes was fixed at 2 cm due to high performance of electro-Fenton process (Atmaca, 2009). Fe^{2+} can be produced from iron anode while Fe^{3+} can be regenerated to Fe^{2+} at iron cathode. Magnetic stirrer was used in experiment to completely mixing of the solution. After synthetic wastewater was prepared and adjusted to desired pH, desired electrical current was applied. Then, hydrogen peroxide was external added into the solution to start the reaction. Later, most procedures were similar to a typical Fenton reaction. The flow chart of electro-Fenton experiments are provided in Figure 3.5.

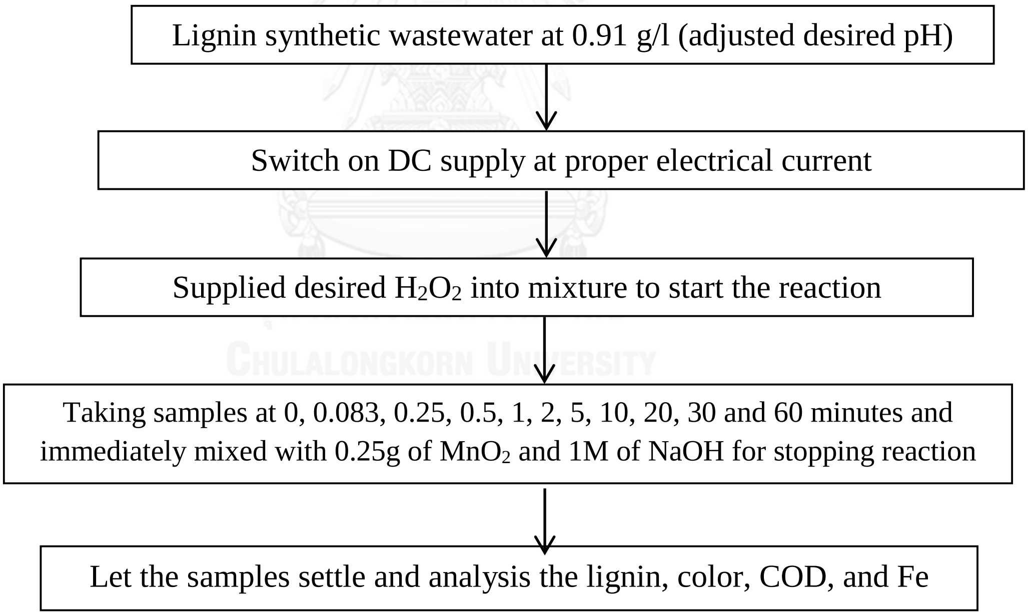


Figure 3. 5 Electro-Fenton experiment procedures

3.4.2 Modified-Fenton scenario

3.4.2.1 Operation feeding

3.4.2.1.1 Step feeding of H_2O_2 (scenario D)

To investigate the H_2O_2 feeding on the degradation of lignin and color to enhance the oxidation efficiency with the condition as shown in Table 3.5.

Table 3. 5 Detail of scenario D

Lignin (g/l)	pH	Fe^{2+}:H_2O_2	Feeding
0.91	From scenario B	From scenario A	Single Step feeding

3.4.2.1.2 Step feeding of ferrous and H_2O_2 (scenario E)

This experiment aims to study the effect of step feeding of ferrous and H_2O_2 on lignin and color removal.

Table 3. 6 Detail of scenario E

Lignin (g/l)	pH	Fe^{2+}:H_2O_2	Feeding
0.91	From scenario B	From scenario A	Single 6 injections 12 injections

3.4.2.2 Electro-Fenton scenario

The studied operating parameters in modified-Fenton experiment are shown in Table 3.7.

Table 3. 7 Studied operating parameters in electro-Fenton

Lignin concentration (g/l)	Operating parameters
0.91	1. Fe^{2+}: H_2O_2 2. current density 3. step feed of H_2O_2

3.4.2.2.1 Effect of Fe^{2+}:H_2O_2 ratio (scenario F)

To investigate the impact of Fe^{2+}:H_2O_2 ratio on lignin and color degradation is the goal of this part. The experiments was carried out at optimum pH obtained from previous part and H_2O_2 dosage is varied as shown in Table 3.8.

Table 3. 8 Detail of scenario F

Lignin concentration (g/l)	pH	Fe^{2+}:H_2O_2	current (A)
0.91	From scenario B	1:0.6 1:1 1:2.5 1:5 1:10 1:15	1

3.4.2.2.2 Effect of current density (scenario G)

An objective of this part is to determine the optimum current density on color and lignin removal with conditions is given in Table 3.9.

Table 3. 9 Detail of scenario G

Lignin concentration (g/l)	pH	H_2O_2 (mg/l)	current (A)
0.91	From scenario B	From scenario F	0.75 1 1.25

3.4.2.2.3 Effect of H_2O_2 feeding (scenario H)

An objective is to investigate the effect of step feed to improve the process efficiency. The experiments are conducted under condition as shown in Table 3.10.

Table 3. 10 Detail of scenario H

Lignin concentration (g/l)	pH	Fe^{2+}:H_2O_2	current (A)	H_2O_2 feeding
0.91	From scenario B	From scenario F	From scenario G	Single Step feeding

3.5 Analytical methods

3.5.1 Lignin measurement

For real and synthetic wastewater, UV-VIS spectrophotometer was used to analyzed lignin concentration with detection wavelength of 280 nm (Ksibi et al., 2003; Pessala, 2004)

For calibration curve preparation, the stock solution has lignin of 1,000 mg/l is prepared by dissolved 1 g of alkali lignin in distilled water and dilute to 1,000 ml. After that, standard lignin solution were prepared in the concentration of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/l by diluting 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ml of stock solution with distilled water in 100 ml of volumetric flasks. Then, the standard lignin solution were detected by spectrophotometer at wavelength of 280 nm.

3.5.2 Chemcal oxygen demand (COD) measurement

Closed reflux titrimetric method used to analyze COD in samples based on the standard method (APHA, 1992). Organic can be oxidized by dichromate solution in the presence of silver sulphate catalyst. The excess dichromate is titrated with standard ferrous ammonium sulphate using ferroin (thophenanthroline ferrous complex) as indicator.

3.5.3 Measurement of ferrous and total iron concentration

For determination of both ferrous and total iron concentration, UV-VIS spectrophotometer was used to detect based on the standard method at 510 nm (APHA, 1992). For total iron measurement, hydroxylamine was added into solution to convert ferric ions to ferrous irons before analysis.

For calibration curve preparation of ferrous, the stock solution was prepared by mixing 1.404g of ferrous ammonium sulphate with 20 ml of sulfuric acid and dilute to 1,000 ml. This stock solution had 200 mg/l of ferrous concentration. Then, ferrous standard solutions was prepared in the concentration of 0.5, 1, 2, 3, 4 and 5 mg/l by diluting 0.25, 0.5, 1, 1.5, 2 and 2.5 ml of stock solution with distilled water. After that, 20 ml of phenanthroline solution and 10 ml of acetate buffer solution was mixed into the solution and dilute to 100 ml before measuring the solution by spectrophotometer at 510 nm.

For determination of total iron calibration curve, prepared standard having iron concentration of 0.5, 1, 2, 3, 4 and 5 mg/l by diluting 0.125, 0.25, 0.5, 0.75,1 and 1.25 ml of stock solution with distilled water to 50 ml. After that, 2 ml of HCl and 1 ml of hydroxylamine solution was added into standard solution and heat to boiling until volume was reduced to 15 to 20 ml. Then, 4 ml of phenanthroline solution and 10 ml of acetate buffer solution was supplied into the standards and allowed a minimum of 10 minutes for maximum color development. The standards were analyzed by spectrophotometer at 510 nm.

3.5.4 pH measurement

pH value was carried out by digital pH meter, seven easy, METTER TOLEDO.

3.5.5 Color measurement

The color from real and synthetic wastewater were analyzed by Platinum-Cobalt method following the standard method with detection wavelength of 475 nm

(APHA, 1992). This method is used as the indicator of water where a yellow color is due to the leachates of naturally occurring organic materials. Before color analysis in real wastewater, the sample was filtrated with 0.45 µm membrane filter to remove fine particles.

For preparation for calibration curve of color, the color stock solution with color concentration of 500 Pt-co unit was prepared by dissolved 1.246g of K_2PtCl_6 and 1g of $CoCl_2 \cdot 6H_2O$ in distilled water with 100 ml of HCl and dilute to 1,000 ml. After that, prepared standard having color concentration of 20, 40, 50, 100, 200, 300, 400 and 500 Pt-co by diluting 4, 8, 10, 20, 40, 60, 80 and 100 ml of stock solution with distilled water in 100 ml of volumetric flasks. The standards were measured by spectrophotometer at 475 nm.

CHARPTER 4
RESULTS AND DISCUSSIONS

The degradation of color, lignin and COD were studied by using two main processes including Fenton and modified-Fenton processes to compare the removal efficiency, performance of reaction and cost of each process. In this work, the detail explanation on each factor such as Fe^{2+}:H_2O_2 ratio, initial pH, Fenton's dosage, effect of step feeding and current density will be shown.

4.1 Characteristic of wastewater determination

Wastewater samples were received from pulp mill located in Ratchaburi province. The characteristic of pulp mill wastewater used in the experiment showed in Table 4.1.

Table 4. 1 Characteristic of pulp mill wastewater collected in September, 2014

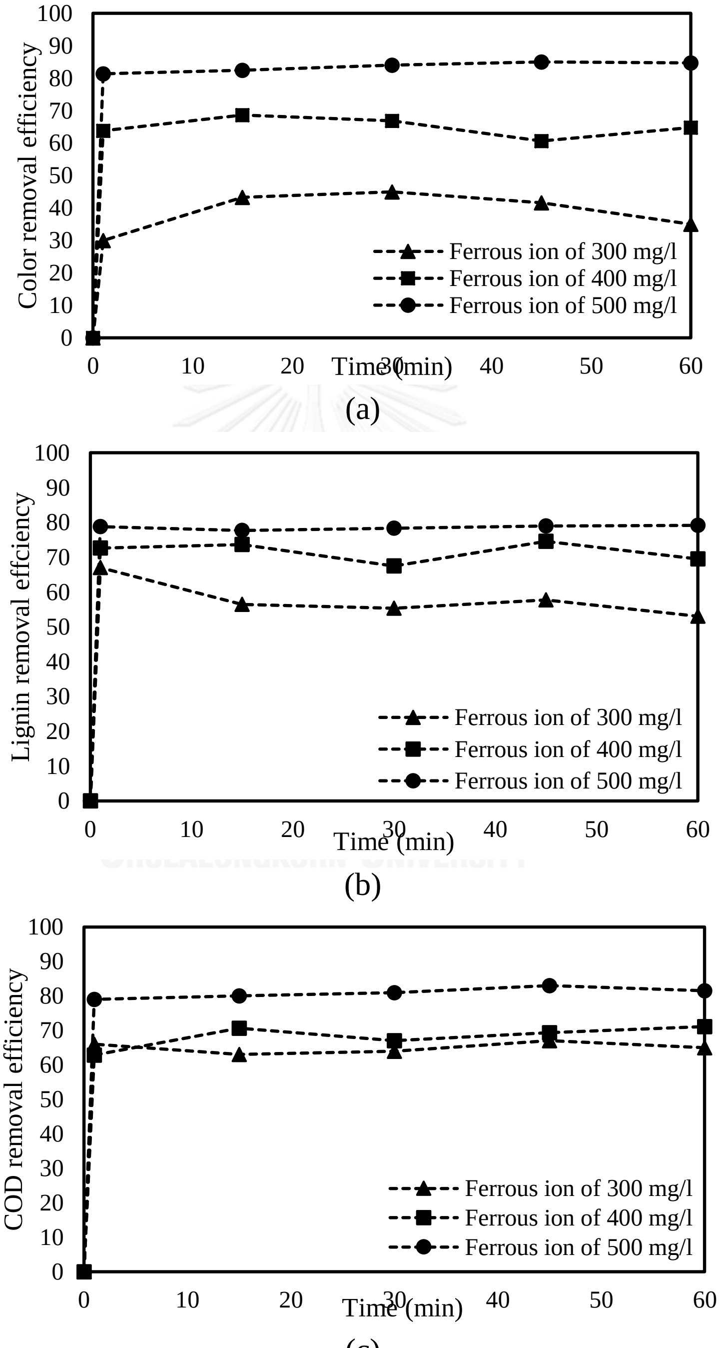
Parameters	Values
pH	7.5-8.5
COD (mg/l)	2,800-3,100
Lignin (mg/l)	900-1,100
Color (pt-co)	7,200-7,400
Suspended solids (mg/l)	4,400-4,700

Wastewater samples containing 900-1,100 mg/l of lignin collected at the first stage after pulp disintegration process. Real wastewater was kept at 4 degree Celsius to inactivated microorganism. Before determine the characteristic of wastewater samples, wastewater was filtrated through 0.45 glass microfilter to remove suspended solid from samples before analysis.

4.2 Control experiments

4.2.1 Ferrous control on Fenton process

In this study, Fe^{2+} in the range of 300-500 mg/l was added into the synthetic wastewater to determine the effect of Fe^{2+} on chemical reaction and coagulation which occurred under alkaline conditions. During coagulation, the coagulant can neutralized the electrical charges of the fine particles in the water, allowing the particles to come closer together and form floc. Then, they can be more easily separated from the water by precipitation. The results in Figure 4.1 showed that color, lignin and COD concentration were reduced in all control experiment. For color removal, coagulation efficiencies were 35%, 65% and 83.5% when Fe^{2+} was applied in the concentration of 300, 400 and 500 mg/l, respectively. Moreover, analysis of sample indicated that lignin removal efficiency was 58%, 72% and 78.5% and 65%, 68% and 81% for COD removal with the Fe^{2+} concentration of 300, 400 and 500 mg/l, respectively. Thus, these control experiment indicated that overall Fenton efficiency composes of coagulation efficiency and oxidation efficiency.



(a)

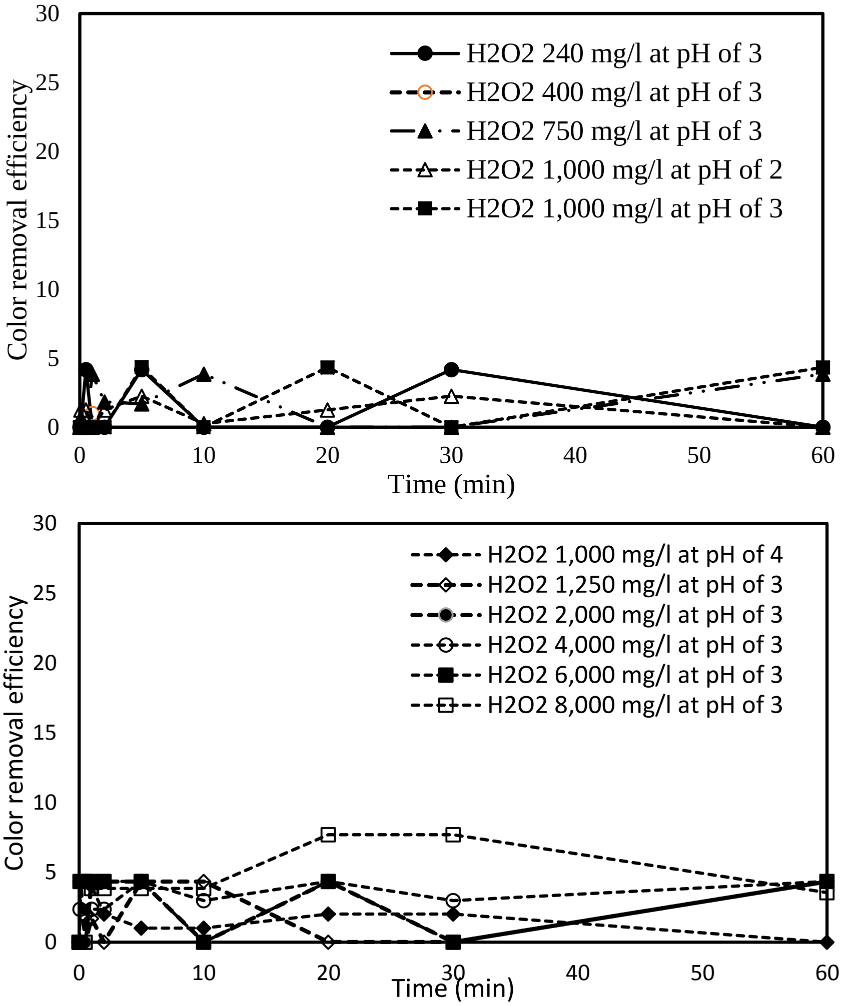
(b)

(c)

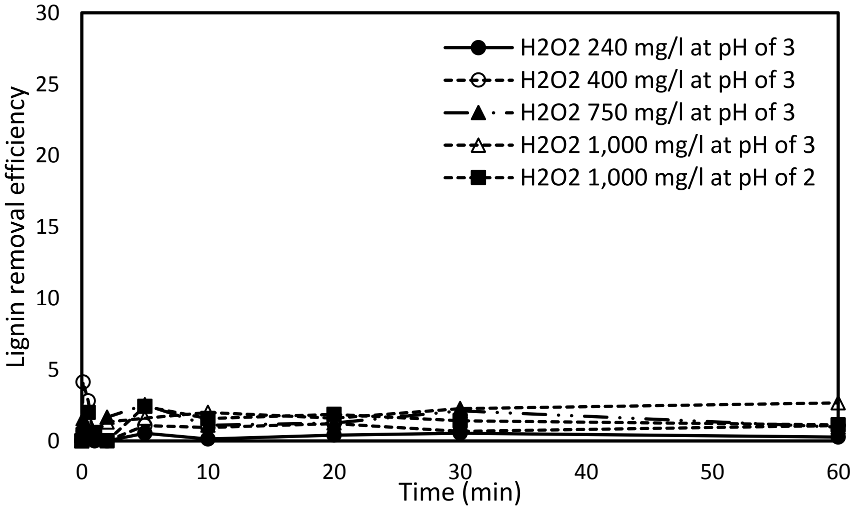
Figure 4. 1 Effect of coagulation from ferrous ions precipitation in alkaline condition at initial pH of 3 on (a) color removal (b) lignin removal (c) COD removal in Fenton process

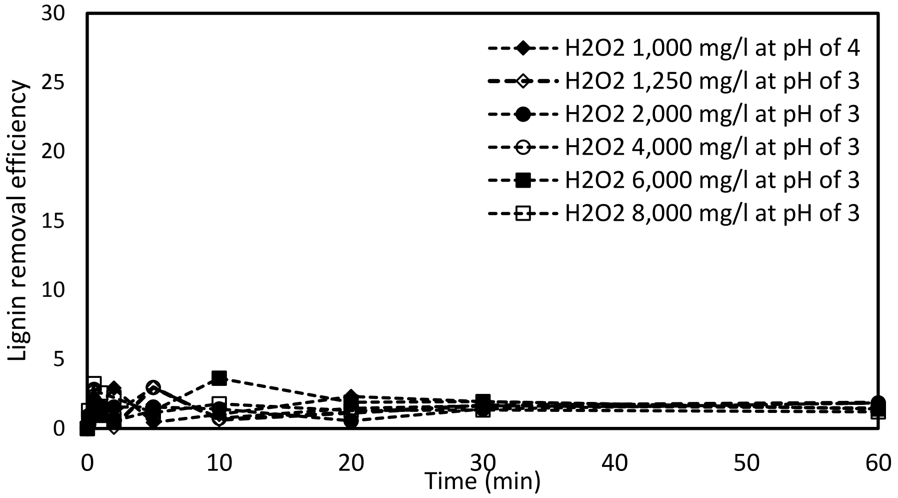
4.2.2 Hydrogen peroxide control on Fenton process

H_2O_2 is one of the most powerful oxidizers that can be oxidized the organic material in wastewater. To investigate the effect of direct oxidation by H_2O_2 on color, lignin and COD removal, the results in Figure 4.2 showed that color, lignin and COD were not significantly affect in the reaction at varied H_2O_2 to be applied in the synthetic wastewater. For color removal, H_2O_2 concentration of 240, 400, 750, 1,000, 1,250, 2,000, 4,000, 6,000 and 8,000 mg/l at initial pH of 3 and 1,000 mg/l at initial pH of 2 and 4 resulted in color removal of 1.2%, 1.4%, 1.6%, 1.3%, 1.5%, 2.6%, 2.8%, 3%, 3.4% 1% and 1.2%, respectively. Moreover, these H_2O_2 concentration can provide lignin removal efficiency to 0.3%, 1.2%, 1.2%, 1.3%, 1.4%, 1.2%, 1.5%, 1.3%, 1.6%, 1.1% and 1.3%, respectively and COD removal efficiency of 1.1%, 0.9%, 1.1%, 1.5%, 1.9%, 4.4%, 5.1%, 6.4%, 8.1%, 1.3% and 1.5% were noted on this experiment. As a result from this part, it can be concluded that H_2O_2 alone was not powerful enough to oxidize lignin in synthetic wastewater.

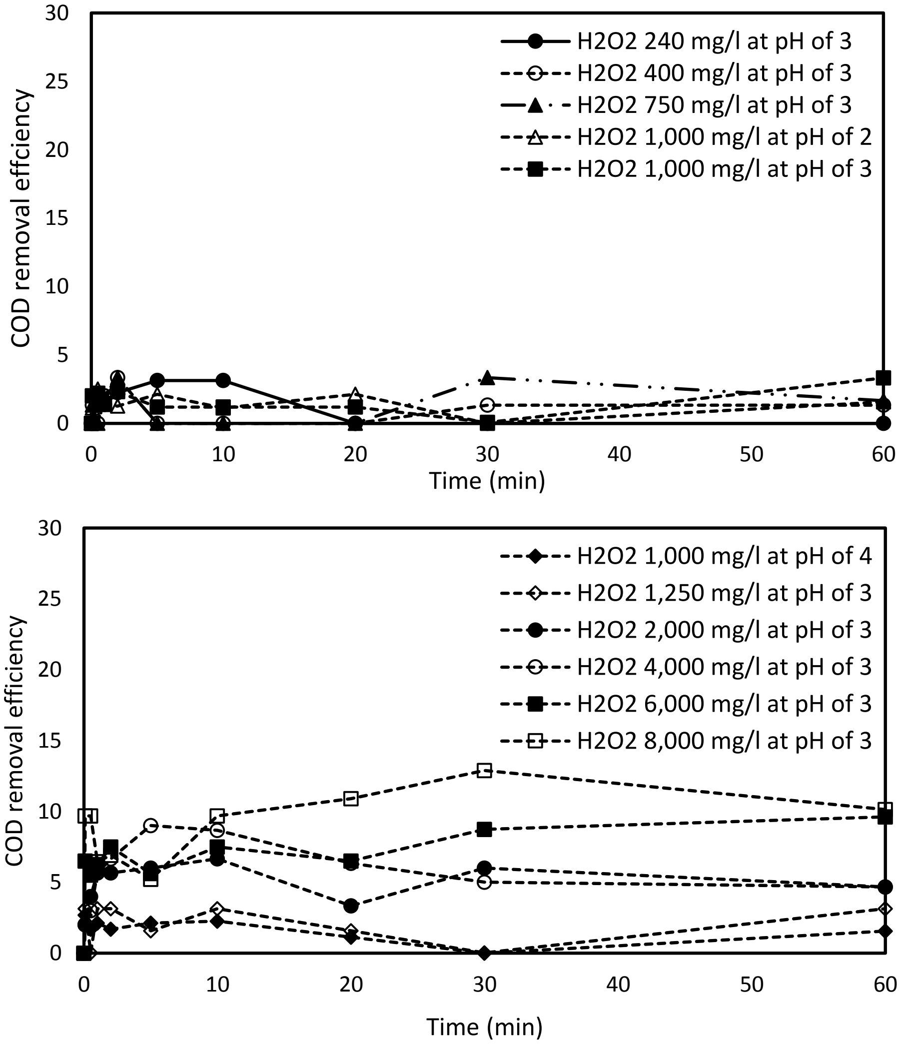

30
25
20
15
10
5
0
Color removal efficiency
0
10
20
30
40
50
60
Time (min)
H2O2 240 mg/l at pH of 3
H2O2 400 mg/l at pH of 3
H2O2 750 mg/l at pH of 3
H2O2 1,000 mg/l at pH of 2
H2O2 1,000 mg/l at pH of 3
30
25
20
15
10
5
0
Color removal efficiency
0
10
20
30
40
50
60
Time (min)
H2O2 1,000 mg/l at pH of 4
H2O2 1,250 mg/l at pH of 3
H2O2 2,000 mg/l at pH of 3
H2O2 4,000 mg/l at pH of 3
H2O2 6,000 mg/l at pH of 3
H2O2 8,000 mg/l at pH of 3

(a)


30
25
20
15
10
5
0
Lignin removal efficiency
0
10
20
30
40
50
60
Time (min)
H2O2 240 mg/l at pH of 3
H2O2 400 mg/l at pH of 3
H2O2 750 mg/l at pH of 3
H2O2 1,000 mg/l at pH of 3
H2O2 1,000 mg/l at pH of 2



(b)



(c)

Figure 4. 2 Effect of direct oxidation by varied H_2O_2 on (a) color removal (b) lignin removal (c) COD removal in Fenton process

4.2.3 Ferrous control on step feeding operation

4.2.3.1 Step feeding of H_2O_2

Since Fe^{2+} is effective to degrade lignin by coagulation process, in the study of its degradation using advanced oxidation process, its removal by coagulation has to be considered. 40 mg of Fe^{2+} was provided into the synthetic wastewater under pH of 3. The result showed that removal efficiency of color, lignin and COD was 1.7%, 2.2% and 2.2%, respectively as shown in Figure 4.3. It can indicate that only Fe^{2+} could remove lignin at a lower efficiency and could be ignored in this experiments.

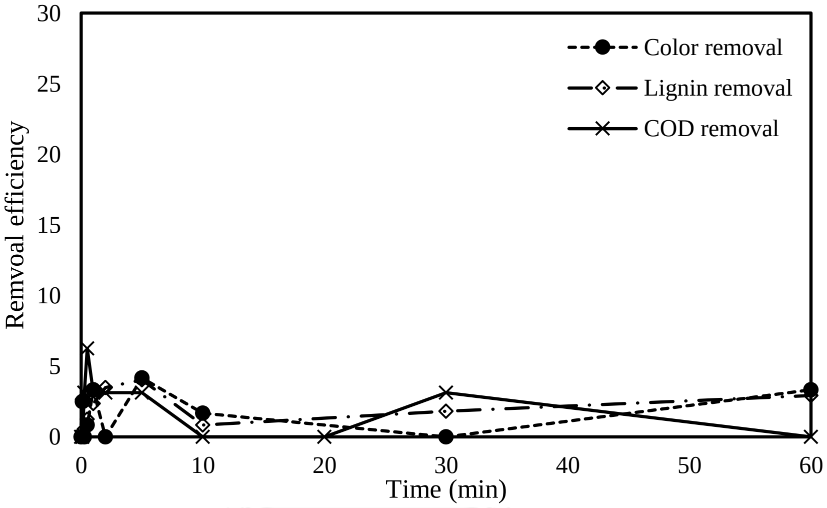
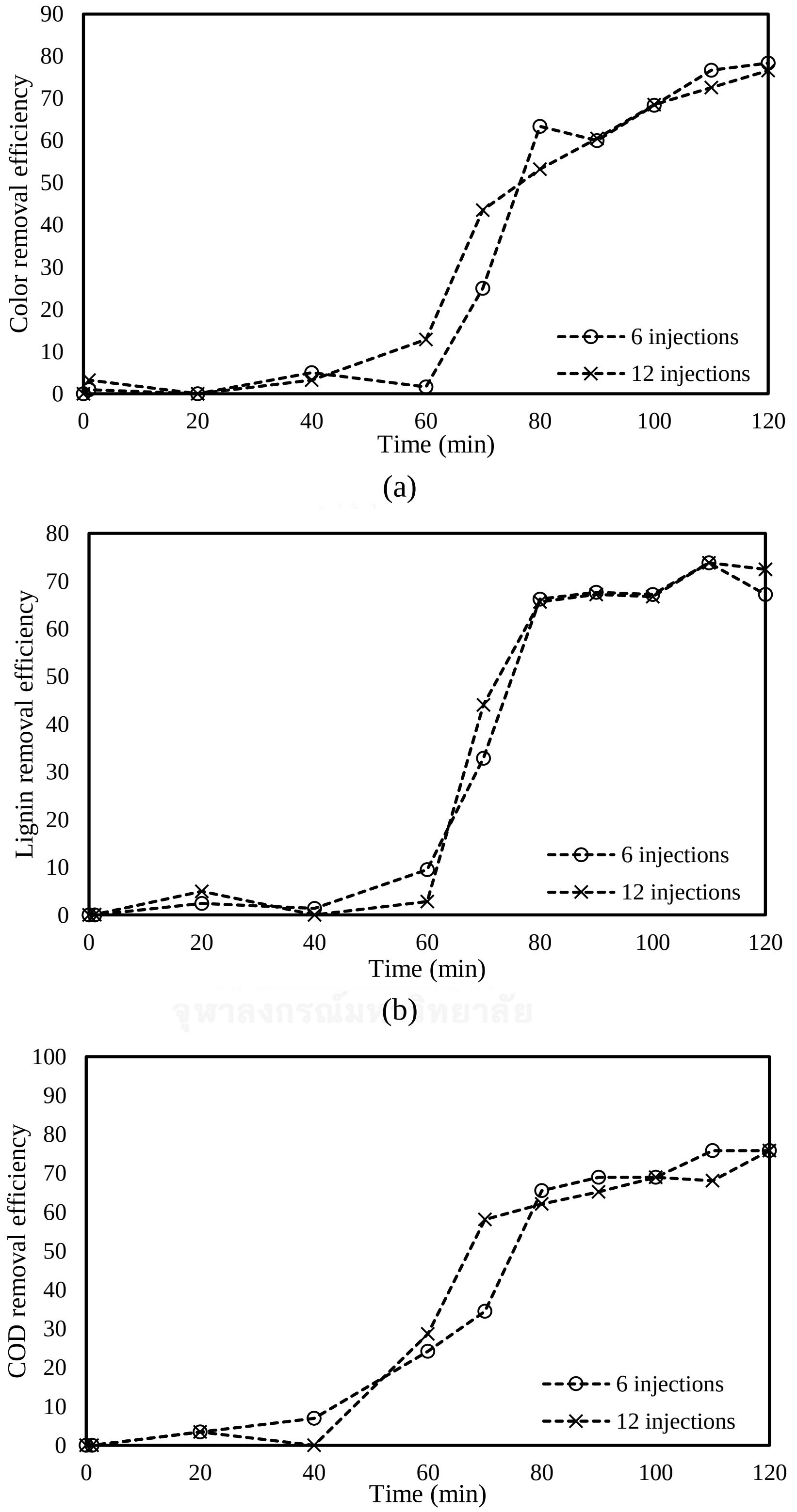


Figure 4. 3 Effect of coagulation on H_2O_2 step feeding operation

4.2.3.2 Step feeding of Fe^{2+} and H_2O_2

This control experiment was performed to study the effect of Fe^{2+} on precipitation under alkaline solution. Fe^{2+} was provided in the function of six feedings (0, 20, 40, 60, 80 and 100 min) and twelve feedings (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 min) under pH of 3. From the results shown in Figure 4.4, it was found that removal efficiency from coagulation increased with increasing the dosage of Fe^{2+} in solution. Thus, the removal efficiency in step feeding of Fe^{2+} and H_2O_2 experiment composed of coagulation and oxidation efficiency.



(a)

(b)

(c)

Figure 4. 4 Effect of coagulation in step feeding of Fe^{2+} *and* H_2O_2 *on (a) color removal (b) lignin removal (c) COD removal*

4.2.4 Hydrogen peroxide control on step feeding operation

4.2.4.1 Step feeding of H_2O_2

To study the effect of H_2O_2 on color, lignin and COD removal, the control experiment was performed. 1,000 mg/l of H_2O_2 can be divided in 10-times feeding was added into the synthetic wastewater at pH of 3. The results in Figure 4.5 showed that removal efficiency of color, lignin and COD was 1.2%, 1.5% and 1.5%, respectively. Direct oxidation of lignin in this experiment had a small effect on process efficiency and can be ignored in this experiment period.

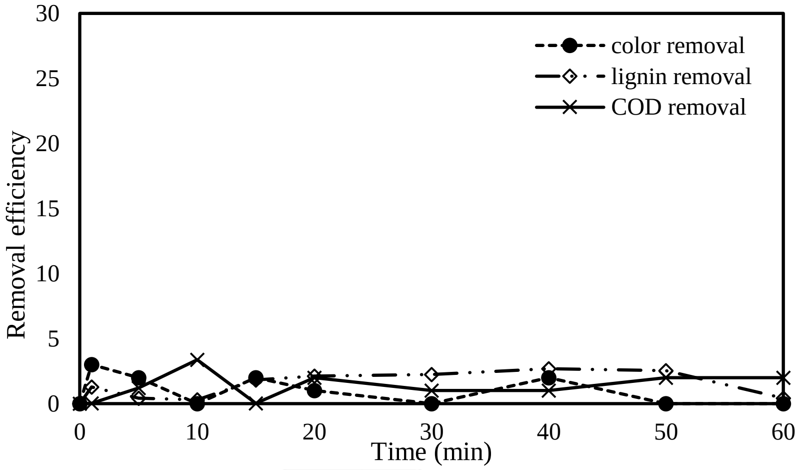


Figure 4. 5 Control experiment for direct H_2O_2 oxidation in step feeding of H_2O_2 experiment

4.2.4.2 Step feeding of Fe^{2+} and H_2O_2

This part was to observe the effect of direct of oxidation by H_2O_2, the control experiment was performed into 2 different ways. The first was 6 additions and the second was 12 additions of H_2O_2. Total reaction time was kept at 120 minutes and total H_2O_2 dosage was 1,000 mg/l. For 6 step feeding, one sixth of the reagent was added initially and then another five sixth of reagent was provided at 20 minutes of interval. Similarly 12 step feeding was done at 10 minutes of interval. As can be seen in Figure 4.6, removal efficiency of color, lignin and COD were 1.5%, 1.7% and 1.7%, respectively on 6 step feeding operation and 1.2%, 1.8% and 1.6%, respectively on 12 step feeding. It can be concluded that direct oxidation by H_2O_2 was provided low process efficiency and cannot oxidize lignin completely.

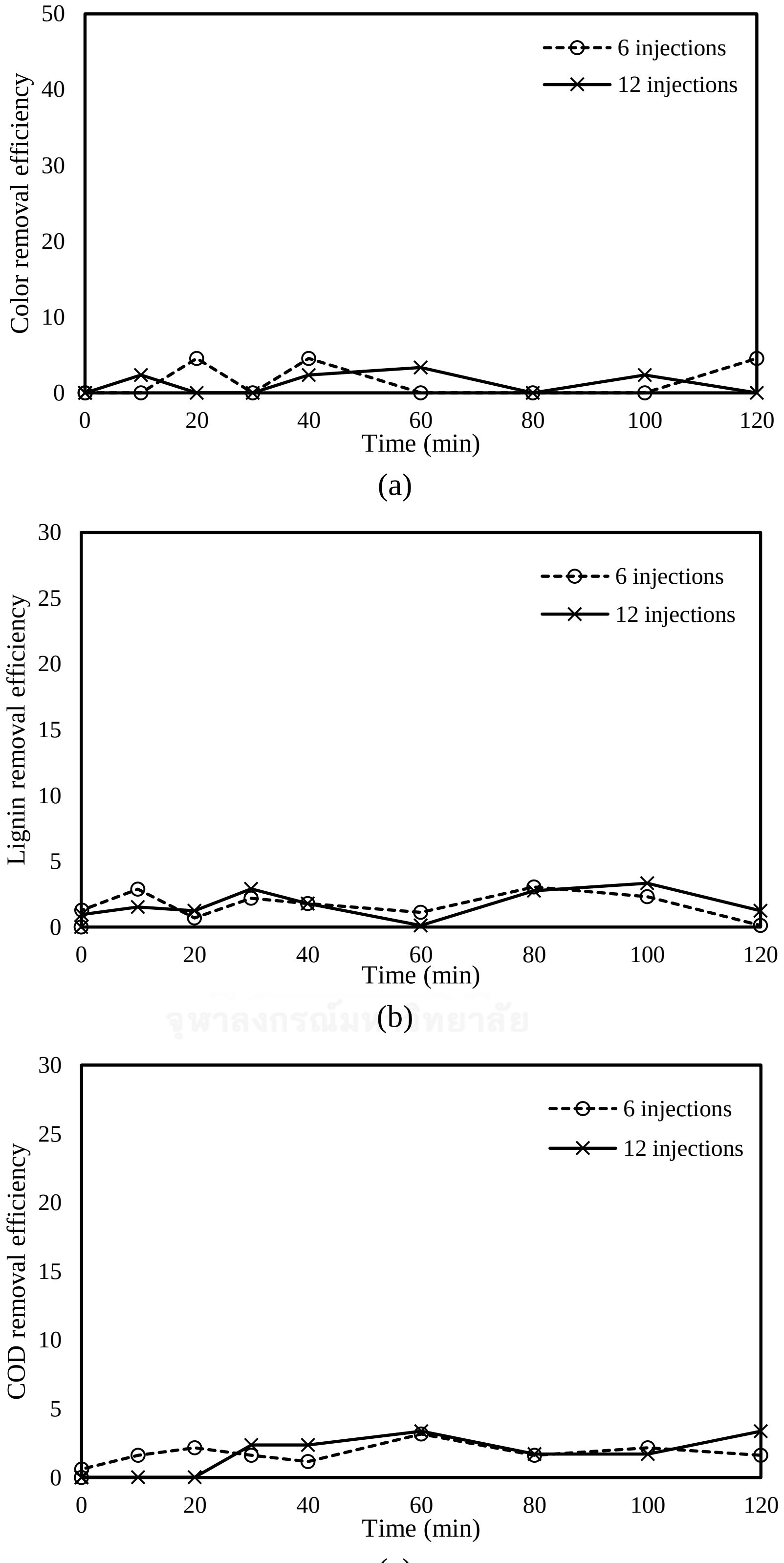
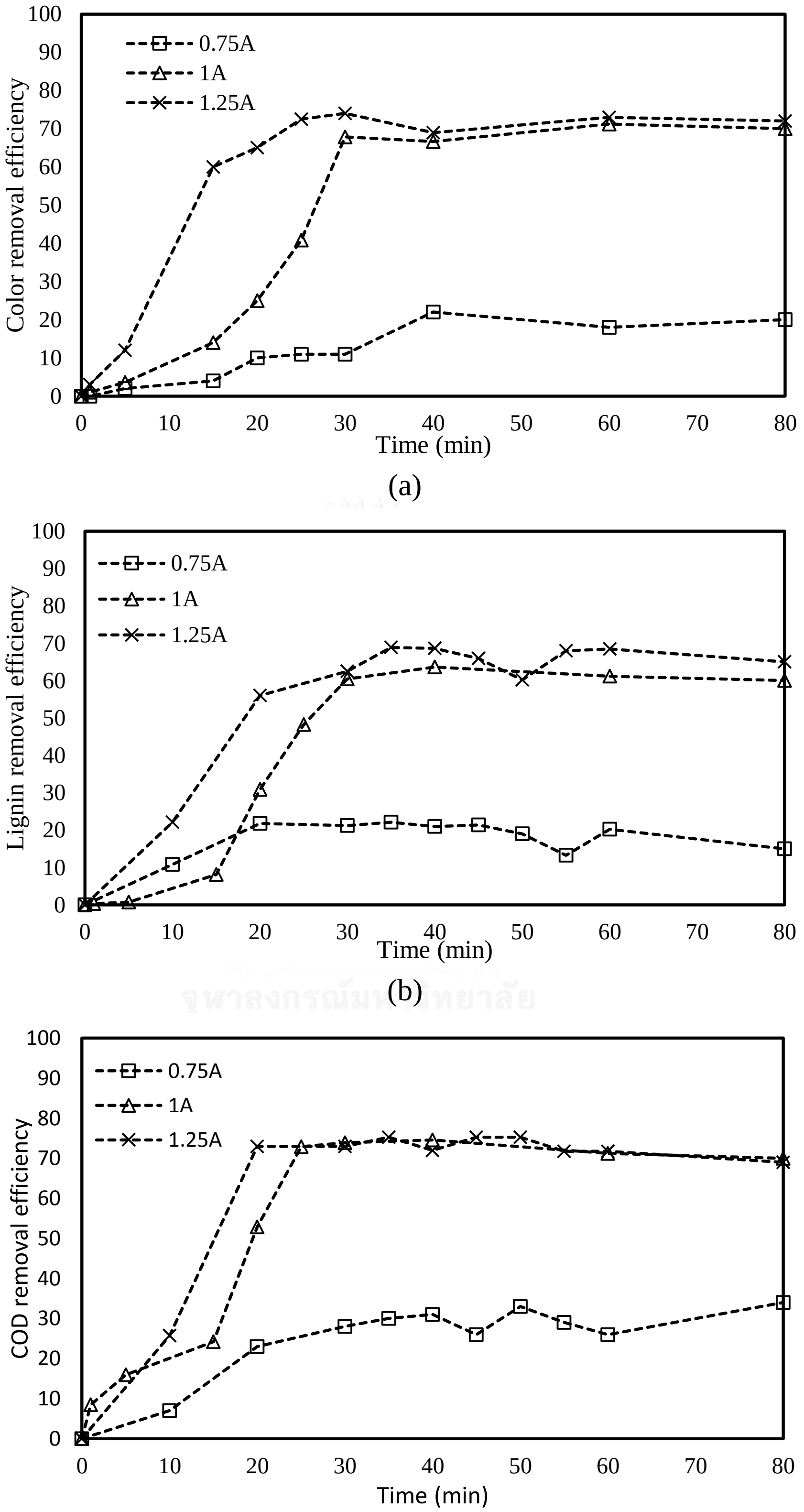


Figure 4. 6 Control experiment for direct H_2O_2 oxidation in step feeding of Fe^{2+} and H_2O_2 experiment on (a) color removal (b) lignin removal (c) COD removal

4.2.5 Ferrous control on electro-Fenton process

In electro-Fenton experiment, iron electrodes were used for the production of Fe^{2+} in solution. To study the effect of Fe^{2+} on precipitation after neutralization, a series of experiment was conducted as control experiment without any addition of H_2O_2. Electrical current was increased from 0.75A, 1A to 1.25A at initial pH of 3. As can be seen in Figure 4.7, color, lignin and COD removal increased when applied electrical current was increased, indicating an increasing of coagulation process. This is due to the higher of Fe^{2+} production in system. From this section, it was concluded that coagulation has a great effect on the removal of color, lignin and COD in Fenton process.



(a)

(b)

(c)

Figure 4. 7 Effect of coagulation in electro-Fenton process on (a) color removal (b) lignin removal and (c) COD removal

4.2.6 Hydrogen peroxide control on electro-Fenton process

Control experiments were conducted to investigate the effect of direct oxidation with H_2O_2 on color, lignin and COD removal. From the results shown in Figure 4.3, it was found that H_2O_2 alone, with H_2O_2 dosage of 240, 400, 1,000, 2,000, 4,000 and 6,000 mg/l, could remove color, lignin and COD at a lower percentage range. Thus, this effect can be negligible.

4.3 Fenton experiments

In this part, the treatment of lignin in synthetic wastewater were investigated to determine the optimum operating conditions. Treatment efficiency of color, lignin and COD by Fenton process were studied under different Fe^{2+}:H_2O_2 ratio (1:0.6, 1:1, 1:2.5, 1:5, 1:10, 1:15 and 1:20), initial pH (2,3 and 4) and Fenton's dosage (300, 400 and 500 mg/l). The detail of each parameter effect is shown below.

4.3.1 Effect of Fe^{2+}:H_2O_2 ratio

Fe^{2+} and H_2O_2 are main reagent in Fenton process to produce OH• with powerful oxidizing power to degrade the pollutants. However, Fe^{2+} and H_2O_2 also can act as the scavengers of OH• as shown in equation below (Pignatello, 1992).

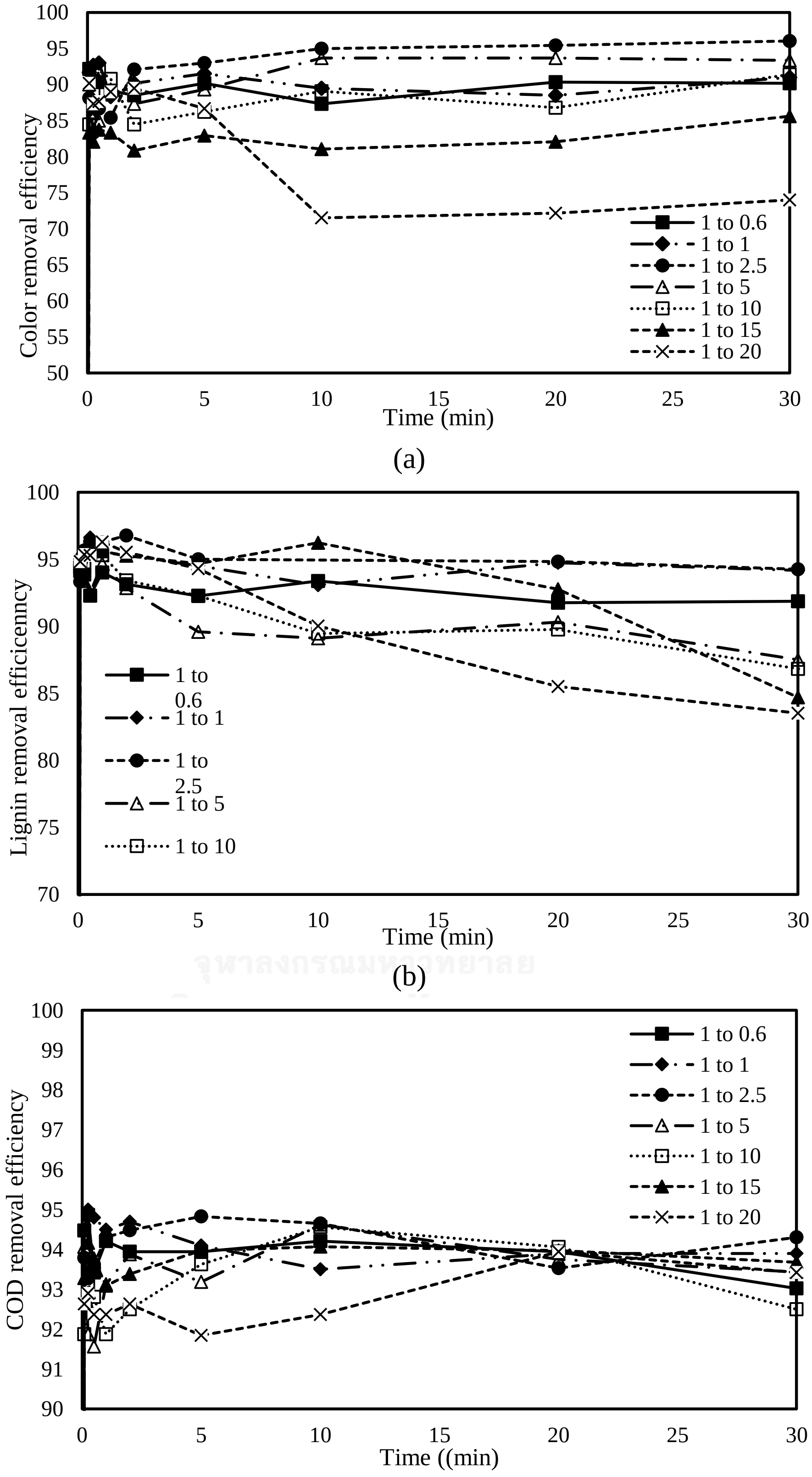
$$Fe^{2+} + OH\bullet \rightarrow OH^- + Fe^{3+} \tag{4.1}$$

$$H_2O_2 + OH\bullet \rightarrow HO_2^{\bullet} + H_2O \tag{4.2}$$

$$\text{Reactant} + H_2O_2 \rightarrow O_2 + \text{products} \tag{4.3}$$

To evaluate the effect of Fe^{2+}:H_2O_2 ratio on color, lignin and COD removal, the experiment was conducted on various ratio as 1:0.6, 1:1, 1:2.5, 1:5, 1:10, 1:15 and 1:20 as shown in Figure 4.8. Initial lignin concentration of 910 mg/l, initial ferrous ion concentration of 400 mg/l and initial pH of 3 was used under this experiment.

The result showed that increasing Fe^{2+}:H_2O_2 ratio from 1:0.6 to 1:2.5 can enhance color, lignin and COD removal. The color removal increased from 89%, 90% to 91% when Fe^{2+}:H_2O_2 ratio was applied from 1:0.6, 1:1 to 1:2.5, respectively. These ratio provided lignin removal efficiency of 93%, 94% and 95% and COD removal of 93%, 94% and 94%, respectively. However, increasing Fe^{2+}:H_2O_2 ratio by more than 1:2.5 was not effective for the increasing of process efficiency. The color removal of 90%, 88%, 83% and 81%, lignin removal efficiency of 91%, 91%, 92% and 91% and COD removal of 93%, 93%, 93% and 92% were indicated in this experiment when Fe^{2+}:H_2O_2 ratio were applied in the range of 1:5, 1:10, 1:15 to 1:20, respectively. As a result, it can be concluded that Fe^{2+}:H_2O_2 ratio of 1:2.5 was chosen as optimum condition in this experiment based on the highest in process efficiency. The lower removal efficiency would by come from a lower and higher Fe^{2+}:H_2O_2 ratio. In Fe^{2+}:H_2O_2 ratio below 1:2.5 or excess of Fe^{2+}, it can react with OH•. Thus, the amount of OH• in solution will be decreased and the organic degradation will be reduced also as shown in equation 4.1 (Masomboon, 2008). On the other hand, in Fe^{2+}:H_2O_2 ratio over 1:2.5 or excess amount of H_2O_2, oxidation reaction can be limited by generation of oxygen instead of OH• and inhibition due to H_2O_2 consuming OH• as shown in equation 4.2 and 4.3 (Masomboon, 2008). At higher ratio, removal efficiency was decreased with time due to the interference of iron species in the solution. H_2O_2 would decrease the pH in solution thus some Fe^{3+} did not precipitated forming $Fe(OH)_3$. Iron in solution can interfere with the estimation of color and lignin degradation.



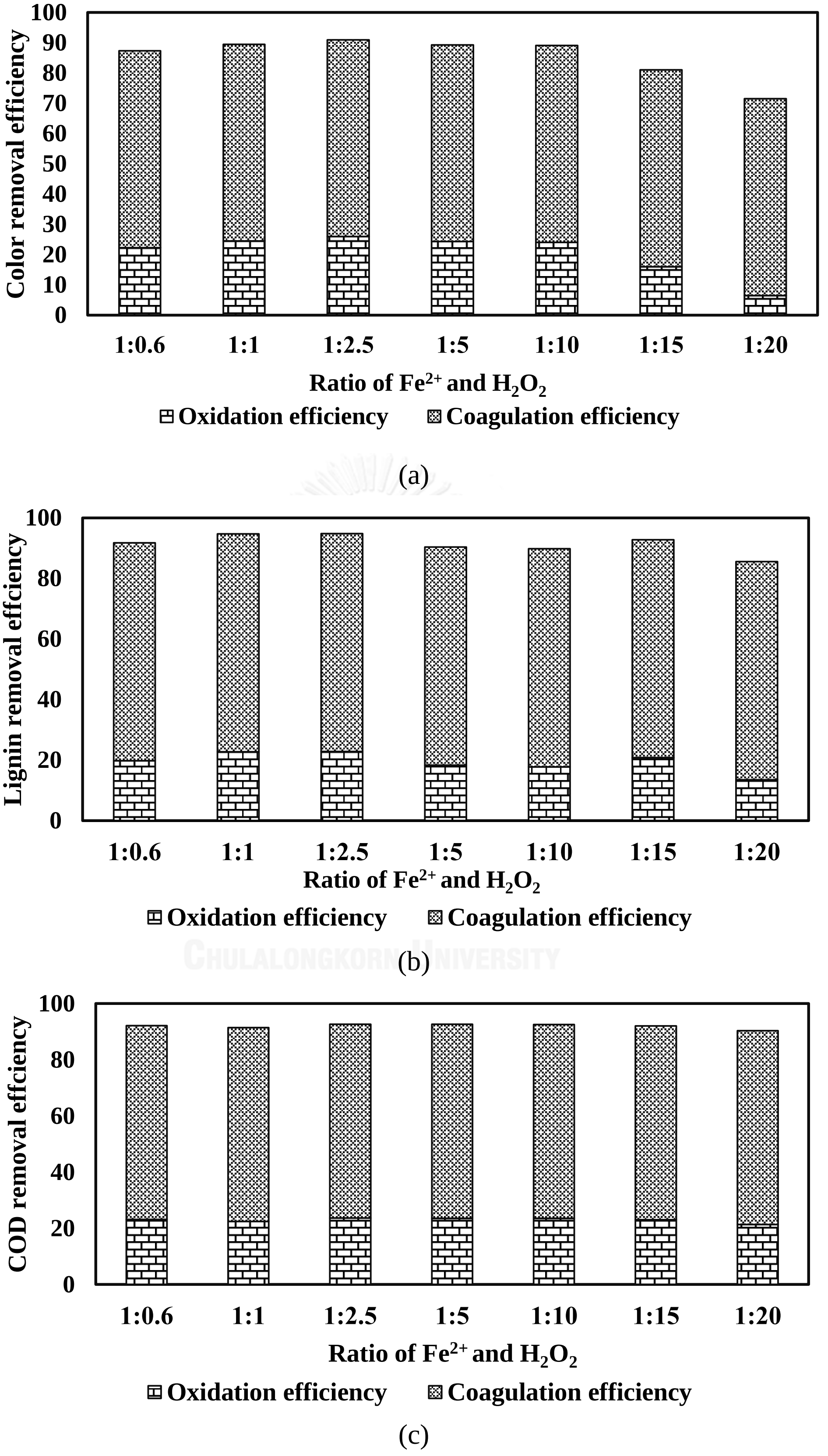
(a)

(b)

(c)

Figure 4. 8 Effect of Fe^{2+}:H_2O_2 ratio on (a) color removal (b) lignin removal (c) COD removal

The overall removal efficiency was the results of coagulation and oxidation. However, oxidation efficiency cannot be measured directly. From the control experiment, it was found that coagulation efficiencies on color, lignin and COD removal were 65%, 72% and 68%, respectively. In addition, the control experiment on direct oxidation by H_2O_2 showed that H_2O_2 alone did not effectively power to oxidize lignin. Thus minimum oxidation efficiency can be calculated from the difference between overall removal efficiency and coagulation efficiency. The calculated oxidation efficiency on color, lignin and COD removal at different ratio of Fe^{2+} and H_2O_2 was shown in Figure 4.9. The results confirmed that optimum ratio of Fe^{2+} and H_2O_2 was 1:2.5 for this experiment with the color, lignin and COD removal of 26%, 23% and 23%, respectively. An example of calculation on oxidation efficiency was mentioned in Appendix C.



(a)

(b)

(c)

Figure 4. 9 Oxidation efficiency at different Fe^{2+}:H_2O_2 ratio on (a) color removal (b) lignin removal (c) COD removal

The optimum ratio of Fe^{2+}:H_2O_2 in Fenton process was reported to be varied different. Torrades et al. (2011) reported the optimum ratio of Fe^{2+}:H_2O_2 by weight at 1:5 to achieve the maximal degradation efficiency in black liquor effluent from pulp industry. Mehmet F. Sevimli (2005) investigated the treatment of board mill effluent which collected at the biological treatment process. The results showed that optimum Fe^{2+}:H_2O_2 was 1:2 with color removal efficiency of 95% and 83% of COD removal. While Catalkaya and Kargi (2007) showed that the optimum Fe^{2+}:H_2O_2 ratio was 1:12. Moreover, Wang C. et al (2014) studied the performance of lignin degradation using Fenton process and found that optimum ratio of Fe^{2+}:H_2O_2 to reach the removal efficiency of lignin up to 87.5% was 1:30. All these findings indicated that ratio varied highly with characteristic of waste and its concentration.

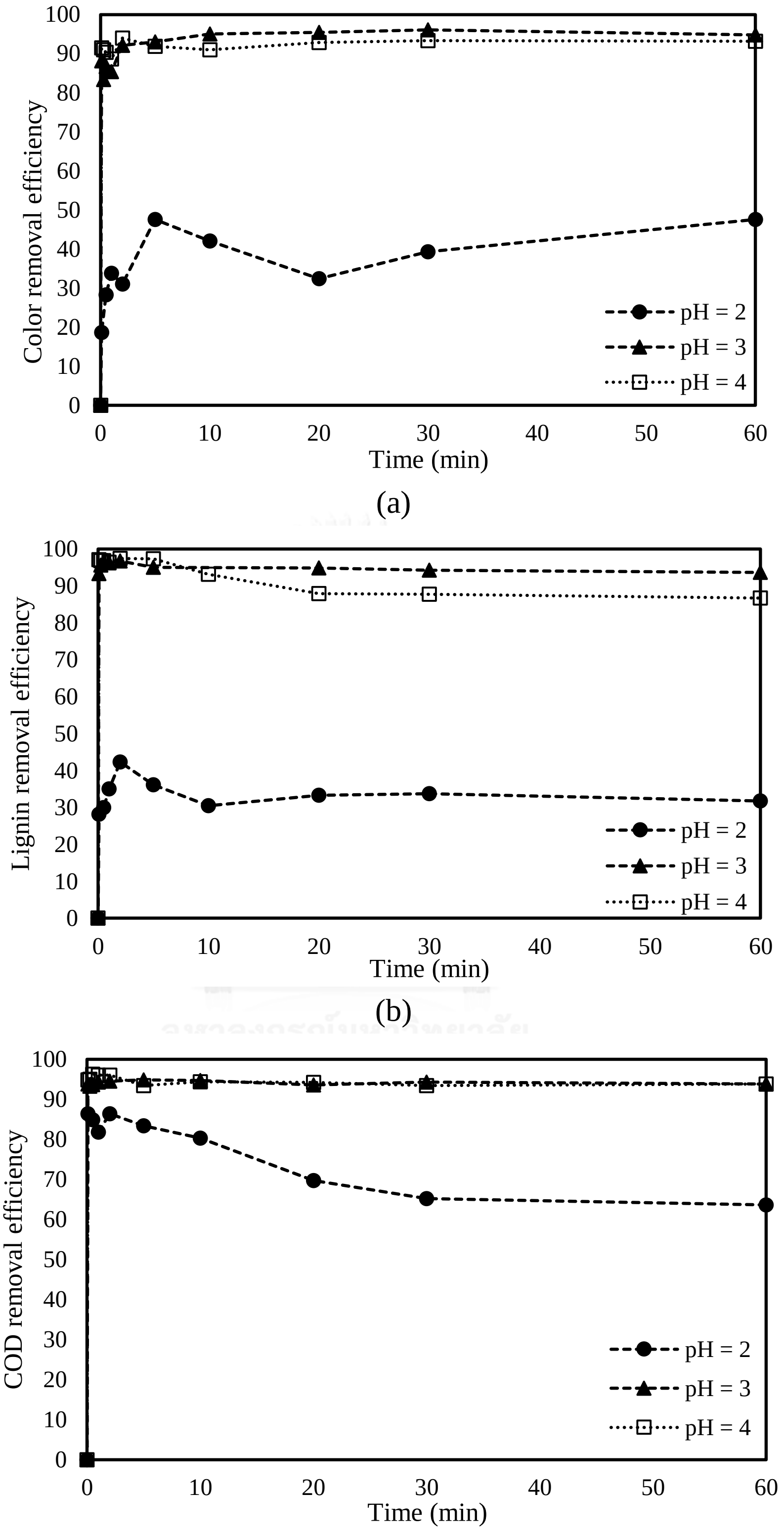
4.3.2 Effect of initial pH

pH is one of important parameters in Fenton process. Generally, Fenton reaction provided the highest removal efficiency at 2-4. pH in the solution controls the production of OH• and the concentration of Fe^{2+}. To evaluate the effect of initial pH, the experiments were conducted under optimum Fe^{2+}:H_2O_2 ratio and varied pH as shown in Figure 4.10. It can be seen from Figure 4.10 that pH affected on color, lignin and COD removal efficiency in Fenton process. The color, lignin and COD removal efficiency increased 55%, 62% and 16%, respectively when pH increased from 2 to 3 and decreased 2%, 2% and 0.7%, respectively when pH increased from 3 to 4. The experimental data indicated that the optimum pH was around 3.

At pH below 3, the excess H^+ can be reacted with H_2O_2 to produce $H_3O_2^+$ which was stable and did not react with Fe^{2+} thus there was a decreased the generation of OH• (Oliveira et al., 2014). In addition, iron complex $[(Fe(H_2O)_6)^{2+}]$ was found at lower pH which reacted more slowly with H_2O_2 and less OH• production. This reduced the degradation efficiency. Moreover, the formation of $FeOOH^{2+}$ was inhibited at lower pH. The generation was the important step for regeneration of Fe^{3+} to Fe^{2+} as shown in equation 4.4. When the production of $FeOOH^{2+}$ was inhibited, the reaction tended to go to the left side of equation 4.4 leading to reduce the process efficiency.

$$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH^{2+} + H^+ \qquad (4.4)$$

At pH over 3, Fe^{2+} was unstable and easily form Fe^{3+} which tends to produce ferric hydroxo complexes or ferric oxyhydroxides (Anna Goi, 2010). Therefore, the oxidation efficiency of Fenton’s reagent might decrease because these complexes had low the activity and cannot react with H_2O_2. Moreover, the stability of H_2O_2 is lower at high pH by decomposition to waster and oxygen (Mohajeri et al., 2010). Thus, the experimental results can be concluded that the optimum initial pH of this process should be pH of 3.



(a)

(b)

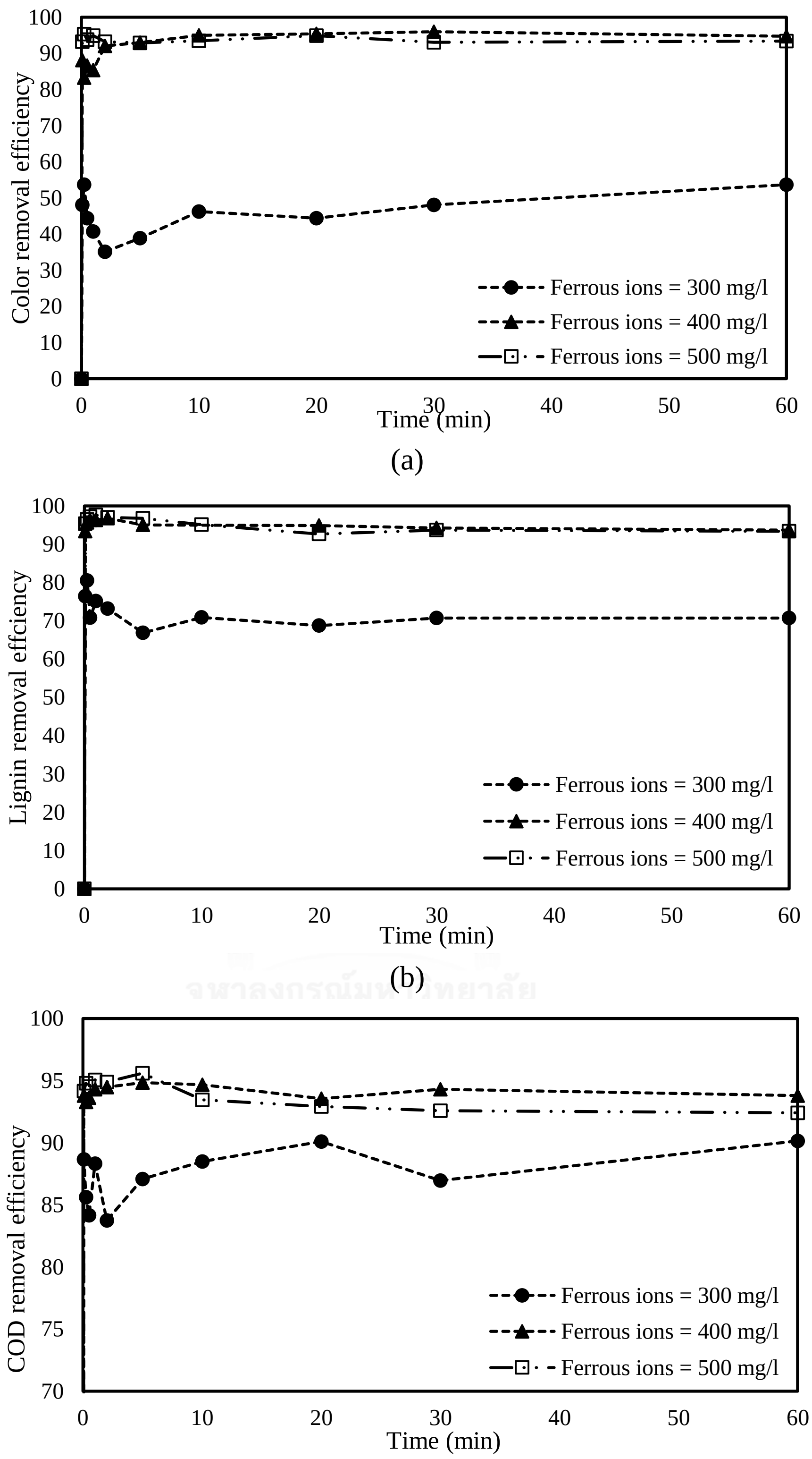
(c)

Figure 4. 10 Effect of initial pH in Fenton process on (a) color removal (b) lignin removal (c) COD removal

The effect of pH was considered as a very significant operating parameter by many researchers, because it impacted to the treatment efficiency. Torrades et al. (2011) reported that the optimum pH was 3 for degrading organic compounds in black liquor which was comparable to Mohajeri et al. (2010). While Catalkaya and Kargi (2007) found that the favorable pH was 5. Moreover, Mehmet Faik Sevimli, Deliktaş, Şahinkaya, and Güçlü (2014) studied on the degradation of organic compound in paper wastewater discharged from the point of an existing wastewater treatment plant. The results showed that pH of 7.3 was provided the highest in degradation efficiency in term of COD removal.

4.3.3 Effect of Fenton's reagent dosage

The amount of Fenton's reagent is one necessary parameter for treatment of wastewater. The generation of OH• depends on the amount of Fe^{2+} and H_2O_2. Therefore, in order to assess the relationship between removal efficiency and reagent's dosage, a set of experiments was conducted by fixing Fe^{2+}:H_2O_2 ratio at 1:2.5 as optimum ratio and varied the amount of both reagents. In experiments, Fe^{2+} concentration was applied at 300, 400 and 500 mg/l. The results showed that increasing the Fenton's dosage improve the removal efficiency as shown in Figure 4.11. For color removal efficiency, it was 45%, 91% and 94% when Fe^{2+} concentration was applied at 300, 400 and 500 mg/l, respectively. Moreover, these Fe^{2+} dosage was provided 72%, 95% and 95% for lignin removal and 87%, 94% and 94% for COD removal, respectively. However, Mohajeri et al. (2010) report that the removal efficiency increased with increasing amount of Fenton's reagent, up to optimum dosage. Higher dosage can provide in lower removal efficiency because OH• may be scavenged by the reaction with excess Fe^{2+} and H_2O_2.



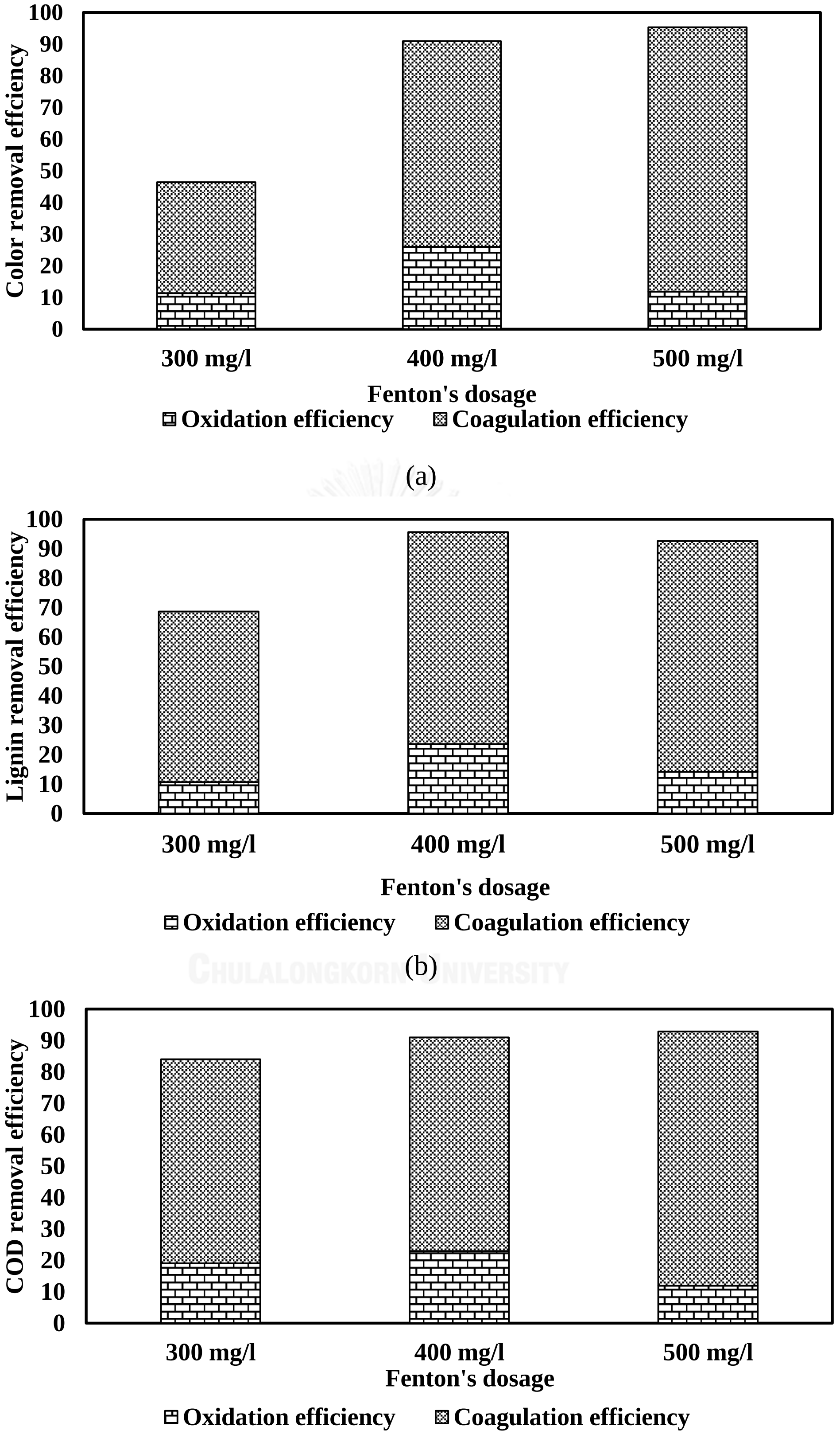
(a)

(b)

(c)

Figure 4. 11 Effect of Fenton's reagent dosage on (a) color removal (b) lignin removal (c) COD removal

In this section, oxidation efficiency in term of color, lignin and COD removal were compared to determine the optimum chemical usage. From control experiment, the minimum oxidation efficiency can be determined by the difference between overall removal efficiency and coagulation efficiency. Increasing the initial concentration of Fe^{2+} from 300 to 500 mg/l can have an increasing on color oxidation efficiency to 10%, 26%, 10%, respectively. The oxidation efficiency of lignin removal was 14%, 23% and 17% and 22, 23% and 14% for COD oxidation efficiency. As can be seen from Figure 4.12 that the highest oxidation efficiency was obtained when the Fe^{2+} concentration was 400 mg/l. Higher in oxidation removal efficiency, more economic in term of chemical cost and an enormous increase in the Fe^{2+} leaded to an increase of the total dissolved solids content of the effluent and this was not permitted. Thus, laboratory scale studies were used 400 mg/l of Fe^{2+} to oxidize lignin synthetic wastewater.



(a)

(b)

(c)

Figure 4. 12 Oxidation efficiency at different Fenton's dosge on (a) color removal (b) lignin removal (c) COD removal

4.3.4 UV-VIS-absorption spectra during Fenton process

UV-VIS spectra of the Fenton reaction for lignin degradation was shown in Figure 4.13. The results showed that Fenton reaction changed the peak of the reaction in solution. Light absorption of lignin's absorption peak at 280 nm decreased with time. Moreover, a new peak of 230 nm appeared at 30 minutes in the spectra. These results indicated that the degradation of lignin and formation of intermediates with characterizing absorption at 230 nm. At 60 minutes, the peak of lignin disappeared and it absorption at 230 nm also decreased. Thus, it can be concluded that lignin has been oxidized to form intermediates and can be further oxidized to CO_2 and water. A dominant absorption band at 224-230 nm indicated the presence of $-NH_2$, -COOH, COO^- or –CN bond Prasad and Sinha, 1981). Moreover, Thongkrua (2010) identified the patterns of by-products from lignin removal by oxidation process as 2,6-Dimethyl-5-methylphenyl, aminopyridine-3,4-dicarboxyimide, 1-methyl-2-phynylindole, 2-ethylacridine, 2-methylbenzaldehyde, glucine, 7H-dibenzo[b,g] carbazole, 5H-naphtho[2,3-c]carbazole, 2,4 dimethylbenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde (vanillin).

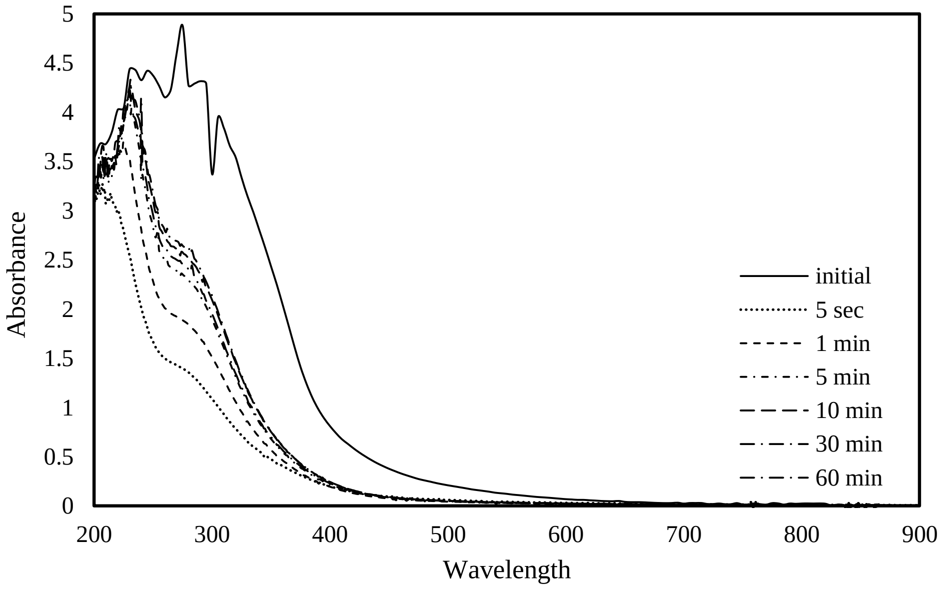


Figure 4. 13 UV-VIS absorption spectra during Fenton process

4.3.5 Sludge production

Fenton technology has strong advantage in treatment of toxic wastewater but produces chemical sludge. Sludge generation in Fenton is expected as catalyst in the form of Fe^{3+} precipitated during the neutralization step (Kiril Mert, Yonar, Yalili Kiliç, & Kestioğlu, 2010). The results indicated that suspended solid was 1,088 mg/l at optimum operating conditions as shown in Figure 4.14. Unlike in biological processes where sludge production is high and the sludge treatment reported to cost approximately 35-50% of total operating costs of wastewater treatment, Fenton oxidation, sludge production is minimal (Dewil, Baeyens, & Neyens, 2005). Moreover, Mahiroglu, Tarlan-Yel, and Sevimli (2009) reported that Fenton sludge was easily formed and handle. However, improvement of operating feeding from initial feeding to step feeding condition may have a positive role to reduce the sludge generation, cost of wastewater treatment and make a certain economic benefit.

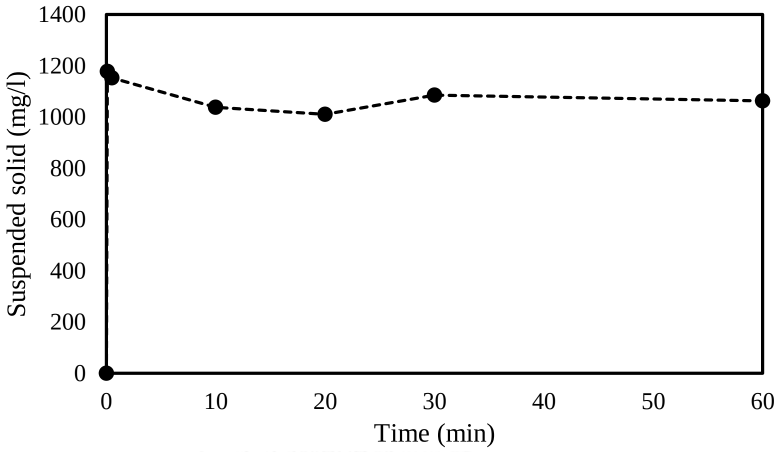


Figure 4. 14 Sludge production

4.4 Modified-Fenton experiments

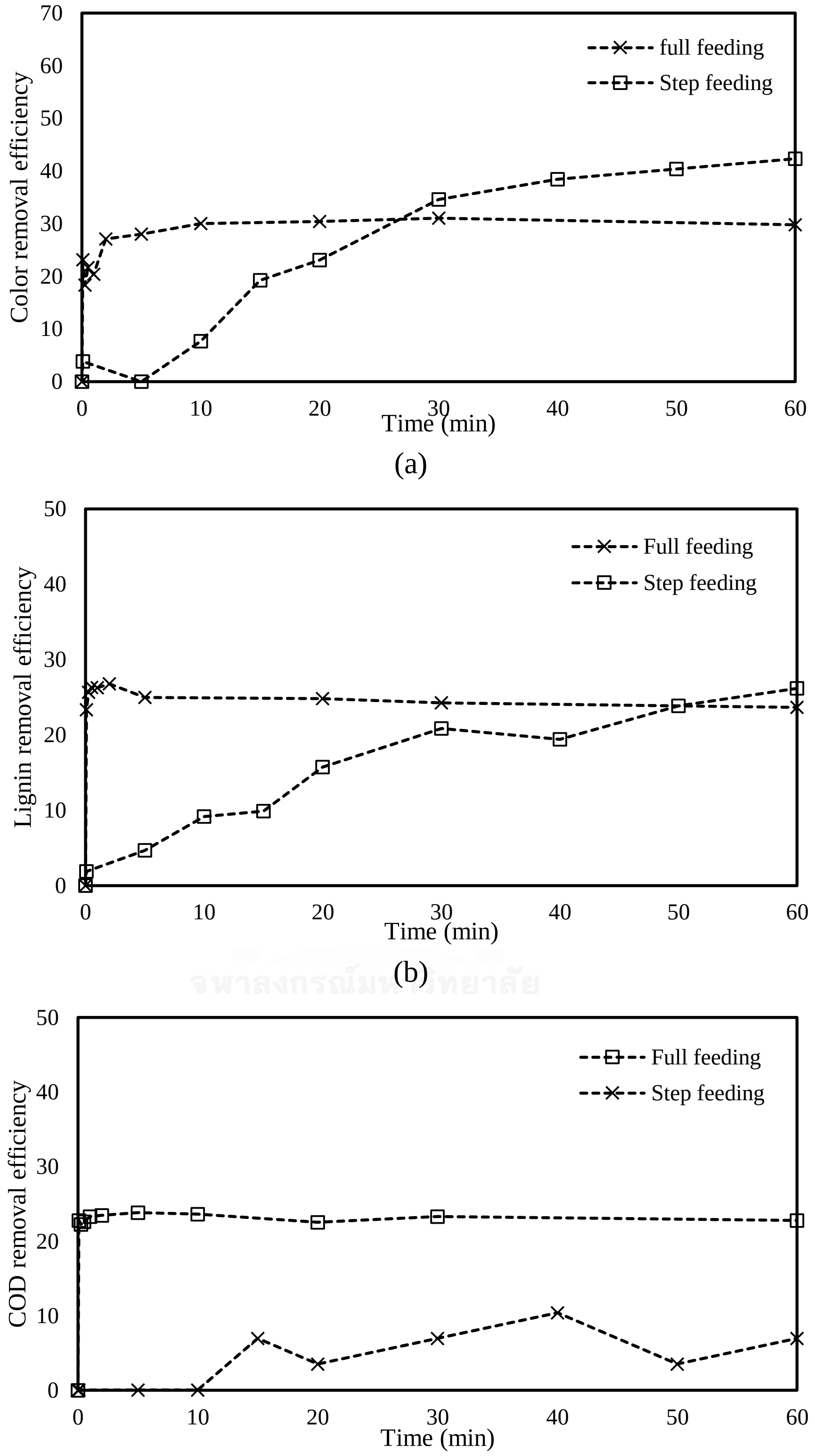
4.4.1 Step feeding operation

Step feeding operation in this work was conducted in two different ways which were H_2O_2 step feeding and step feeding of Fe^{2+} and H_2O_2. These two operations were compared in term of oxidation efficiency on color, lignin and COD removal, sludge generation and chemical used. From the previous work, there are some benefits of step feeding mode over initial feeding which are higher removal efficiency, reduce the sludge production and lower in chemical usage. However, initial feeding was faster in removal organic compounds in wastewater than that of step feeding operation.

4.4.1.1 H_2O_2 step feeding operation

Previous work showed that step feeding of H_2O_2 or continuous mode could improve the process efficiency . Thus, the effect of H_2O_2 feeding on color, lignin and COD removal by Fenton process was investigated. This condition was compared between initial feeding mode and H_2O_2 step feeding mode at 5 minutes interval. Total reaction time was performed at 60 minutes and total H_2O_2 dosage was 1,000 mg/l. Initial concentration of Fe^{2+} of 40 mg/l was used in this section. The removal efficiency from coagulation can be ignored due to low level of Fe^{2+} was added.

From the control experiment, 40 mg of Fe^{2+} cannot affect on the removal efficiency by coagulation process. Thus, the overall removal efficiency in this section was the same as oxidation efficiency. From the results in Figure 4.15, the oxidation efficiency of color removal at 60 minutes increased from 26% to 42% when step feeding of H_2O_2 was applied. The same tend was found in lignin removal efficiency. The lignin removal increased from 23% to 26% at 60 minutes. However, the efficiency in COD removal decreased from 23% to 6% when H_2O_2 was gradually applied. The cause of this result might be the regeneration of Fenton's reagent in term of Fe^{2+} concentration for generating OH• on the reaction. It can be seen in the reaction between Fe^{3+} and H_2O_2 by equation 4.4. Moreover, the use of sufficient H_2O_2 concentration in the step feeding operation and the optimum ratio of Fe^{2+}:H_2O_2 could be decreased the scavenging effect on the reactions of OH•. The major advantage of this operation was to minimize the sludge production.



(a)

(b)

(c)

Figure 4. 15 Effect of step feeding of H_2O_2 on oxidation efficiency of (a) color removal (b) lignin removal and (c) COD removal

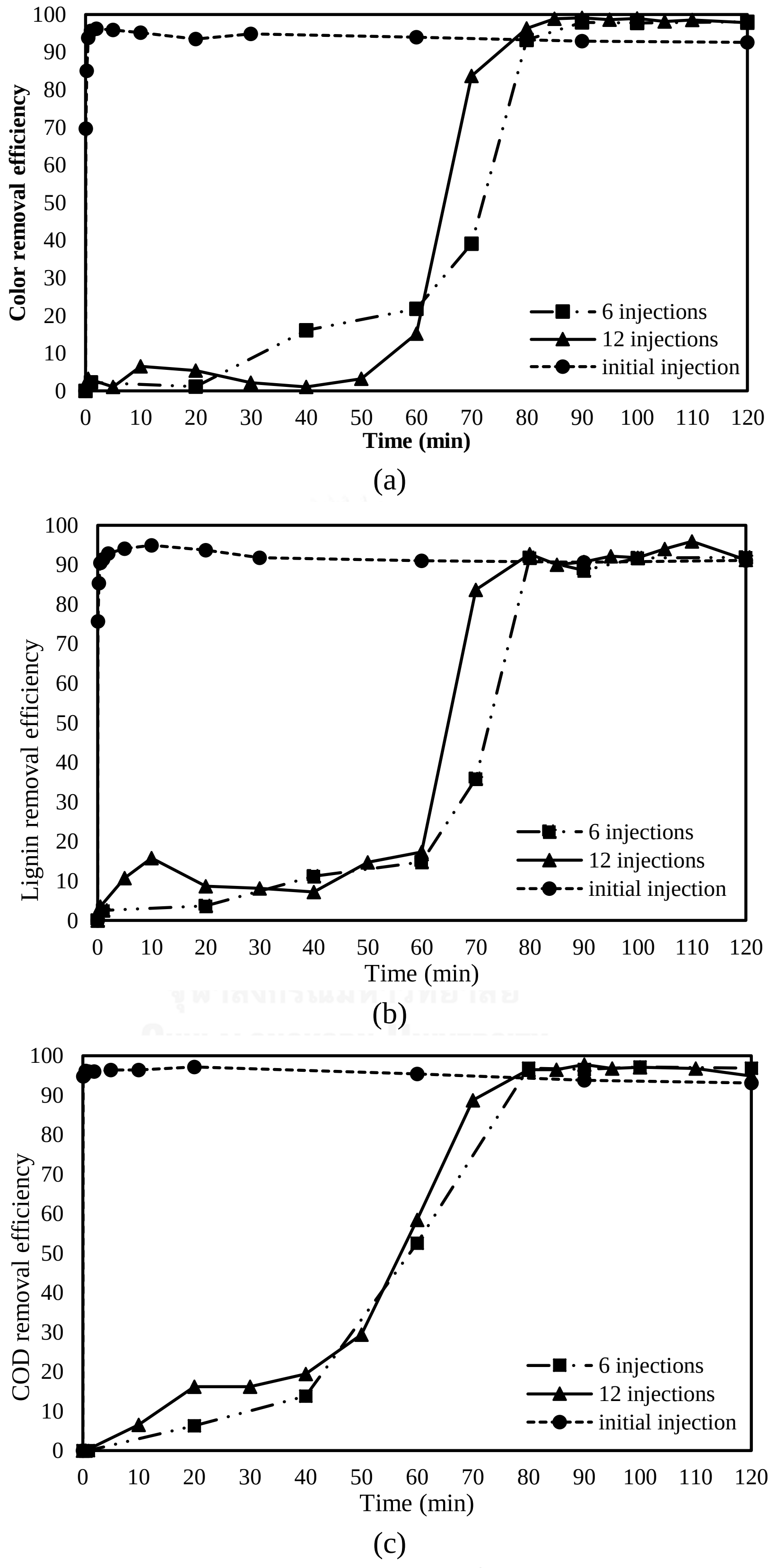
The result of another study, Mohajeri et al. (2010) found that increasing number of feeding affected on the increase in COD and color removal efficiency because more OH• was produced and used to oxidize the pollutants. Moreover, L. Jiang and Mao (2012a) indicated that continuous feeding of H_2O_2 increased COD removal efficiency. One step feeding of H_2O_2 caused faster consumption of H_2O_2. The hydroperoxy radicals were produced by the decomposition of H_2O_2 as shown in equation 4.2. However, Zhang, Choi, and Huang (2005) found that initial COD removal rate increased with the decreasing feeding time and it becomed the highest efficiency when H_2O_2 was added all at once. They reported that with the decrease of feeding time, the concentration of H_2O_2 at the beginning period would increase. Thus, more OH• can be generated by the reaction between Fe^{2+} and H_2O_2.

4.4.1.2 Fe^{2+} and H_2O_2 step feeding operation

When applying a large dose of H_2O_2, the scavenging effect of OH• increased, so it can be reduced the oxidation efficiency of organic compounds. On the other hand, when large amount of Fe^{2+} was used, Fe^{2+} can react with OH•. In order to investigate the feeding mode effect, Fenton’s reagent was fed with two different methods as follows:

(1) Both Fe^{2+} and H_2O_2 were added simultaneously in six-time feedings (at 0, 20, 40, 60, 80 and 100 minutes).
(2) Both Fe^{2+} and H_2O_2 were divided in 12 additions (at 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 minutes)

Total reaction time was 120 minutes. The total concentration of Fe^{2+} and H_2O_2 were 400 and 1,000 mg/l, respectively under initial pH of 3. The result in Figure 4.16 showed that multiple feeding of Fenton’s reagent provided in higher process efficiency. The removal efficiency of color, lignin and COD with 6 additions were 97%, 91% and 96%, respectively in 120 minutes and about 3%, 0.5% and 2% higher than that of a single dose. In 12 feedings, it provided higher color, lignin and COD removal efficiency of 4%, 1% and 3%, respectively compared to single feeding. This cause of this result was to the reduction of scavenging effect of OH•. When excess Fe^{2+} or H_2O_2 was applied into the solution, they can react with OH• to reduce the oxidation removal rate of organic material. Moreover, chemical used in 12-times feeding was less than that of 6-times feeding at the same removal efficiency. Thus, multiple feeding of Fenton’s reagent increased with the decreasing chemical used leading to reduce the sludge production. Low percentage of removal efficiency was obtained at the earlier stage of reaction. After that, removal efficiency significantly increased due to precipitation of iron as $Fe(OH)_3$.



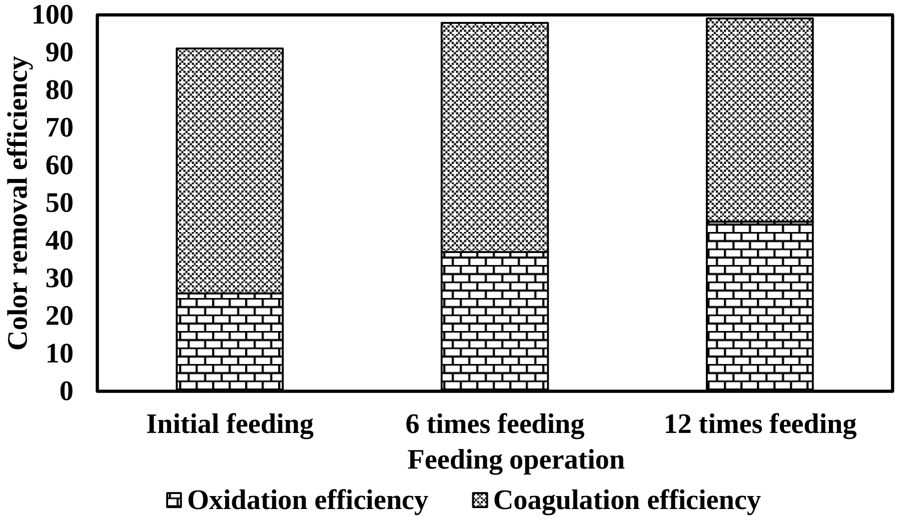
(a)

(b)

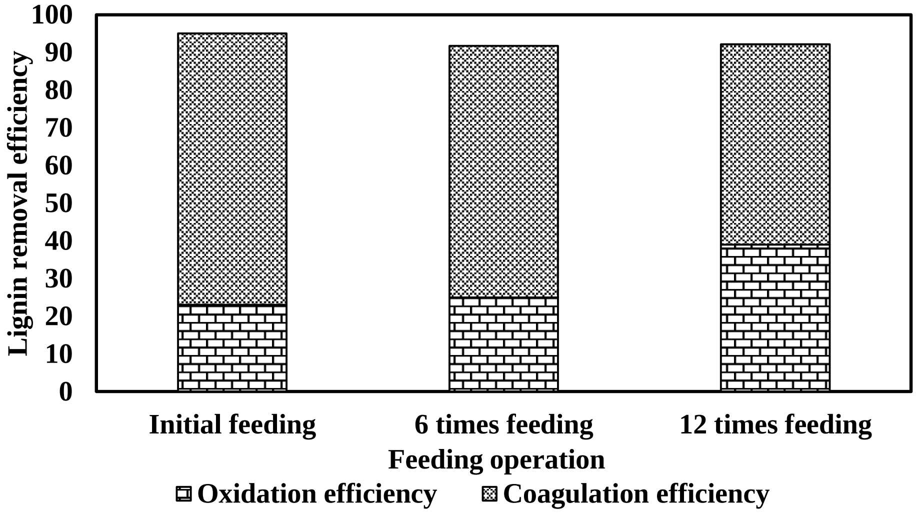
(c)

Figure 4. 16 Effect of step feeding operation of Fe^{2+} and H_2O_2 on (a) color removal (b) lignin removal (c) COD removal

To compare the oxidation efficiency between single feeding and step feeding operation, the results in Figure 4.17 was found that the oxidation efficiency in color removal increased from 26% to 37% when feeding operation was applied from initial feeding to step feeding with 6 injection, and increased from 37% to 45% when number of feedings increased from 6 injections to 12 injection as shown in Figure 4.19. For lignin removal, oxidation efficiency were 23%, 25% and 39% when single feeding, 6 time-feeding and 12-time feedings were applied, respectively. Oxidation efficiency of COD removal were 23%, 31% and 38% were reported in this experiment. From the results, it can be concluded that step feeding operation with 12 injection provided higher removal efficiency, reduce the chemical used at the same removal efficiency.



(a)



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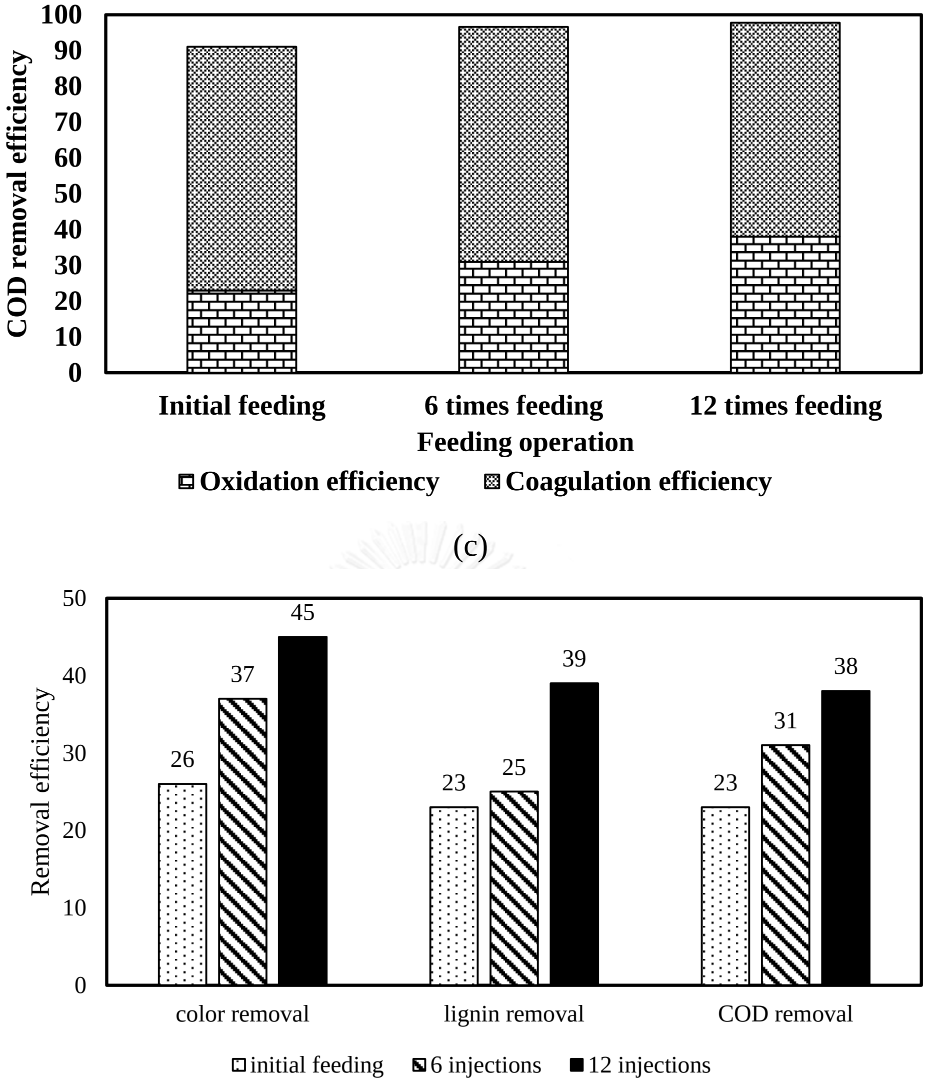


(c)

(d)

Figure 4. 17 Effect of step feeding of F^{2+} and H$_2$O$_2$ on oxidation efficiency of (a) color removal (b) lignin removal (c) COD removal (d) oxidation efficiency comparison

The results in another study, Yoo, Cho, and Ko (2001) reported that multiple feeding could improve the organic content removal rate and also the cost of reagent and disposal of sludge could be lowered. This is similar to the of Zhang et al. (2005), they found that the process efficiency of Fenton enhanced by adding Fenton’s reagent in multiple step than that in a single step. In addition, they reported that step addition of both Fe^{2+} and H_2O_2 was more effective than that of H_2O_2 only due to the scavenging effect was minimized. Moreover, Mahmud et al. (2011) found that modifications of the mode of addition of Fenton reagents can improve the removal of organic materials. The results showed that step addition of Fenton’s reagents increased COD removal efficiency. However, Rivas, Beltrán, Gimeno, and Alvarez (2003) found that COD removal efficiencies were not different for single, two and three-step feeding of Fenton's reagent.

To investigate the effect of feeding interval on color as shown in Figure 18, lignin and COD removal, the experiment was conducted at varied time interval as 5 minutes interval and 3 minutes interval. 12 feedings and optimum Fe^{2+}:H_2O_2 were obtained in previous part under pH of 3. The total concentration of Fe^{2+} and H_2O_2 were 400 and 1,000 mg/l and total reaction time was at 60 minutes. As can be seen in Figure 4.20, the results showed that step feeding operation with interval time of 3 minutes provided color removal efficiency of 96% in 36 minutes while multiple addition of Fenton's reagent with interval time of 5 minutes provide 95% of color removal in 40 minutes. For lignin removal, feeding mode at 3 minutes interval required reaction time of 33 minutes to achieve the same efficiency as initial feeding while feeding mode at 5 minutes required reaction time of 40 minutes. These was the same trend to COD removal. Thus, it can be indicated that reaction time to achieve the same efficiency as single feeding decreased with decreasing the feeding interval.

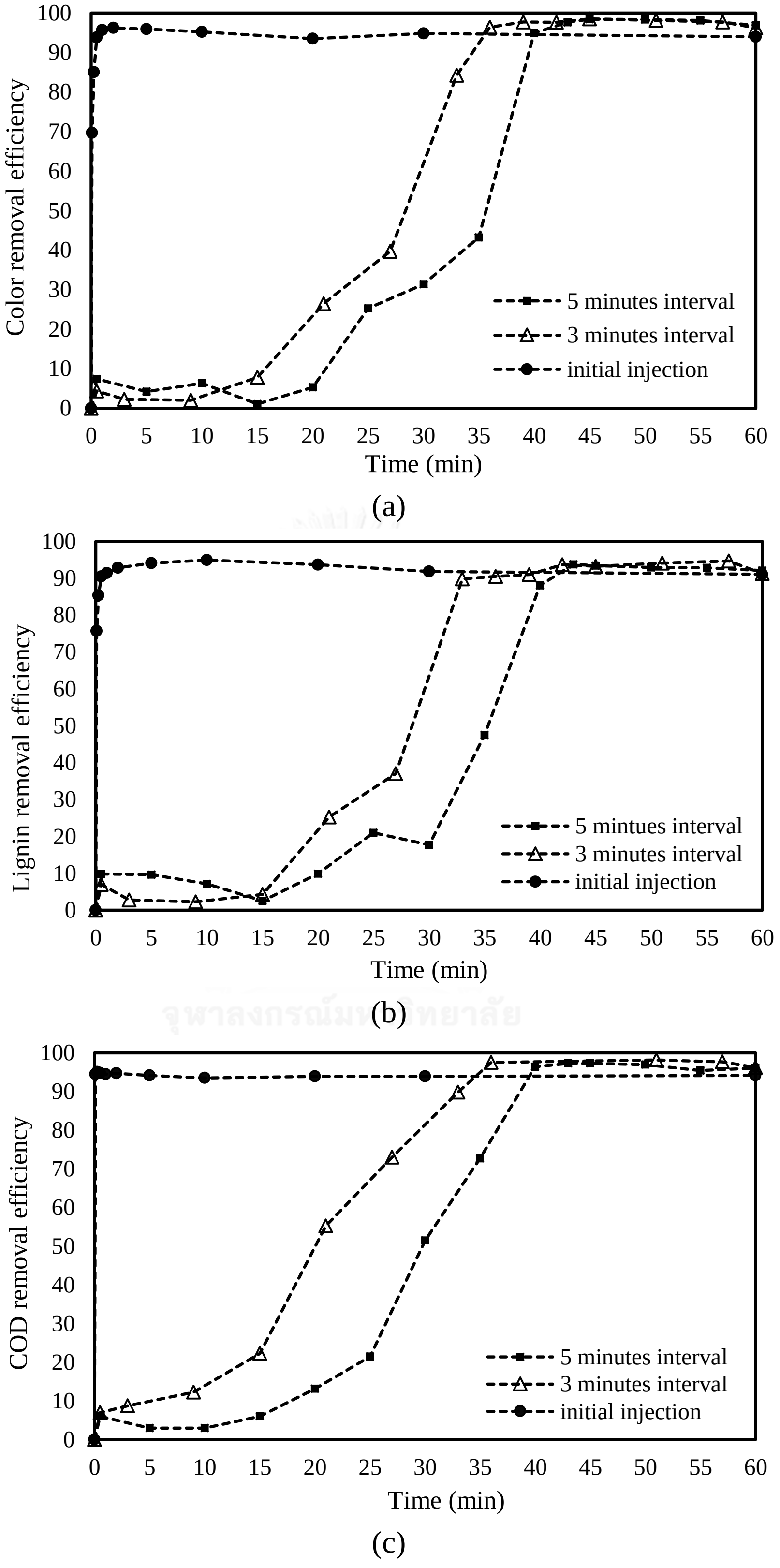


Figure 4. 18 Effect of feeding interval in step feeding Fe^{2+} and H_2O_2 on (a) color removal (b) lignin removal (c) COD removal

Fenton treatment of wastewater is limited by the final production of iron sludge, which requires for sludge disposal (Plgnatello, 1992). Thus, step feeding operation was comducted in order to reduce the generation of sludge. Figure 4.22 showed the comparison of sludge production between initial feeding and step feeding of Fe^{2+} and H_2O_2, the results showed that sludge production in multiple feeding increased with number of feedings. However, single dose feeding produced more sludge than multiple feeding at the same removal efficiency. Step feeding of Fe^{2+} and H_2O_2 could reduce the sludge generation of 20.7% at the same removal efficiency as initial feeding. The cause of this result was that Fe^{2+} was used at low concentration in step feeding operation. For other study, Mahmud et al. (2011) studied the effect of multiple feeding to minimize the sludge production. They found that sludge production reduced significantly 17% when applied multiple dosages of Fenton reagents with greater removal of COD and color. The similar results was reported by Yoo et al. (2001) that report that the cost of reagent and final disposal of sludge could be lower because reduced amount of Fe^{2+} was added at step addition operation.

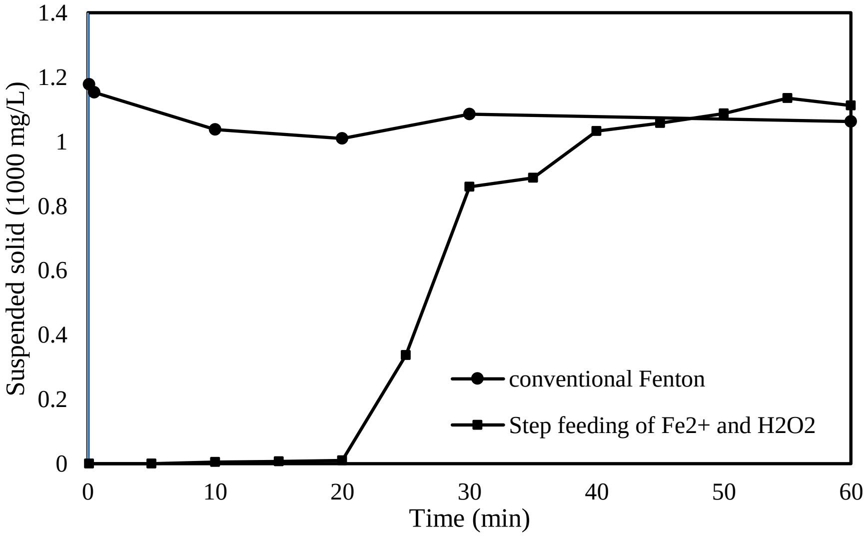


Figure 4. 19 Comparison of sludge production at initial feeding and step feeding operation

4.4.2 Electro-Fenton process

In Fenton reaction, OH• are produced in the solution by chemical reaction between Fe^{2+} and H_2O_2 to complete destruction of pollutants into harmless compounds, for example, CO_2, water and inorganic salts (Neyens & Baeyens, 2003). However, the results from the previous section indicated that calculated oxidation efficiency in this process is quite low. Thus, electro-Fenton process is developed to minimize the disadvantage of conventional Fenton process.

In experiment, cathode and anode electrode were made from steel with working surface area of 50 cm^4. Fe^{2+} was produced from iron electrode while H_2O_2 was external added to start the reaction. Moreover, the regeneration of Fe^{2+} can be occurred at the cathode electrode. This part aimed to determine the optimum Fe^{2+}:H_2O_2 ratio (varied at 1:0.6, 1:1, 1:2.5, 1:5, 1:10 and 1:15) and optimum current density (varied at 150, 200 and 250 A/m^2). Then, step feeding of electro-Fenton was performed to enhance the oxidation efficiency under optimum operating conditions. The detail of each experiment was shown below.

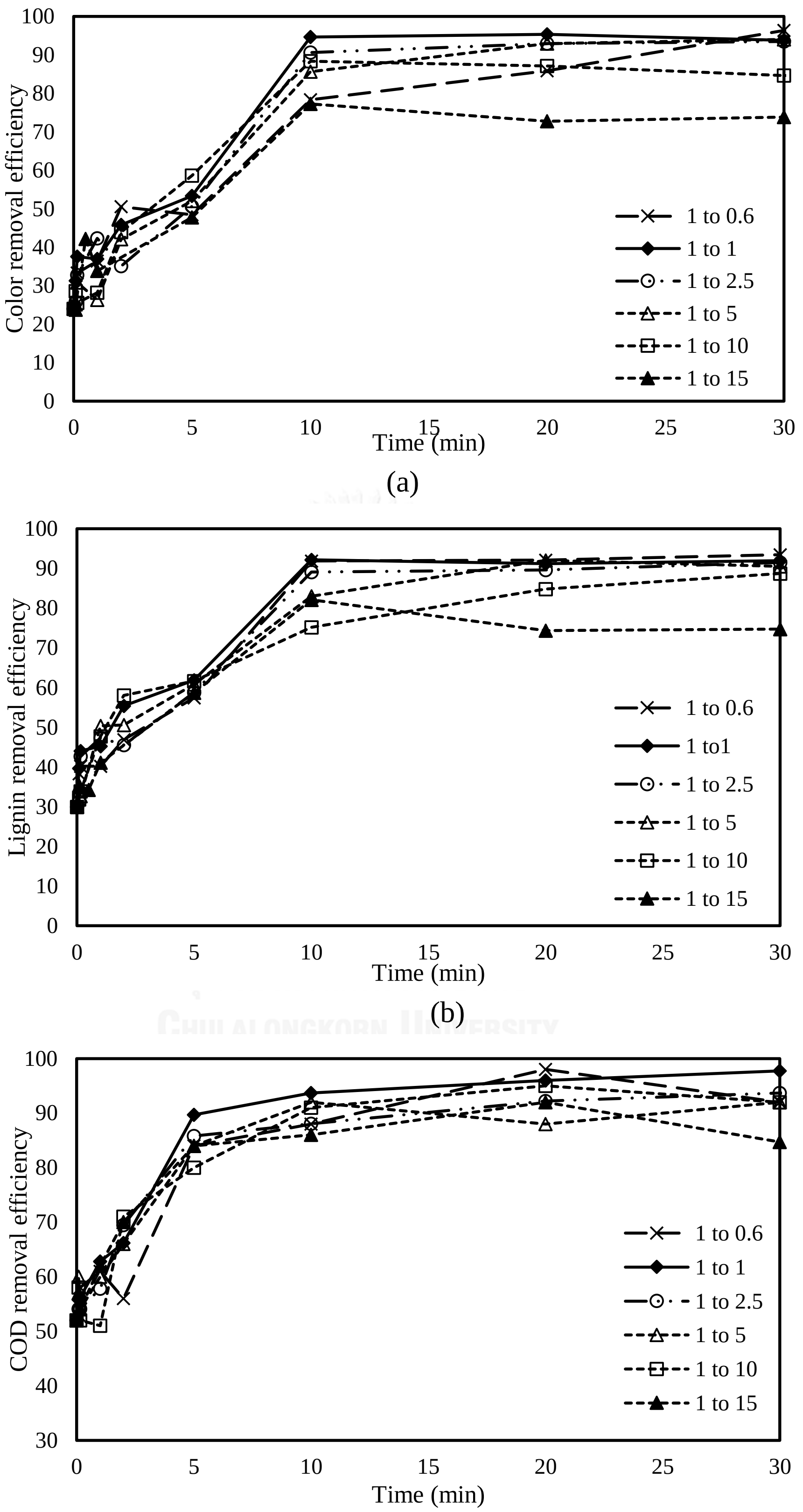
4.4.2.1 Effect of Fe^{2+}:H_2O_2 ratio

The dosage of Fe^{2+} and H_2O_2 in solution has a greater effect on process. The effect of Fe^{2+}:H_2O_2 ratio on color lignin and COD removal was studied in this solution.

In experiment, electrical current of 1A was supplied to the synthetic wastewater to produce Fe^{2+} in solution for 30 minutes. Then, H_2O_2 in the concentration of 120, 200, 500, 1,000, 2,000 and 3,000 mg/l was added after 20 minutes to start the reaction. The ratio was varied at 1:0.6, 1:1, 1:2.5, 1:5, 1:10 and 1:15 under pH of 3.

The results indicated that increasing Fe^{2+}:H_2O_2 ratio from 1:0.6 to 1:1 could accelerated process efficiency. Figure 4.20 showed that the Fe^{2+}:H_2O_2 ratio of 1:1 was the maximized the condition for electro-Fenton process. At Fe^{2+}:H_2O_2 ratio below 1:1 or excess Fe^{2+}, the rate of oxidation was found to decrease due to scavenging effect of OH• by Fe^{2+}. The Fe^{2+} and organic compounds competed to react with OH• resulting in decreasing in the rate of oxidation as shown in equation 4.1 (Rosales, Pazos, & Sanromán, 2012). On the other hand, at Fe^{2+}:H_2O_2 ratio over 1:1 or excess of H_2O_2, an excess H_2O_2 had a scavenging effect on OH• leading to the production of hydroperoxyl radical (HO_2•) which is weaker oxidizing power than OH• as shown in equation 4.2. Moreover, excess amount of H_2O_2 could decompose to water and oxygen as shown in equation 4.5 (San Sebastián et al., 2003). Therefore, it can be concluded that the optimum Fe^{2+}:H_2O_2 ratio was 1:1 for this experiment based on the highest removal efficiency. At optimum ratio, the overall removal efficiency on color, lignin and COD were 93%, 91% and 92%, respectively at the end of reaction time.

$$H_2O_2 \quad \rightarrow \quad H_2O + O_2 \qquad (4.5)$$



(a)

(b)

(c)

Figure 4. 20 Effect of Fe^{2+}:H$_2$O$_2$ ratio in electro-Fenton process on (a) color removal (b) lignin removal and (c) COD removal

This section aimed to compare the oxidation efficiency on color, lignin and COD removal at different ratio of Fe^{2+} and H_2O_2 in electro-Fenton process, but oxidation efficiency could not measure directly. Thus, the minimum oxidation efficiency could be determined from the difference between overall removal efficiency and coagulation efficiency. From the results in Figure 4.21, it showed that oxidation efficiency of color were 24%, 28%, 27%, 23%, 16% and 11% at 30 minutes of reaction time when Fe^{2+}:H_2O_2 ratio was varied at 1:0.6, 1:1, 1:2.5, 1:5, 1:10 and 1:15, respectively. At these ratio, oxidation efficiency were 19%, 22%, 17%, 17%, 14% and 8% for lignin removal and 18%, 20%, 21%, 16%, 18% and 4% for COD removal. The highest oxidation efficiency was obtained when Fe^{2+}:H_2O_2 ratio of 1:1 was applied. Thus, Fe^{2+}:H_2O_2 of 1:1 was applied as the optimum process in this electro-Fenton experiment.

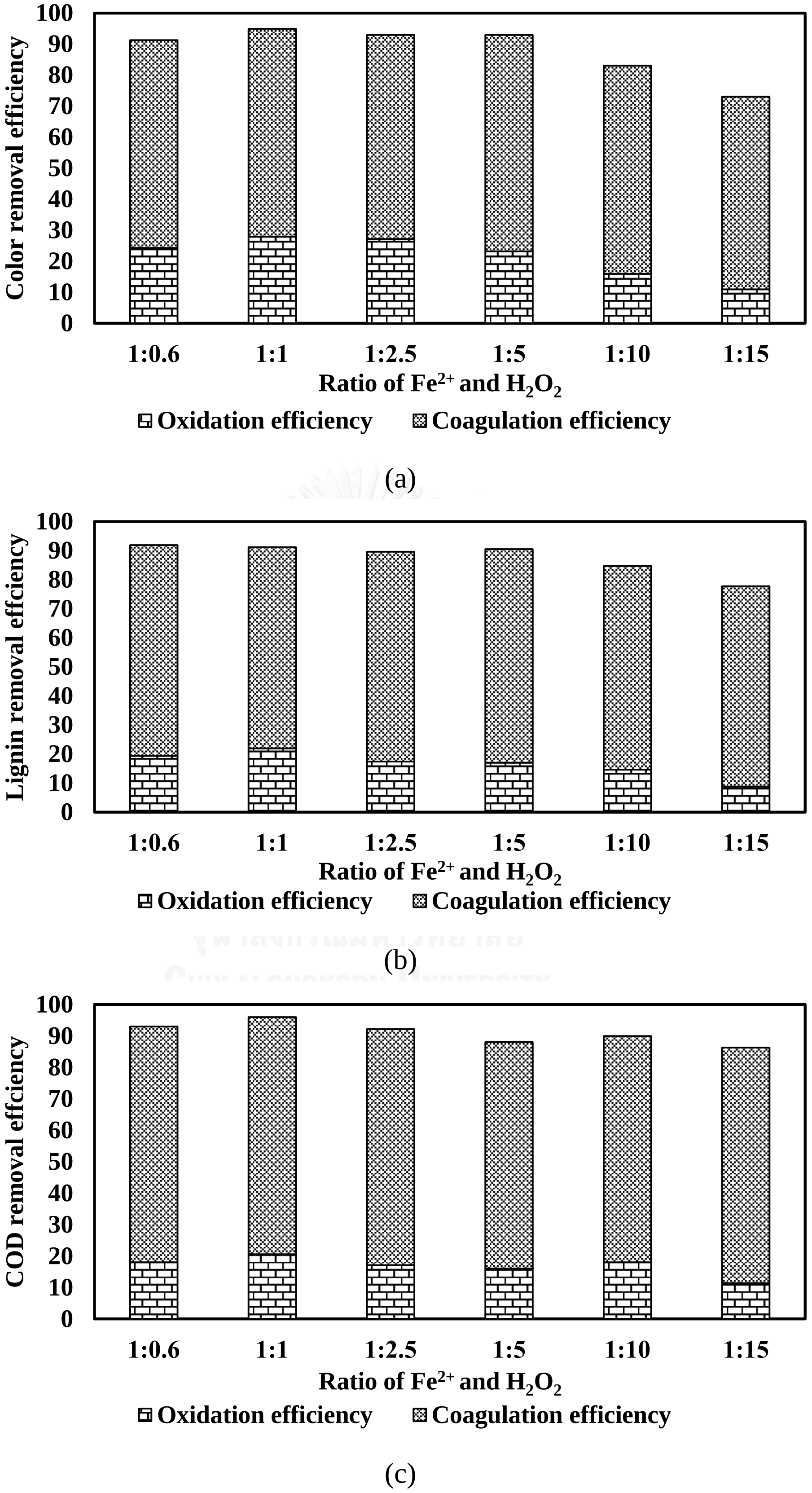


Figure 4. 21 Effect of Fe^{2+}:H_2O_2 *ratio on oxidation efficiency of (a) color removal (b) lignin removal (c) COD removal*

Figure 4.22 showed the comparison the oxidation efficiency on color, lignin and COD removal between conventional Fenton and electro-Fenton process. The results indicated that Fenton process provided higher oxidation efficiency of lignin and COD than electro-Fenton process. The cause of this result might be low regeneration of Fenton’s reagent in term of Fe^{2+} concentration for generating OH• in electro-Fenton process. It can be concluded that electro-Fenton using iron as electrode was not effective to treat lignin synthetic wastewater.

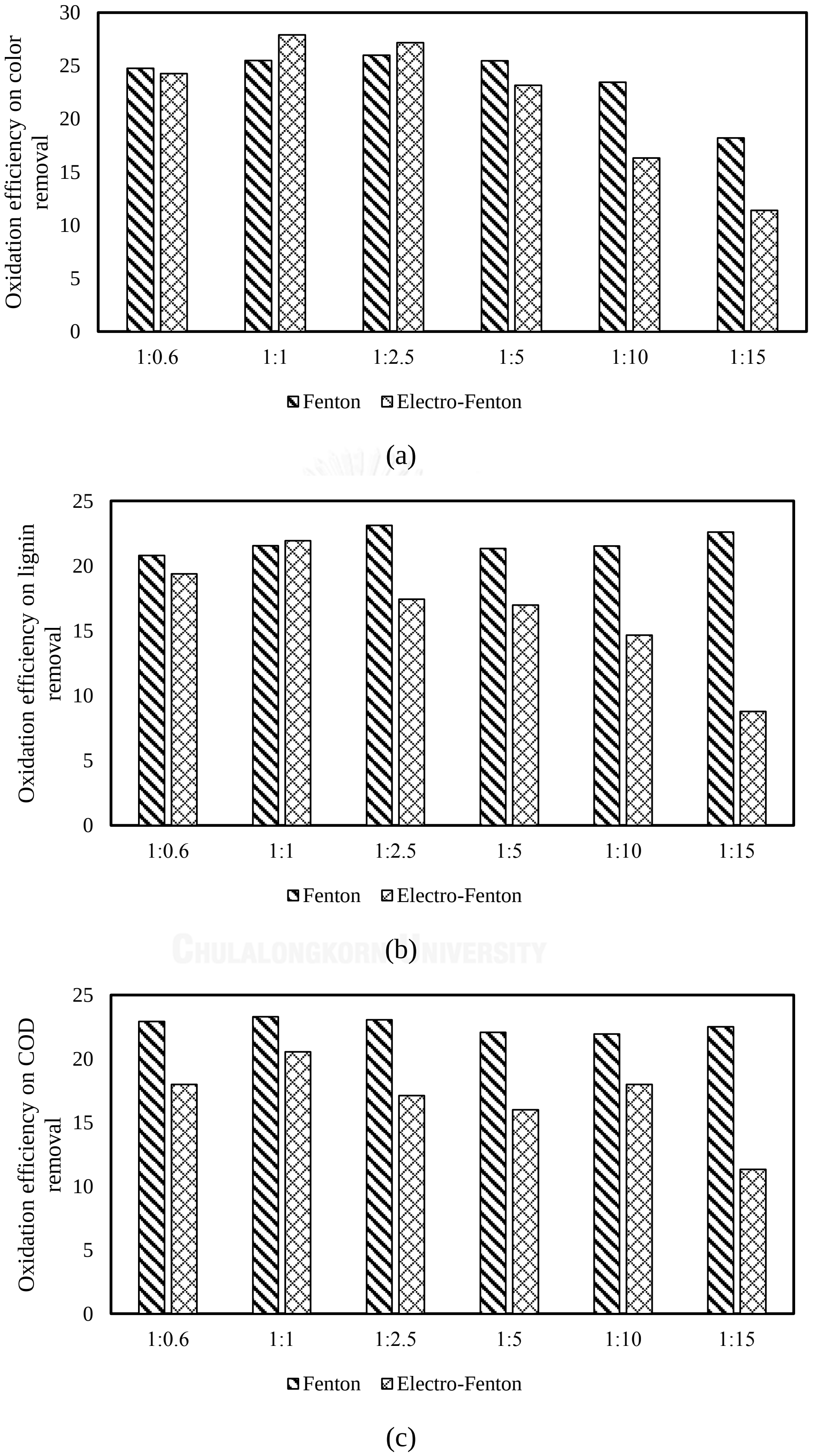


Figure 4. 22 Comparison oxidation efficiency on (a) color removal (b) lignin removal (c) COD removal between Fenton and electro-Fenton process

To compared with the other studies, Babuponnusami and Muthukumar (2012) concluded that the optimum weight ratio of 1:12 was provided in the highest removal efficiency and less time for degradation in phenol-containing wastewater. This was similar results to Selvabharathi G. and Kanmani S. (2010). They found that the maximum color removal up to 95% and COD removal up to 90% in pulp and paper wastewater were obtained at $Fe^{2+}:H_2O_2$ of 1:12. On the other hand, Mehmet F. Sevimli (2005) reported a smaller optimum ratio of 1:3 to complete the maximal degradation efficiency in pulp mill wastewater. The dosage of Fenton's reagent reported for Fenton treatment were very different depending on waste characteristic to be oxidized and its concentration (Alijuboury, Palaniandy, Aziz, & Feroz, 2014).

4.4.2.2 Effect of current density

Current density is one of factor that affect the efficiency of electro-Fenton processes. In experiment, current density of 150, 200 and 250 A/m^2 were varied under pH of 3. The results in Figure 4.23 showed that the most effective on color, lignin and COD removal efficiency with a greater energy saving was obtained when the current density of 200 A/m^2 was used in experiment. From Figure 4.26, it can be showed that increasing the current density from 150 A/m^2 to 250 A/m^2 improve the color, lignin and COD removal efficiency. The color removal in percentage value were 43%, 94% and 95% at the end of reaction time when the current density was applied at 150, 200 and 250 A/m^2. The lignin removal of 45%, 91% and 96% and COD removal of 54%, 92% and 95% were noted in the experiments respectively. The removal was increased when the applied current density increased due to more production of Fe^{2+} dosage at the anode according to equation (4.6), which promoted more OH• production. From the results, it showed that the maximum process efficiency was achieved when the current density was 250 A/m^2. However, in term of removal efficiency was less difference and more economic in term of operation cost, the current density of 200 A/m^2 was found to be the most effective for this work.

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (4.6)$$

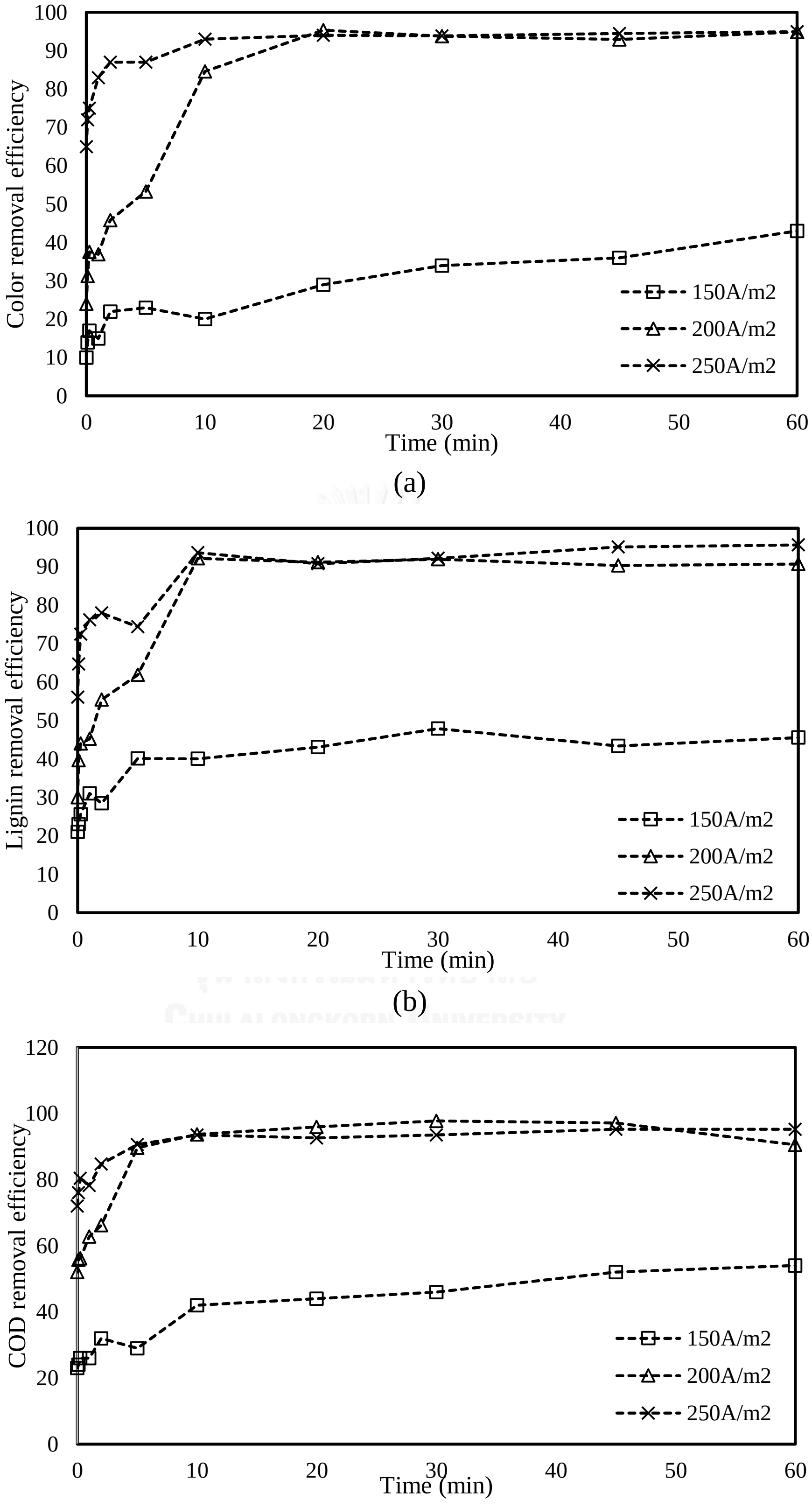
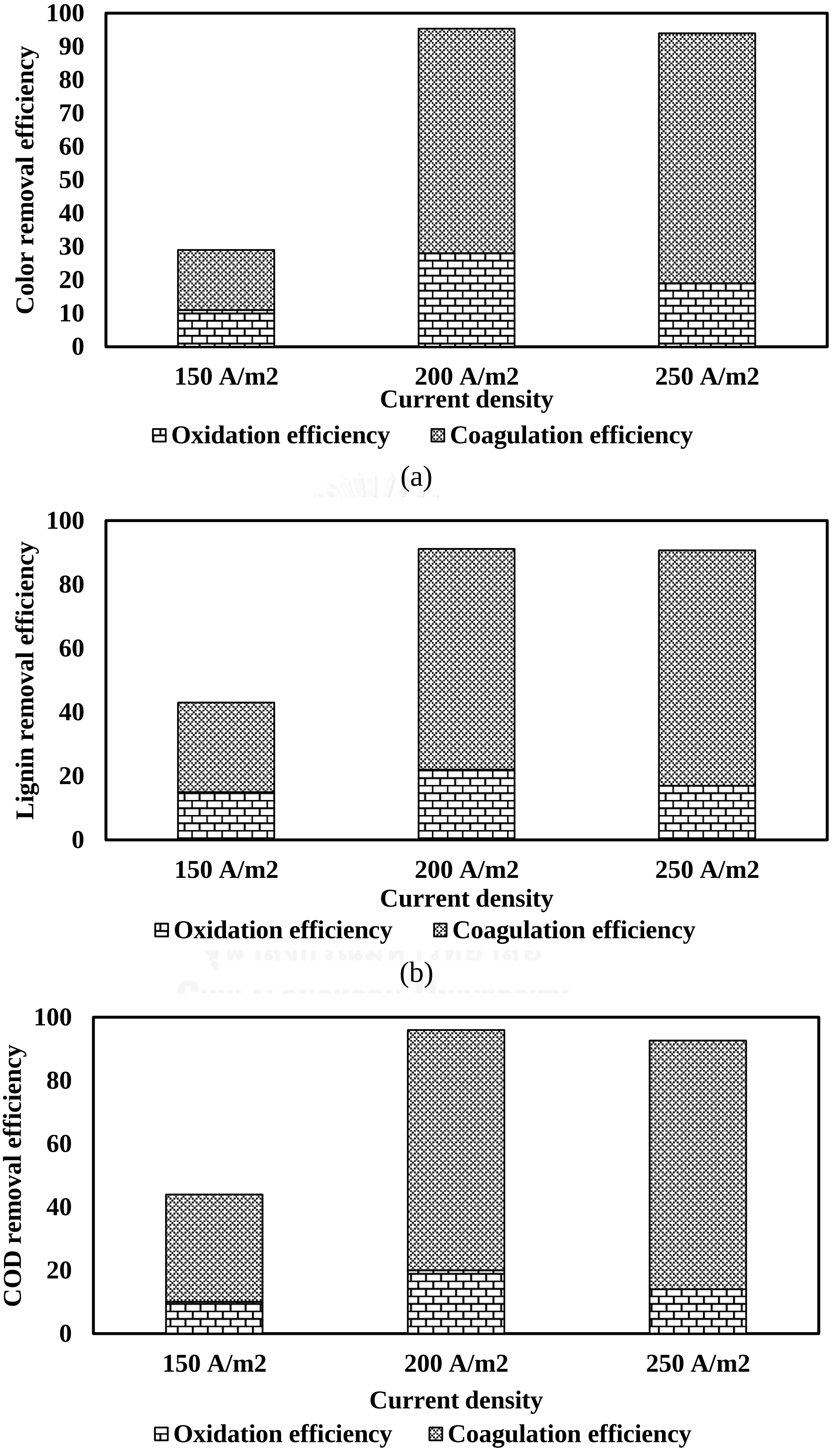


Figure 4. 23 Effect of current density in electro-Fenton process on (a) color removal (b) lignin removal (c) COD removal

To compare the oxidation efficiency on color, lignin and COD removal at different current density, minimum oxidation efficiency was calculated by the subtraction of overall removal efficiency by coagulation efficiency. The results that oxidation efficiency of color removal were 14%, 28% and 23% at the steady of reaction time when current density of 150, 200 and 250 A/m^2 was applied to the system as shown in Figure in 4.24. Moreover, oxidation efficiency of 22%, 22% and 20% for lignin removal and 19%, 20% and 18% for COD removal were obtained in this experiment. Therefore, current density of 200 A/m^2 was obtained as optimum operating condition based on high removal efficiency and economic cost in this work.



(a)

(b)

(c)

Figure 4. 24 Effect of current density on the oxidation efficiency of (a) color removal (b) lignin removal (c) COD removal

The performance of electro-Fenton process was determined by the current efficiency (η) which is shown in equation 4.7 (Masomboon, 2008).

$$\eta = \left(\frac{FV}{A}\right)\left(\frac{[Fe2+]}{t}\right)x100\% \qquad (4.7)$$

where F represents the Faraday constant, $[Fe^{2+}]$ represents the concentration of prodiced ferrous ions, V is the volume of solution, A is current and t represents the reaction time. Since the current was stayed constant, the amount of Fe^{2+} generated was proportional to the time of electrolysis. Current efficiency for 150, 200 and 250A/m^2 of current density was 28.82%, 36.92% and 40.35%, respectively. The energy cost of electro-Fenton process was also discussed and shown in Figure 4.28 and equation 4.8 (Masomboon, 2008).

$$\text{Energy cost (kWh/m}^3\text{)} \quad = \quad \frac{VIt}{Volumn} x \frac{[initial\ unit\ color]}{[\Delta color]} \qquad (4.8)$$

Where V is the voltage until time (t), I is electrical current (A) used in this study, t is given in time, Volumn is amount of solution in experiment (l), [initial unit color] is the initial concentration of color and [Δcolor] is the difference between initial color concentration and the final lignin after treatment process. By calculated the energy cost from equation 4.8, current density of 150 A/m^2, 200 A/m^2 and 250 A/m^2 provided energy consumption of 16.75, 14.83 and 24.1 kW·h/m^3. This results confirmed that the optimum current density for this process should be current density of 200A/m^2. The energy cost was one major parameter which should be considered when applied electrical current into Fenton reaction.

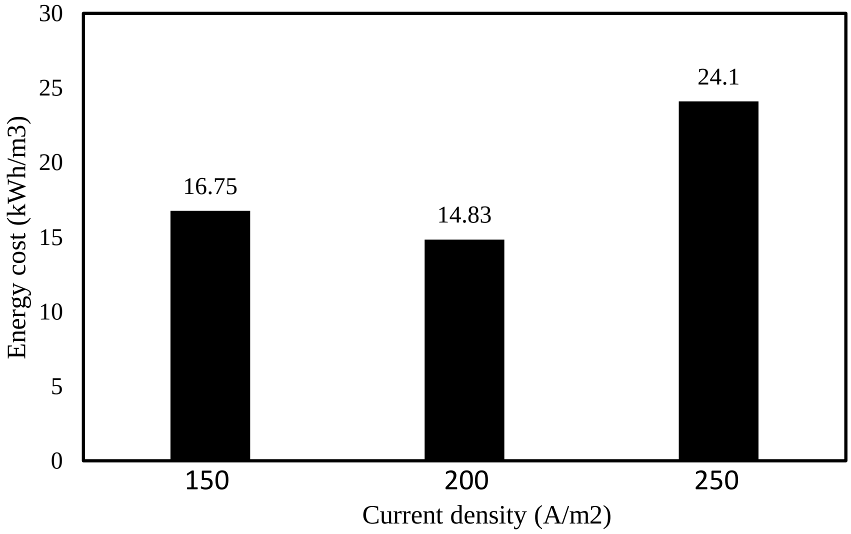


Figure 4. 25 Energy cost at different current density

For other study, Un et al. (2014) report that the optimum current density for the treatment of tissue paper wastewater by electro-Fenton was found to be around 200 A/m^2 with removal efficiency of 80%. While Babuponnusami and Muthukumar (2012) reported that the current density of 120 A/m^2 was obtained for the optimized process.

The results in Figure 4.26 showed sludge production in electro-Fenton process under optimum Fe^{2+}:H_2O_2 and optimum current density. It showed that sludge generation increased with time. At the end of reaction, sludge of 1,137 mg/l was produced. However, sludge production in conventional Fenton and electro-Fenton were not significantly different. Thus, H_2O_2 of stepwise addition during electro-Fenton process was conducted to minimize the sludge production.

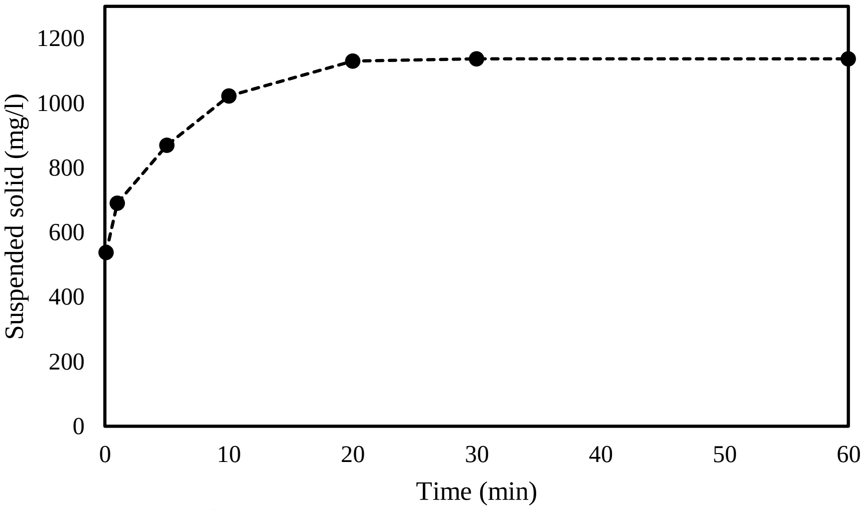
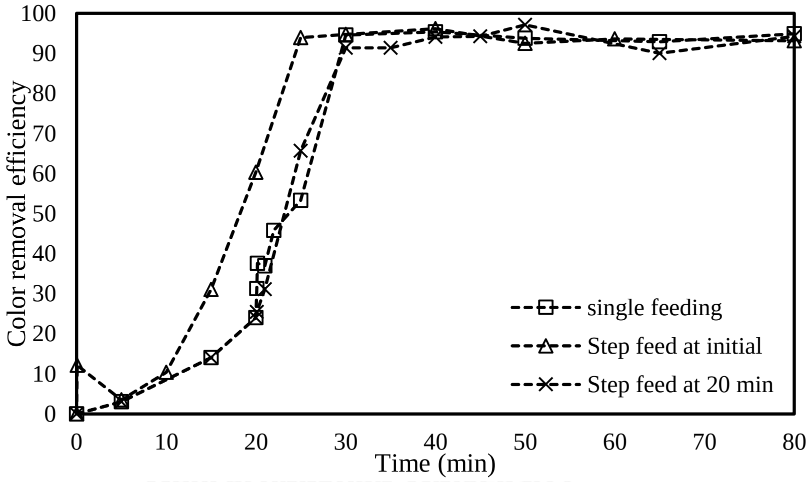


Figure 4. 26 Sludge production in electro-Fenton process

4.4.2.3 Step feeding in electro-Fenton process

The step addition of H_2O_2 was conducted in this part at total H_2O_2 concentration of 400 mg/l under optimum ratio and optimum current density obtained from previous section. H_2O_2 was added in 10-time feeding with 2 different ways; the first was added at initial and the second was added at 20 minutes. Total reaction time was at 80 minutes. The results from this operation was shown in Figure 4.27. The results showed that the removal efficiency increased with time. At the end of reaction time, color removal efficiency were 93%, 94% and 95% when H_2O_2 was applied at single feeding, step feeding at 20 minutes and step feeding at initial, respectively. In addition, lignin removal efficiency of 91%, 86% and 93% and COD removal efficiency of 92%, 92% and 95% were obtained from this experiment. However, at the earlier stage of reaction, the removal efficiency of color, lignin and COD in step feeding operation at initial was the highest. It can be concluded that multiple feeding mode in electro-Fenton process can reduce the reaction time to achieve the same efficiency as single feeding. The reason might be that step feeding operation could generate OH• continuously and also help to avoid the presence of excessive OH• concentration at the earlier stages. Moreover, the sufficient level of H_2O_2 concentration in the multiple feeding mode and optimum ratio could reduce the scavenging effect on Fenton reaction. Thus, the step feeding was better than initial feeding mode in removal of color, lignin and COD.

Hence, from the experimental results in this section, it can be concluded that step feeding operation at initial should be the optimum operation based on the highest removal efficiency and less reaction time. For step feeding mode, oxidation efficiency on color, lignin and COD were 30%, 24% and 23% with higher than conventional Fenton process due to the scavenging effect of OH• as shown in Figure 4.28.



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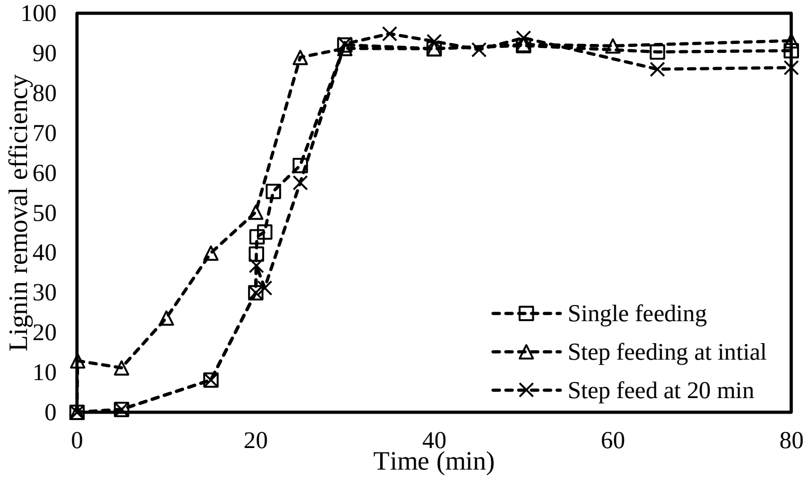

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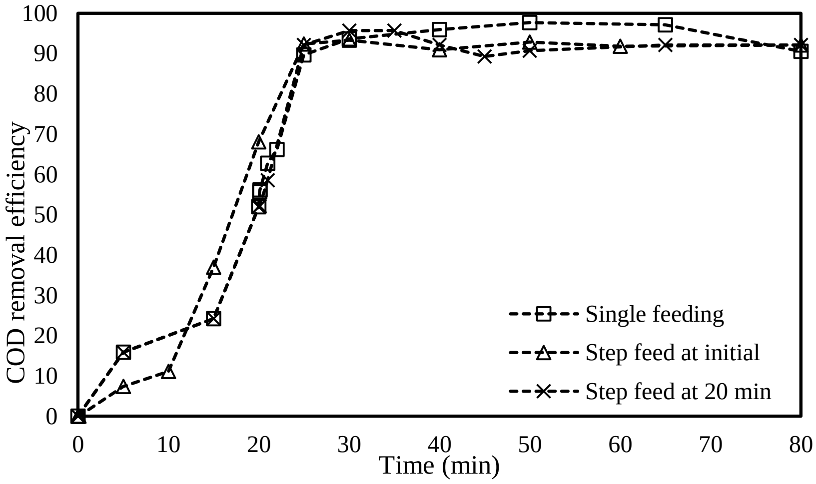

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Figure 4. 27 Effect of step feeding operation in electro-Fenton on (a) color removal (b) lignin removal (c) COD removal

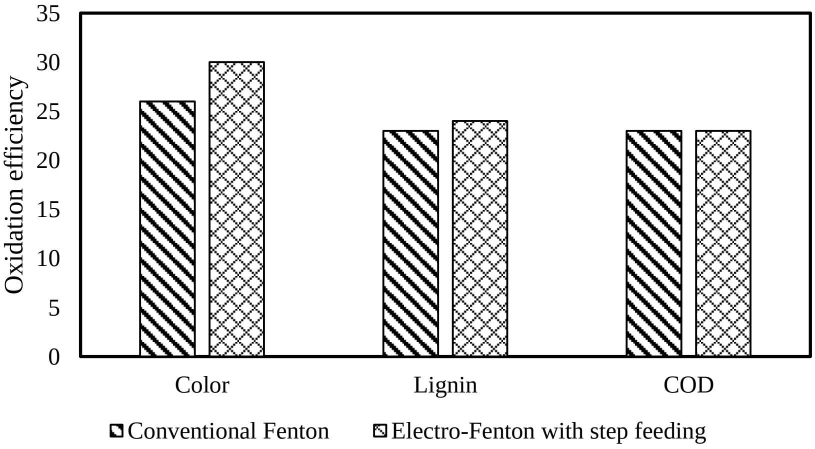


Figure 4. 28 The comparison of oxidation efficiency between conventional Fenton and step feeding of electro-Fenton process at optimum conditions

From other studies, Nidheesh and Gandhimathi (2012) studied the treatment of wastewater by electro-Fenton process to enhance the removal efficiency. They found that step addition of H_2O_2 was more effective than a single step addition. Moreover, the results indicated that removal efficiency increased with the frequency of H_2O_2 feeding and became the highest at continuous operation. The same trend can be found in the research of L. Jiang and Mao (2012b)J. They reported that the removal efficiency in continuous addition of H_2O_2 increased and exceeded than that of the single step feeding way. For one step feeding of H_2O_2, high concentration of H_2O_2 in solution was formed, can cause the faster consumption of H_2O_2. Thus the decomposition of H_2O_2 was occurred to produce HO_2• with weaker oxidative species than OH•. Moreover, Zhang, Fei, Zhang, and Tang (2007) provided the highest removal efficiency at the end of reaction time. Therefore, the best efficiency was observed in step feeding operation.

One of limitations of Fenton oxidation is the production of sludge approximately 1-2 Euro/m^{3}of wastewater is spent for sludge treatment ((Di Iaconi, Lopez, Ramadori, Di Pinto, & Passino, 2002). Thus, step feeding experiment was performed to enhance the oxidation efficiency and also reduced the sludge production. Figure 4.34 showed the comparison of sludge between one time feeding and step feeding operation. At the same removal efficiency, the sludge production reduced significantly 45% for multiple feeding in electro-Fenton process. Since Fe^{2+} was required at lower concentration leading to lower the formation of ferric hydroxo complex and thus to the sludge production.

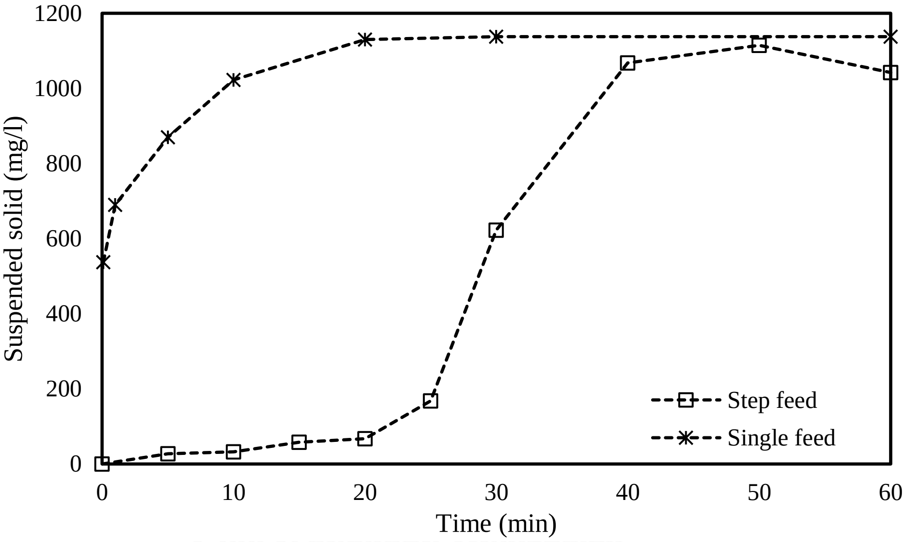


Figure 4. 29 Comparison of sludge production between one time feeding and step feeding operation in electro-Fenton process

From all of study in electro-Fenton process, it can be seen that Fe^{2+}:H_2O_2 ratio, current density and step feeding operation were the important parameter in order to achieve the highest removal efficiency of color, lignin and COD.

4.4.3 Comparison between conventional and modified-Fenton

In this section, the degradation of color, lignin and COD were evaluated by various process to study the performance of Fenton process and modified-Fenton process. As shown in Figure 4.30, the results showed that the oxidation efficiency by conventional Fenton process can reach to 26% for color removal when using 400 mg/l of Fe^{2+} and 1,000 mg/l of H_2O_2 at pH of 3. The 42% of oxidation efficiency on color removal achieved by H_2O_2 step feeding operation was nearly 16% higher than that of the conventional Fenton process. The reason that step feeding mode can remove lignin more than the initial one-time feeding mode was due to reduction the scavenging effect, thus minimizing the H_2O_2 that was not efficient consumption. Moreover, when step feeding mode was applied, Fe^{2+} can be regenerated by the reduction of Fe^{3+} with H_2O_2 or organic radical intermediates (Masomboon, 2008) as shown in equation 4.4 and 4.9.

$$Fe^{3+} + R\bullet \rightarrow Fe^{2+} + R^{+} \qquad (4.9)$$

Meanwhile, the oxidation efficiency on color removal of 45% was found when applied step feeding operation of Fe^{2+} and H_2O_2 during 60 minutes. This operation achieved the oxidation efficiency that was 19% higher than that of the conventional Fenton process. Thus, it indicated that two feeding operation was effective for synthetic pulp mill wastewater. However, initial feeding and step feeding in electro-Fenton provided 28% and 30%, respectively for color degradation with lower than multiple feeding in Fenton process. This indicated that electro-Fenton process using iron as electrode could not regenerate Fe^{3+} to Fe^{2+}. Hence, multiple feeding in Fenton can extend the effective performance of Fenton's reagent.

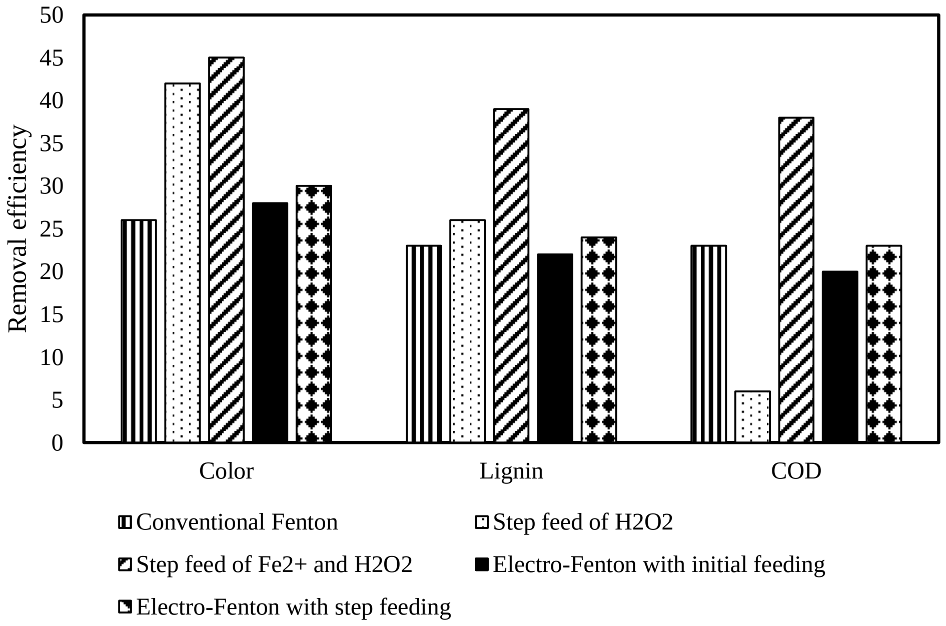
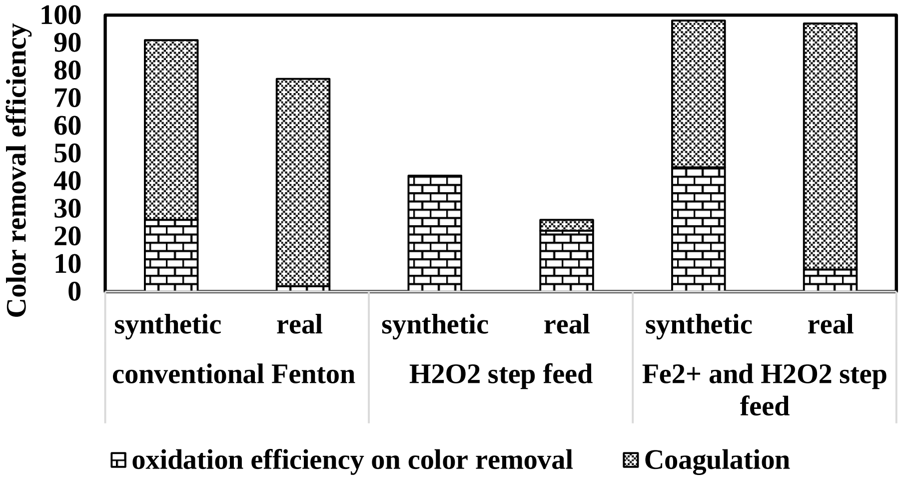


Figure 4. 30 Comparison of oxidation efficiency on various kind of process

4.4.4 Real wastewater treatment

From previous section, the best oxidation efficiency was obtained when two different feeding mode were applied. The first was H_2O_2 step feeding and the second was multiple feeding of Fe^{2+} and H_2O_2. Thus, real wastewater experiment was conducted with two operations. Under the similar conditions, it can be seen that overall and oxidation removal efficiency in real wastewater were lower than those obtained from synthetic wastewater as shown in Figure 4.31. This was due to the presence of other organic pollutants in real wastewater which can compete with lignin or OH•. Moreover, improvement of operation feeding from initial feeding to step feeding condition could provide higher removal efficiency. The cause of this result was to multiple feeding operation could reduce the scavenging effect on the reaction process. However, oxidation efficiency in H_2O_2 step feeding operation of real wastewater was higher than that of synthetic wastewater due to the interference of other organic compound containing phenolic unit. They can be absorbed at the same detection wavelength of lignin measurement.



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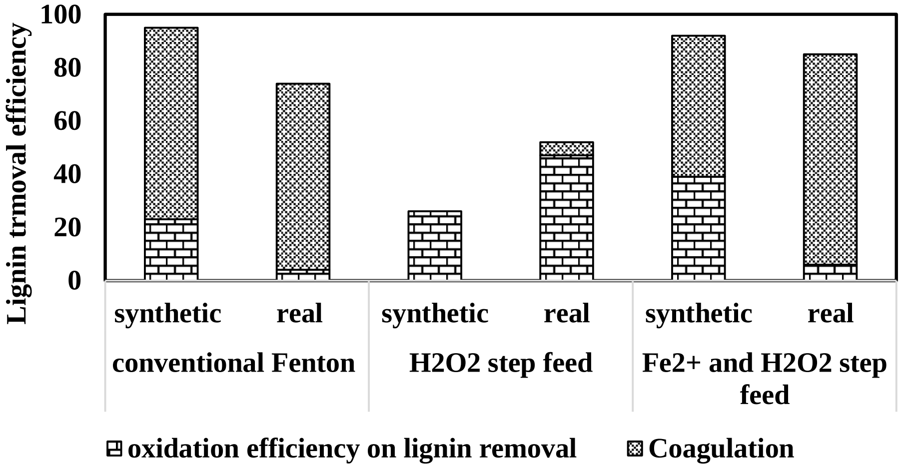

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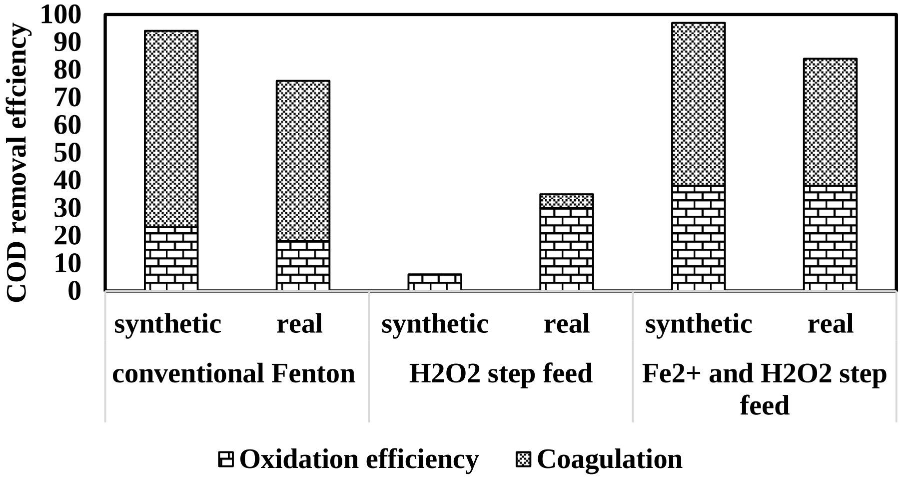

(c)

Figure 4. 31 Treatment efficiency of (a) color removal (b) lignin removal and (c) COD removal in synthetic and real wastewater at the same experimental conditions

4.4.5 Cost estimation

The decisions for industrial wastewater treatment plant are certainly influenced by the cost of treatment facilities (El-Kamah, Tawfik, Mahmoud, & Abdel-Halim, 2010). The optimization of operating conditions, for example, Fe^{2+}:H_2O_2 ratio, initial pH, Fenton's dosage, operation feeding and current density will not only affect the treatment process, but will also influence the operation cost. The operating costs include chemical reagents and required energy. Staff costs are not calculated in this estimation for the simplicity of the calculations. The costs of chemicals including pH adjustment reagents are calculated as the concentration multiplied by the unit price. Prices of chemicals were taken as the average values from different suppliers. The energy cost can calculated by equation 4.9.

$$\text{Energy cost (kWh/m}^3\text{)} = \frac{VIt}{1000Vt} \qquad (4.9)$$

Where V is given in voltage, I is electrical current, t is operating time and V_t represents volume of treated wastewater

Conventional Fenton treatment provided higher cost in term of chemical reagents which will further imply an associated higher cost for iron sludge disposal. While electro-Fenton treatment requires a higher cost in term of energy consumption. The calculated treatment cost under optimum conditions with different operating process was shown in Table 4.2

Table 4. 2 Comparison of treatment by various kind of operating mode

Process	Lignin (mg/l)	Chemical costs (THB/m^3)	Operating costs (THB/m^3)	Total costs (THB/m^3)	Oxidation efficiency (%)		
					Color	Lignin	COD
Conventional Fenton	910	125.5	-	125.5	26	23	23
Step feeding of H_2O_2	910	80.5	-	80.5	42	26	6
Step feed of Fe^{2+} and H_2O_2	910	106	-	106	45	39	38
Electro-Fenton on initial feed	910	97.5	40.6	138.1	28	22	20
Electro-Fenton on step feeding operation	910	96.5	40.4	137.1	30	24	23

From the results, it showed that step feeding operation provided in higher oxidation efficiency and reduced the treatment cost. Thus, it is one effective for pulp mill treatment system.

CHARPTER 5
CONCLUSION

5.1 Conclusion

5.1.1 Fenton and modified Fenton are effective among the treatment of synthetic and real pulp mill wastewater.

5.1.2 Operating parameters which are Fe^{2+}:H_2O_2 ratio, initial pH, Fenton's dosage, current density and feeding operation mode are the important parameters in degradation of lignin by Fenton and modified-Fenton process.

5.1.3 The optimum operating conditions for 910 mg/l of lignin removal was found at Fe^{2+}:H_2O_2 of 1:2.5, initial pH of 3 and initial Fe^{2+} of 400 mg/l for Fenton process. For electro-Fenton, the current density of 200 A/m^2 and Fe^{2+}:H_2O_2 of 1:1 were found to be the optimum conditions in this process.

5.1.4 Step feeding operation could enhance the process efficiency. This operation could reduce the scavenging effect on the reaction, thus the oxidation efficiency can be increased. Moreover, increased number of feeding provided higher removal efficiency and less reaction time.

5.2 Suggestions for future work

5.2.1 The performance of Fenton and modified-Fenton processes should be studied under continuous operation.

5.2.2 The rate constant of lignin with hydroxyl radicals should be investigated and compared with other advanced oxidation processes.

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APPENDIX

Appendix A
Analytical Methods

Appendix A-1

Analytical method of lignin (Ksibi et al., 2003 and Pessala et al., 2004)

1. General discussion

Lignin contains phenolic groups that the maximum absorbance at 280 nm was used. Lignin concentration was determine based on a calibration curve created with different lignin concentration.

2. Reagents

Stock solution: The stock solution was prepared by dissolving 1 g of alkali lignin with 1000 ml of distilled water. The solution has a lignin of 1,000 mg/l.

3. Procedures

3.1 Calibration curve preparation: Standard solution in the lignin concentration of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/l were prepared by diluting 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ml of stock solution with 100 ml of distilled water. Then, UV-VIS spectrophotometer was used to measure lignin concentration with detection wavelength of 280 nm as shown in Figure A.1.

3.2 Samples analysis: the effluent samples were diluted of 3 ml samples in 10 ml distilled water for initial lignin concentration of 910 mg/l. Later, samples were measured the absorbance by UV-VIS spectrophotometer and determined lignin concentration by calibration curve.

Table A. 1 Absorbance of lignin detected by spectrophotometer at 280 nm

Lignin concentration (mg/l)	Absorbance
10	0.155
20	0.310
30	0.467
40	0.623
50	0.777
60	0.942
70	1.108
80	1.253
90	1.403
100	1.558

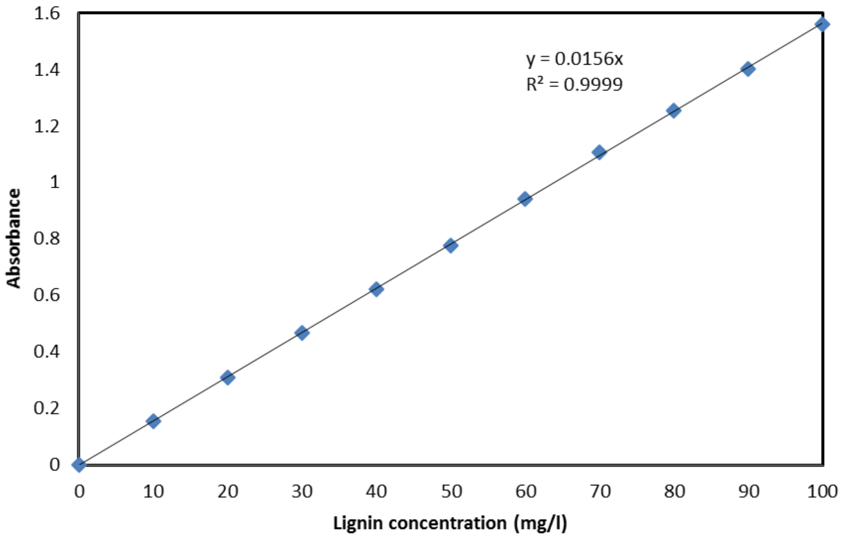


Figure A. 1 Calibration curve of lignin detected by spectrophotometer at 280 nm

Appendix A-2

Analytical method of color (Standard methods, APHA, 1992)

1. General discussion

The platinum-cobalt method is used as a way to determine amount of pollution levels in water. It is useful for measuring color of water derived from natural occurring materials such as lignin, vegetable residues and humus. The term color is used in this study to mean true color that is the color of water which turbidity is removed. Suspended particles should be removed before measurement.

2. Interference

2.1 pH dependent

2.2 Amount of turbidity interferes with determination, thus turbidity in sample should be clarified before measurement.

3. Reagents

3.1 Potassium hexachloroplatinate (K_2PtCl_6)
3.2 Cobalt chloride ($CoCl_2 \cdot 6H_2O$)
3.3 Hydrochloric acid (HCl)

4. Procedures

4.1 Standard preparation for calibration curve: Dissolved 1.246g of K_2PtCl_6 and 1g of $CoCl_2 \cdot 6H_2O$ in distilled water containing 100 ml of HCl and diluted to 1,000 ml. This stock solution has a color of 500 Pt-Co unit. The standard solution having Pt-Co unit of 20, 40, 50, 100, 200, 300 and 400 were prepared by diluting 4, 8, 10, 20, 40, 60 and 80 ml of stock solution with distilled water into 100 ml. After that, the standards were analyzed using UV-VIS spectrophotometer with detection wavelength at 475 nm and obtained standard curve as shown in Figure A.2 and Table A.2.

Table A. 2 Absorbance of color solution detected by spectrophotometer at 475 nm

Color (Pt-Co)	Absorbance
20	0.005
40	0.009
50	0.011
100	0.022
200	0.046
300	0.069
400	0.093
500	0.116

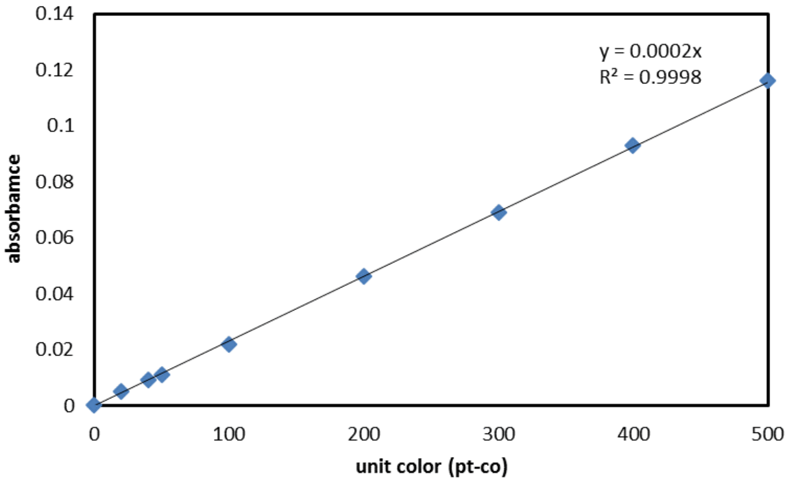


Figure A. 2 Calibration curve of color solution detected by spectrophotometer at 475 nm

4.2 Sample analysis: 10 ml of synthetic wastewater stayed overnight to removal suspended solid and was analyzed light absorbance by using UV-VIS spectrophotometer at 475 nm and calculated the color concentration using standard curve.

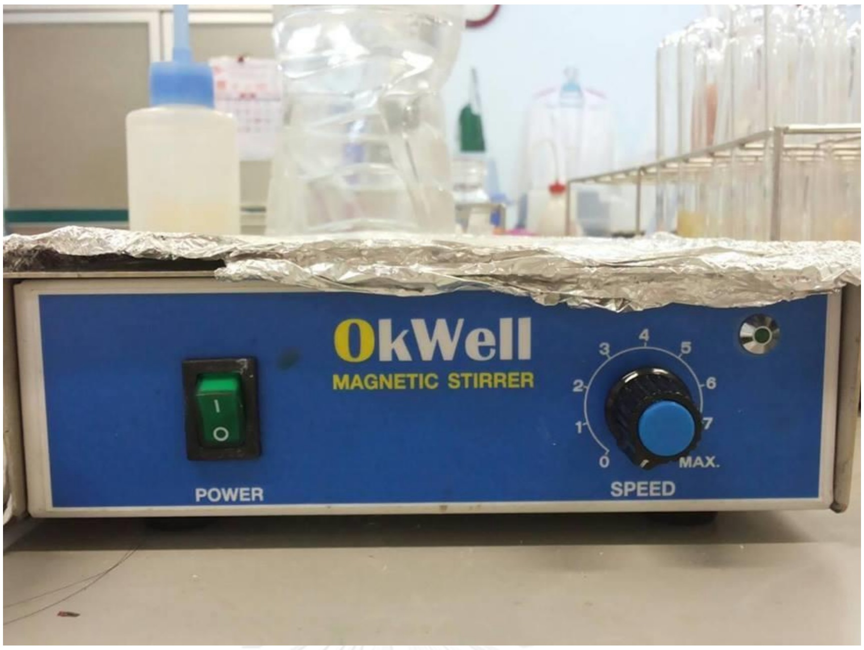
Appendix B

Experimental Figures

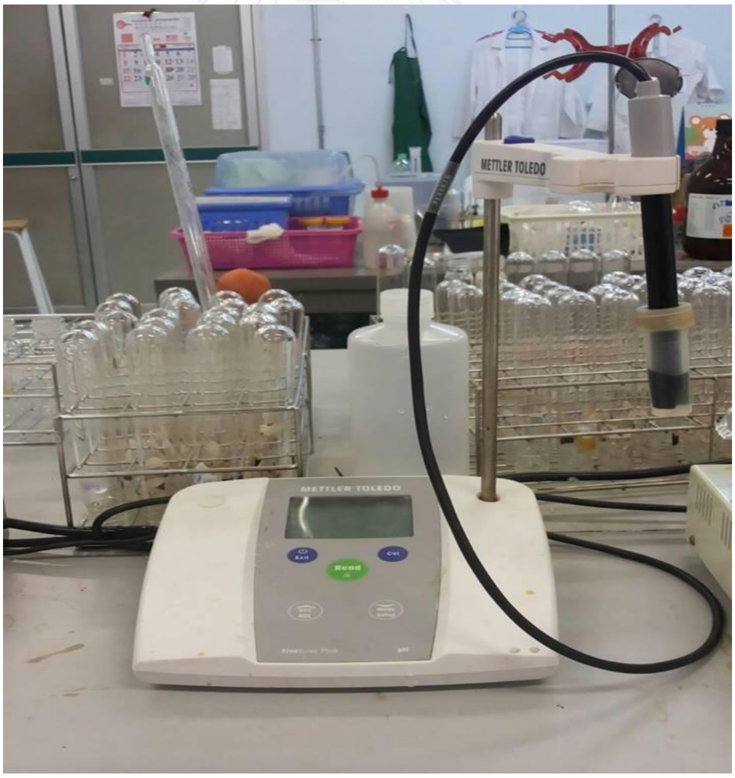
Figure B. 1 Fenton experiment setup

Figure B. 2 Electro-Fenton setup

Figure B. 3 Electrode



(a) Magnetic stirrer



(b) pH meter

(c) DC power supply

(d) Spectrophotometer

(e) Hot oven for COD measurement

Figure B. 4 Experimental instruments

Appendix C

Raw data

Table C. 1 Coagulation efficiency on color, lignin and COD removal by conventional Fenton process

Time (min)	**Color removal efficiency**			**Lignin removal efficiency**			**COD removal efficiency**		
	300	**400**	**500**	**300**	**400**	**500**	**300**	**400**	**500**
0	0	0	0	0	0	0	0	0	0
1	30.00	63.79	81.38	67.04	72.59	78.80	66.00	62.89	79.00
15	43.33	68.62	82.41	56.44	73.64	77.70	63.00	70.67	80.00
30	45.00	66.90	84.05	55.30	67.48	78.35	64.00	67.00	81.00
45	41.67	60.69	85.00	57.71	74.53	78.95	67.00	69.33	83.00
60	35.00	64.83	84.74	53.04	69.51	79.19	65.00	71.11	81.50

Note: initial lignin concentration = 910 mg/l, initial pH = 3, initial ferrous ion = 300-500 mg/l

Table C. 2 H_2O_2 *direct oxidation efficiency at different* H_2O_2 *concentration on color removal by Fenton process*

Time (min)	**H_2O_2 concentration (mg/l)**										
	240	**400**	**750**	**1,000**	**1,250**	**2,000**	**4,000**	**6,000**	**8,000**	**1,000 at pH2**	**1,000 pH4**
0	0	0	0	0	0	0	0	0	0	0	0
0.083	0.00	1.69	0.69	0.00	0.00	4.35	2.35	4.35	0.00	1.26	0.00
0.5	4.17	1.69	0.00	0.00	0.00	0.00	1.98	4.35	0.00	1.26	0.00
1	0.00	0.00	3.85	0.00	1.70	4.35	2.35	4.35	3.85	0.00	4.00
2	0.00	3.85	1.85	0.00	0.00	4.35	2.35	4.35	3.85	1.26	2.00
5	4.17	1.85	1.69	4.35	4.35	4.35	4.35	4.35	3.85	2.26	1.00
10	0.00	3.85	3.85	0.00	4.35	0.00	2.98	0.00	3.85	0.26	1.00
20	0.00	0.00	0.00	4.35	0.00	4.35	4.35	4.35	7.69	1.26	2.00
30	4.17	0.00	0.00	0.00	0.00	0.00	2.98	0.00	7.69	2.26	2.00
60	0.00	1.85	3.85	4.35	4.35	4.35	4.35	4.35	3.54	0.00	0.00

Note: initial lignin concentration = 910 mg/l, initial pH = 2 and 3, initial H_2O_2 concentration = 240-8,000 mg/l

Table C. 3 H_2O_2 direct oxidation efficiency at different H_2O_2 concentration on lignin removal by Fenton process

Time (min)	**H_2O_2 concentration**										
	240	**400**	**750**	**1,000**	**1,250**	**2,000**	**4,000**	**6,000**	**8,000**	**1,000 pH2**	**1,000 pH4**
0	0	0	0	0	0	0	0	0	0	0	0
0.083	0.68	4.12	1.53	0.93	0.91	0.28	0.91	0.75	1.28	0.43	0.50
0.5	0.13	2.79	0.54	0.13	2.82	2.00	2.82	1.01	3.22	1.99	1.19
1	0.01	0.27	0.25	0.53	1.59	1.11	1.59	0.94	2.56	0.57	1.67
2	0.01	0.00	1.66	1.33	0.09	1.53	1.09	0.54	2.24	0.00	2.91
5	0.54	1.06	2.53	1.60	2.96	1.53	2.96	1.27	1.12	2.41	0.42
10	0.13	0.93	1.09	1.99	0.63	1.39	0.73	3.62	1.78	1.57	1.02
20	0.40	1.20	1.25	1.60	1.14	0.56	1.44	1.88	1.30	1.85	2.30
30	0.54	0.67	2.10	2.26	1.64	1.39	1.64	1.94	1.34	1.42	1.94
60	0.27	1.06	0.95	2.66	1.86	1.84	1.46	1.41	1.20	1.12	1.39

Note: initial lignin concentration = 910 mg/l, initial pH = 2 and 3, initial H_2O_2 concentration = 240-8,000 mg/l

Table C. 4 H_2O_2 direct oxidation efficiency at different H_2O_2 concentration on COD removal by Fenton process

Time (min)	**H_2O_2 concentration**										
	240	**400**	**750**	**1,000**	**1,250**	**2,000**	**4,000**	**6,000**	**8,000**	**1,000 pH2**	**1,000 pH4**
0	0	0	0	0	0	0	0	0	0	0	0
0.083	0.00	1.33	1.33	2.00	3.15	2.00	2.00	6.50	9.68	1.12	2.69
0.5	1.50	0.00	0.00	2.19	0.02	4.00	3.00	5.50	9.68	2.50	1.69
1	1.38	2.00	1.67	1.45	3.15	5.67	5.67	6.25	6.45	1.38	2.13
2	2.25	3.33	3.33	2.32	3.15	5.67	6.67	7.50	6.90	1.25	1.69
5	3.13	0.00	0.00	1.19	1.58	6.00	9.00	5.62	5.22	2.13	2.13
10	3.12	0.00	0.00	1.19	3.15	6.67	8.67	7.50	9.68	1.12	2.25
20	0.00	0.00	0.00	1.19	1.58	3.33	6.33	6.50	10.90	2.12	1.12
30	0.00	1.33	3.33	0.06	0.02	6.00	5.00	8.75	12.90	0.00	0.00
60	0.00	1.33	1.67	3.32	3.15	4.67	4.67	9.62	10.13	1.56	1.56

Note: initial lignin concentration = 910 mg/l, initial pH = 2 and 3, initial H_2O_2 concentration = 240-8,000 mg/l

Table C. 5 Coagulation efficiency on color, lignin and COD removal by Fenton process with step feeding operation

Time (min)	**Color**			**Lignin**			**COD**		
	H_2O_2	**Fe^{2+} and H_2O_2**		**H_2O_2**	**Fe^{2+} and H_2O_2**		**H_2O_2**	**Fe^{2+} and H_2O_2**	
		6 feed	**12 feed**		**6 feed**	**12 feed**		**6 feed**	**12 feed**
0	0	0	0	0	0	0	0	0	0
0.083	2.50	-	-	2.65	-	-	0.01	-	-
0.25	0.00	-	-	0.55	-	-	3.13	-	-
0.5	0.83	-	-	1.25	-	-	6.26	-	-
1	3.33	1.00	3.23	2.37	0.02	0.11	3.13	0.00	0.00
2	0.00	-	-	3.49	-	-	3.13	-	-
5	4.17	-	-	4.05	-	-	3.13	-	-
10	1.67	-	-	0.83	-	-	0.01	-	-
20	-	0.00	0.00	-	2.46	4.98	-	3.44	3.44
30	0.00	-	-	1.81	-	-	3.13	-	-
40	-	5.00	3.23	-	1.40	0.03	-	6.89	0.00
60	3.33	1.67	12.90	2.93	9.52	2.80	0.01	24.14	28.62
70	-	25.00	43.55	-	32.89	44.05	-	34.48	58.07
80	-	63.33	53.23	-	66.26	65.68	-	65.52	62.07
90	-	60.00	60.48	-	67.69	67.21	-	68.96	65.17
100	-	68.33	68.55	-	67.23	66.73	-	68.96	68.96
110	-	76.67	72.58	-	73.85	73.83	-	75.86	68.07
120	-	78.33	76.61	-	67.20	72.46	-	75.86	75.86

Note: initial lignin concentration = 910 mg/l, initial pH = 3

Table C. 6 H_2O_2 direct oxidation efficiency on color, lignin and COD removal by Fenton process with step feeding operation

Time (min)	**Color**			**Lignin**			**COD**		
	H_2O_2	**Fe^{2+} and H_2O_2**		**H_2O_2**	**Fe^{2+} and H_2O_2**		**H_2O_2**	**Fe^{2+} and H_2O_2**	
		6 feed	**12 feed**		**6 feed**	**12 feed**		**6 feed**	**12 feed**
0	0	0	0	0	0	0	0	0	0
0.083	3.57	0.00	0.00	1.26	1.28	0.96	3.36	1.54	0.36
5	0.00	-	-	0.42	-	-	0.03	-	-
10	3.57	4.55	4.35	3.09	3.88	3.88	1.69	1.54	0.03
15	5.14	-	-	3.65	-	-	3.36	-	-
20	3.57	4.55	0.00	4.91	0.69	1.24	3.36	2.62	0.03
30	1.57	0.00	0.00	2.24	4.58	2.91	4.69	1.54	1.36
40	0.00	4.55	4.35	4.07	1.80	1.20	1.69	1.62	0.36
50	3.57	-	-	0.98	-	-	1.02	-	-
60	0.00	4.55	4.35	2.81	0.15	0.65	2.69	4.62	3.36
80	-	0.00	0.00	-	4.44	5.27	-	1.54	2.69
100	-	2.09	4.35	-	2.42	4.02	-	4.62	1.02
120	-	4.55	4.35	-	3.59	3.46	-	1.54	1.69

Note: initial lignin concentration = 910 mg/l, initial pH = 2 and 3, initial H_2O_2 concentration = 240-8,000 mg/l

Table C. 7 Coagulation efficiency on color, lignin and COD removal by electro-Fenton process

Time (min)	**Color removal**			**Lignin removal**			**COD removal**		
	1A	**0.75A**	**1.25A**	**1A**	**0.75A**	**1.25A**	**1A**	**0.75A**	**1.25A**
0	0	0	0	0	0	0	0	0	0
1	1.00	0.00	3.00	0.34	-	-	8.47	-	-
5	3.61	2.00	12.00	0.72	-	-	15.92	-	-
10	-	-	-	-	10.85	22.15	-	7.00	25.71
15	13.98	4.00	60.00	8.12	-	-	24.22	-	-
20	24.96	10.00	65.00	30.87	21.75	56.02	52.86	23.00	72.99
25	40.82	11.00	72.50	48.22	-	-	72.86	-	-
30	67.83	11.00	74.00	60.47	21.23	62.51	73.88	28.00	72.99
35	-	-	-	-	-	-	-	-	-
40	66.63	22.00	69.00	63.68	20.97	68.61	74.56	31.00	71.99
45	-	-	-	-	21.37	65.89	-	26.00	75.24
50	-	-	-	-	18.97	60.18	-	33.00	75.24
55	-	-	-	-	13.24	67.97	-	29.00	71.73
60	71.20	18.00	73.00	61.20	20.20	68.48	71.20	26.00	71.73
80	70.00	20.00	72.00	60.00	15.00	65.00	70.00	34.00	69.00

Note: initial lignin concentration = 910 mg/l, initial pH = 3, current = 0.75-1.25A

Table C. 8 Effect of Fe^{2+}*:*H_2O_2 *ratio on overall efficiency of color removal by Fenton process*

Time (min)	**Color removal efficiency**						
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**	**1 to 20**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.08	92.17	91.67	88.13	90.00	84.48	83.33	90.17
0.25	90.50	92.67	83.33	86.00	89.08	82.08	87.33
0.5	90.33	93.00	86.67	85.00	91.95	83.75	87.67
1	89.17	88.33	85.42	89.33	90.80	83.33	89.00
2	88.50	90.17	92.10	87.33	84.48	80.83	89.50
5	90.17	91.50	93.00	89.33	86.21	82.92	86.67
10	87.33	89.50	95.00	93.67	89.08	81.04	71.50
20	90.33	88.50	95.42	93.67	86.78	82.08	72.17
30	90.17	91.00	96.04	93.33	91.38	85.63	74.00
60	88.83	88.50	94.79	97.00	90.23	87.08	66.83

Note: initial lignin concentration = 910 mg/l, initial pH = 3, initial ferrous ion = 400 mg/l

Table C. 9 Effect of Fe^{2+}:H_2O_2 ratio on oxidation efficiency of color removal by Fenton process

Time (min)	**Oxidation efficiency of color removal**						
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**	**1 to 20**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.083	27.17	26.67	23.13	25.00	19.48	18.33	25.17
0.25	25.50	27.67	18.33	21.00	24.08	17.08	22.33
0.5	25.33	28.00	21.67	20.00	26.95	18.75	22.67
1	24.17	23.33	20.42	24.33	25.80	18.33	24.00
2	23.50	25.17	27.10	22.33	19.48	15.83	24.50
5	25.17	26.50	28.00	24.33	21.21	17.92	21.67
10	22.33	24.50	30.00	28.67	24.08	16.04	6.50
20	25.33	23.50	30.42	28.67	21.78	17.08	7.17
30	25.17	26.00	31.04	28.33	26.38	20.63	9.00
60	23.83	23.50	29.79	32.00	25.23	22.08	1.83

Note: initial lignin concentration = 910 mg/l, initial pH = 3, initial ferrous ion = 400 mg/l

Table C. 10 Effect of Fe^{2+}:H_2O_2 ratio on overall efficiency of lignin removal by Fenton process

Time (min)	Lignin removal efficiency						
	1 to 0.6	1 to 1	1 to 2.5	1 to 5	1 to 10	1 to 15	1 to 20
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.08	94.11	94.60	93.34	95.46	94.41	95.21	94.82
0.25	93.86	93.68	95.66	93.37	94.41	95.53	95.34
0.5	92.28	96.62	96.31	92.48	95.35	96.16	95.27
1	94.00	95.54	96.26	94.66	95.30	95.60	96.28
2	93.12	95.25	96.77	92.85	93.41	95.25	95.53
5	92.24	94.52	94.99	89.58	92.28	94.67	94.29
10	93.37	93.06	-	89.10	89.45	96.22	90.02
20	91.76	94.73	94.82	90.30	89.76	92.77	85.50
30	91.85	94.17	94.24	87.49	86.81	84.69	83.52
60	91.34	93.25	93.66	88.12	84.10	80.01	82.19

Note: initial lignin concentration = 910 mg/l, initial pH = 3, initial ferrous ion = 400 mg/l

Table C. 11 Effect of Fe^{2+}:H_2O_2 ratio on oxidation efficiency of lignin removal by Fenton process

Time (min)	Oxidation efficiency of lignin removal						
	1 to 0.6	1 to 1	1 to 2.5	1 to 5	1 to 10	1 to 15	1 to 20
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.083	24.11	24.60	23.34	25.46	24.41	25.21	24.82
0.25	23.86	23.68	25.66	23.37	24.41	25.53	25.34
0.5	22.28	26.62	26.31	22.48	25.35	26.16	25.27
1	24.00	25.54	26.26	24.66	25.30	25.60	26.28
2	23.12	25.25	26.77	22.85	23.41	25.25	25.53
5	22.24	24.52	24.99	19.58	22.28	24.67	24.29
10	23.37	23.06	-	19.10	19.45	26.22	20.02
20	21.76	24.73	24.82	20.30	19.76	22.77	15.50
30	21.85	24.17	24.24	17.49	16.81	14.69	13.52
60	21.34	23.25	23.66	18.12	14.10	10.01	12.19

Note: initial lignin concentration = 910 mg/l, initial pH = 3, initial ferrous ion = 400 mg/l

Table C. 12 Effect of Fe^{2+}:H_2O_2 ratio on overall efficiency of COD removal by Fenton process

Time (min)	**COD removal efficiency**						
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**	**1 to 20**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.08	94.47	94.50	93.79	94.06	91.88	93.28	92.63
0.25	94.87	95.00	93.28	91.88	93.13	94.17	92.89
0.5	93.42	94.80	93.62	91.56	92.81	93.77	92.37
1	94.21	94.50	94.31	93.13	91.88	93.09	92.37
2	93.95	94.70	94.48	93.88	92.50	93.38	92.63
5	93.95	94.10	94.83	93.19	93.63	93.97	91.84
10	94.21	93.50	94.66	94.63	94.56	94.07	92.37
20	93.95	93.90	93.53	93.75	94.06	93.97	93.95
30	93.03	93.90	94.31	93.44	92.50	93.68	93.42
60	93.29	94.10	93.79	91.25	92.50	91.72	92.63

Note: initial lignin concentration = 910 mg/l, initial pH = 3, initial ferrous ion = 400 mg/l

Table C. 13 Effect of Fe^{2+}:H_2O_2 ratio on oxidation efficiency of COD removal by Fenton process

Time	**Oxidation efficiency of COD removal**						
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1:15**	**1 to 20**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.083	23.47	23.50	22.79	23.06	20.88	22.28	21.63
0.25	23.87	24.00	22.28	20.88	22.13	23.17	21.89
0.5	22.42	23.80	22.62	20.56	21.81	22.77	21.37
1	23.21	23.50	23.31	22.13	20.88	22.09	21.37
2	22.95	23.70	23.48	22.88	21.50	22.38	21.63
5	22.95	23.10	23.83	22.19	22.63	22.97	20.84
10	23.21	22.50	23.66	23.63	23.56	23.07	21.37
20	22.95	22.90	22.53	22.75	23.06	22.97	22.95
30	22.03	22.90	23.31	22.44	21.50	22.68	22.42
60	22.29	23.10	22.79	20.25	21.50	20.72	21.63

Note: initial lignin concentration = 910 mg/l, initial pH = 3, initial ferrous ion = 400 mg/l

Table C. 14 Effect of initial pH on color, lignin and COD removal by Fenton process

time	Color removal efficiency			Lignin removal efficiency			COD removal efficiency		
	pH=2	pH=3	pH=4	pH=2	pH=3	pH=4	pH=2	pH=3	pH=4
0	0	0	0	0	0	0	0	0	0
0.08333333	18.62	88.13	91.50	28.12	93.34	97.12	86.36	93.79	94.79
0.25	-	83.33	91.00	-	95.66	96.82	-	93.28	94.99
0.5	28.28	86.67	90.33	29.97	96.31	96.84	84.85	93.62	96.29
1	33.79	85.42	88.67	35.02	96.26	96.43	81.82	94.31	95.99
2	31.03	92.10	94.00	42.30	96.77	97.44	86.36	94.48	95.99
5	47.59	93.00	91.83	36.17	94.99	97.37	83.33	94.83	93.39
10	42.07	95.00	91.00	30.46	-	93.13	80.30	94.66	94.39
20	32.41	95.42	92.83	33.33	94.82	87.94	69.69	93.53	94.19
30	39.31	96.04	93.33	33.73	94.24	87.74	65.15	94.31	93.39
60	47.59	94.79	93.17	31.72	93.66	86.70	63.63	93.79	93.79

Note: initial lignin concentration = 910 mg/l, initial H_2O_2 concentration = 1,000 mg/l, initial ferrous ion = 400 mg/l

Table C. 15 Effect of Fenton's dosage on overall efficiency of color, lignin and COD removal by Fenton process

Time	Color removal efficiency			Lignin removal efficiency			COD removal efficiency		
	Fe^{2+}=300 mg/l	Fe^{2+}=400 mg/l	Fe^{2+}=500 mg/l	Fe^{2+}=300 mg/l	Fe^{2+}=400 mg/l	Fe^{2+}=500 mg/l	Fe^{2+}=300 mg/l	Fe^{2+}=400 mg/l	Fe^{2+}=500 mg/l
0	0	0	0	0	0	0	0	0	0
0.08	48.15	88.13	93.28	76.36	93.34	95.35	88.67	93.79	94.17
0.25	53.70	83.33	95.34	80.49	95.66	96.42	85.63	93.28	94.79
0.5	44.44	86.67	93.86	70.77	96.31	97.17	84.16	93.62	94.52
1	40.74	85.42	94.90	75.12	96.26	97.62	88.33	94.31	95.05
2	35.19	92.10	93.28	73.12	96.77	97.01	83.76	94.48	94.88
5	38.89	93.00	92.93	66.85	94.99	96.75	87.09	94.83	95.58
10	46.30	95.00	93.52	70.84	-	95.09	88.48	94.66	93.46
20	44.44	95.42	94.90	68.71	94.82	92.68	90.09	93.53	92.92
30	48.15	96.04	93.10	70.71	94.24	93.66	86.96	94.31	92.57
60	53.70	94.79	93.45	70.71	93.66	93.35	90.13	93.79	92.39

Note: initial lignin concentration = 910 mg/l, initial H_2O_2 concentration = 750, 1,000 and 1,250 mg/l, initial ferrous ion = 300, 400 and 500 mg/l under pH = 3

Table C. 16 Effect of Fenton’s dosage on oxidation efficiency of color, lignin and COD removal by Fenton process

Time	Color removal efficiency			Lignin removal efficiency			COD removal efficiency		
	Fe^{2+}=300 mg/l	Fe^{2+}=400 mg/l	Fe^{2+}=500 mg/l	Fe^{2+}=300 mg/l	Fe^{2+}=400 mg/l	Fe^{2+}=500 mg/l	Fe^{2+}=300 mg/l	Fe^{2+}=400 mg/l	Fe^{2+}=500 mg/l
0	0	0	0	0	0	0	0	0	0
0.08	15.15	23.13	10.28	18.36	23.34	16.85	17.67	25.79	13.17
0.25	20.70	18.33	12.34	22.49	25.66	17.92	14.63	25.28	13.79
0.5	11.44	21.67	10.86	12.77	26.31	18.67	13.16	25.62	13.52
1	7.74	20.42	11.90	17.12	26.26	19.12	17.33	26.31	14.05
2	2.19	27.10	10.28	15.12	26.77	18.51	12.76	26.48	13.88
5	5.89	28.00	9.93	8.85	24.99	18.25	16.09	26.83	14.58
10	13.30	30.00	10.52	12.84	-	16.59	17.49	26.66	12.46
20	11.44	30.42	11.90	10.71	24.82	14.18	19.09	25.53	11.92
30	15.15	31.04	10.10	12.71	24.24	15.16	15.96	26.31	11.57
60	20.70	29.79	10.45	12.71	23.66	14.85	19.13	25.79	11.39

Note: initial lignin concentration = 910 mg/l, initial H_2O_2 concentration = 750, 1,000 and 1,250 mg/l, initial ferrous ion = 300, 400 and 500 mg/l under pH = 3

Table C. 17 Effect of H_2O_2 step feeding mode on oxidation efficiency of color, lignin and COD removal by Fenton process

Time	Color removal	Lignin removal	COD removal
0	0	0	0
0.083	3.85	1.87	0.07
5	0.00	4.67	0.07
10	7.69	9.17	0.07
15	19.23	9.90	6.97
20	23.08	15.75	3.52
30	34.62	20.86	6.97
40	38.46	19.40	10.41
50	40.38	23.86	3.52
60	42.31	26.17	6.97

Note: initial lignin concentration = 910 mg/l, total H_2O_2 = 1,000 mg/l, initial ferrous ion = 40 mg/l under pH = 3

Table C. 18 Effect of Fe^{2+} and H_2O_2 step feeding mode (number of feeding) on overall efficiency of color, lignin and COD removal by Fenton process

Removal efficiency							
6 injections				**12 injections**			
Time	**Color**	**Lignin**	**COD**	**Time**	**Color**	**Lignin**	**COD**
0	0.00	0.00	0.00	0	0.00	0.00	0.00
1	2.30	2.56	0.00	1	3.26	3.59	0.00
20	1.15	3.75	6.25	5	1.09	10.77	-
40	16.09	11.24	13.75	10	6.52	15.81	6.48
60	21.84	14.79	52.50	20	5.43	8.72	16.15
70	39.08	35.90	-	30	2.17	8.12	16.15
80	93.28	91.81	96.88	40	1.09	7.26	19.38
90	97.87	88.57	96.56	50	3.26	14.70	29.38
100	97.76	91.71	97.19	60	15.22	17.35	58.40
120	98.05	91.86	96.88	70	83.70	83.68	88.71
-	-	-	-	80	96.30	92.71	96.45
-	-	-	-	85	98.86	90.05	96.45
-	-	-	-	90	99.08	90.68	97.74
-	-	-	-	95	98.64	92.14	96.78
-	-	-	-	100	98.97	91.76	97.10
-	-	-	-	105	98.15	94.00	-
-	-	-	-	110	98.53	95.91	96.78
-	-	-	-	120	97.83	91.26	94.84

Note: initial lignin concentration = 910 mg/l, total H_2O_2 = 1,000 mg/l, total ferrous ion = 400 mg/l under pH = 3

Table C. 19 Effect of Fe^{2+} and H_2O_2 step feeding mode (number of feeding) on oxidation efficiency of color, lignin and COD removal by Fenton process

Oxidation removal efficiency							
6 injections				**12 injections**			
Time	**Color**	**Lignin**	**COD**	**Time**	**Color**	**Lignin**	**COD**
0	0.00	0.00	0.00	0	0.00	0.00	0.00
1	1.30	2.59	0.00	1	1.26	2.59	0.00
20	1.15	1.29	2.81	5	1.09	5.77	-
40	11.09	3.00	6.86	10	5.52	3.81	3.48
60	20.17	5.27	28.36	20	3.43	4.72	13.15
70	14.08	3.01	-	30	1.17	4.12	13.15
80	29.94	25.55	31.00	40	1.09	7.26	19.38
90	37.87	20.89	31.05	50	2.26	14.70	29.38
100	29.43	24.47	28.22	60	3.22	15.35	30.40
120	21.38	18.01	27.91	70	40.70	39.68	30.71
-	-	-	-	80	43.30	27.71	34.45
-	-	-	-	85	45.86	25.05	34.45
-	-	-	-	90	39.08	23.68	39.74
-	-	-	-	95	38.64	25.14	38.78
-	-	-	-	100	30.97	25.76	29.10
-	-	-	-	105	30.15	18.00	-
-	-	-	-	110	26.53	12.91	28.78
-	-	-	-	120	21.83	9.26	19.84

Note: initial lignin concentration = 910 mg/l, total H_2O_2 = 1,000 mg/l, total ferrous ion = 400 mg/l under pH = 3

Table C. 20 Effect of Fe^{2+} and H_2O_2 step feeding mode (time interval) on oxidation efficiency of color, lignin and COD removal by Fenton process

Removal efficiency								
5 interval				**3 interval**				
Time	**Color**	**Lignin**	**COD**	**Time**	**Color**	**Lignin**	**Time**	**COD**
0	0.00	0.00	0.00	0	0.00	0.00	0.00	0.00
0.5	7.37	9.80	6.06	1	4.33	7.00	0.50	7.00
5	4.21	9.62	3.03	3	2.22	2.75	3.00	8.75
10	6.32	7.14	3.03	9	2.00	2.28	9.00	12.28
15	1.05	2.47	6.06	15	7.78	4.27	15.00	22.27
20	5.26	9.89	13.18	21	26.44	25.26	21.00	55.26
25	25.26	20.97	21.51	27	39.67	36.98	27.00	72.98
30	31.37	17.67	51.51	33	84.22	89.84	33.00	89.84
35	43.16	47.53	72.73	36	96.33	90.47	36.00	97.47
40	94.89	88.02	96.36	39	97.72	90.94	51.00	98.13
43	97.63	93.71	97.27	42	97.61	93.66	57.00	97.66
45	98.37	93.41	97.27	45	98.44	93.25	60.00	96.21
50	98.32	92.87	96.97	51	98.13	94.13	-	-
55	98.11	92.81	95.45	57	97.66	94.66	-	-
60	96.84	92.06	96.06	60	96.21	91.21	-	-

Note: initial lignin concentration = 910 mg/l, total H_2O_2 = 1,000 mg/l, total ferrous ion = 400 mg/l under pH = 3

Table C. 21 Effect of Fe^{2+}:H_2O_2 ratio on overall efficiency of color removal by electro-Fenton process

Time (min)	**Color removal efficiency**					
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**
0	24.00	24.00	24.00	24.00	24.00	24.00
0.08	25.03	31.26	25.75	23.75	28.55	25.14
0.25	33.28	37.56	32.77	30.77	25.52	42.18
0.5	36.37	36.97	42.28	26.28	28.18	33.86
1	50.52	45.79	35.09	42.09	43.94	47.73
2	48.45	53.31	50.63	52.00	58.64	-
5	78.35	94.62	90.61	85.61	88.38	77.27
10	85.88	95.37	92.91	92.91	87.12	72.73
20	96.39	93.76	93.44	94.00	84.60	73.86
30	93.81	92.94	95.32	90.32	86.62	76.14
60	91.27	94.89	94.15	90.15	83.33	78.41

Note: initial lignin concentration = 910 mg/l, initial pH = 3, electrical current = 1A

Table C. 22 Effect of Fe^{2+}:H_2O_2 ratio on overall efficiency of lignin removal by electro-Fenton process

Time (min)	**Lignin removal efficiency**					
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**
0	30.00	30.00	30.00	30.00	30.00	30.00
0.08	38.28	39.67	31.28	35.28	31.87	35.33
0.25	40.21	44.00	42.64	32.64	33.85	34.26
0.5	40.21	45.24	47.36	50.36	47.75	41.07
1	46.92	55.40	45.56	50.56	58.05	58.68
2	57.44	61.85	58.81	60.81	61.64	-
5	91.90	92.14	89.10	83.00	75.15	82.05
10	92.08	91.16	89.58	92.00	84.81	74.36
20	93.46	91.91	91.48	90.48	88.69	74.75
30	95.53	90.32	88.89	85.89	90.52	66.07
60	92.78	90.68	85.69	91.69	87.39	65.48

Note: initial lignin concentration = 910 mg/l, initial pH = 3, electrical current = 1A

Table C. 23 Effect of Fe^{2+}:H_2O_2 ratio on overall efficiency of COD removal by electro-Fenton process

Time (min)	**COD removal efficiency**					
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**
0	52.00	52.00	52.00	52.00	52.00	52.00
0.08	53.00	55.76	54.07	60.00	58.00	57.00
0.25	58.00	56.21	54.07	54.00	52.00	54.00
0.5	61.00	62.76	57.78	60.00	51.00	62.00
1	56.00	66.21	69.48	66.00	71.00	70.00
2	84.00	89.65	85.80	84.00	80.00	84.00
5	88.00	93.65	88.04	92.00	91.00	86.00
10	98.00	95.98	92.19	88.00	95.00	92.00
20	92.00	97.70	93.65	92.00	92.00	84.67
30	94.00	97.13	89.74	85.00	88.00	83.33
60	91.00	90.55	94.12	89.00	91.00	77.33

Note: initial lignin concentration = 910 mg/l, initial pH = 3, electrical current = 1A

Table C. 24 Effect of Fe^{2+}:H_2O_2 ratio on oxidation efficiency of color removal by electro-Fenton process

Time (min)	**Oxidation efficiency of color**					
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**
0	0.00	0.00	0.00	0.00	0.00	0.00
0.08	1.03	7.26	1.75	3.75	4.55	1.14
0.25	9.28	13.56	8.77	6.77	1.52	3.18
0.5	12.37	12.97	18.28	2.28	4.18	9.86
1	11.52	15.79	11.09	18.09	19.94	7.73
2	13.45	13.31	12.63	12.00	18.64	-
5	11.35	27.62	23.61	18.61	21.38	10.27
10	18.88	28.37	25.91	25.91	20.12	5.00
20	29.39	26.76	26.44	27.00	17.60	6.86
30	26.81	25.94	28.32	23.32	19.62	9.14
60	24.27	27.89	27.15	23.15	16.33	11.41

Note: initial lignin concentration = 910 mg/l, initial pH = 3, electrical current = 1A

Table C. 25 Effect of Fe^{2+}:H_2O_2 ratio on oxidation efficiency of lignin removal by electro-Fenton process

Time (min)	**Oxidation efficiency of lignin**					
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**
0	0.00	0.00	0.00	0.00	0.00	0.00
0.08	8.28	9.67	1.28	5.28	1.87	5.33
0.25	10.21	14.00	12.64	2.64	3.85	4.26
0.5	10.21	15.24	7.36	10.36	7.75	11.07
1	6.92	15.40	12.56	10.56	8.05	10.68
2	9.44	13.85	10.81	12.81	13.64	-
5	26.90	29.14	26.10	20.00	12.15	19.05
10	29.08	28.16	26.58	29.00	21.81	11.36
20	30.46	28.91	28.48	27.48	25.69	11.75
30	32.53	27.32	25.89	22.89	27.52	3.07
60	29.78	27.68	22.69	28.69	24.39	2.48

Note: initial lignin concentration = 910 mg/l, initial pH = 3, electrical current = 1A

Table C. 26 Effect of Fe^{2+}:H_2O_2 ratio on oxidation efficiency of COD removal by electro-Fenton process

Time (min)	**Oxidation efficiency of COD**					
	1 to 0.6	**1 to 1**	**1 to 2.5**	**1 to 5**	**1 to 10**	**1 to 15**
0	0.00	0.00	0.00	0.00	0.00	0.00
0.08	1.00	3.76	2.07	2.00	3.00	5.00
0.25	6.00	4.21	2.07	2.00	0.00	4.00
0.5	9.00	10.76	5.78	8.00	1.00	10.00
1	4.00	14.21	7.00	6.00	9.00	10.00
2	12.00	17.65	13.80	9.00	8.00	12.00
5	15.00	20.65	15.04	9.00	18.00	13.00
10	25.00	22.98	19.19	15.00	22.00	19.00
20	19.00	24.70	20.65	19.00	19.00	11.67
30	21.00	24.13	16.74	22.00	15.00	10.33
60	18.00	17.55	21.12	16.00	18.00	4.33

Note: initial lignin concentration = 910 mg/l, initial pH = 3, electrical current = 1A

Table C. 27 Effect of current density on overall efficiency of color, lignin and COD removal by electro-Fenton process

Time (min)	**Current density (A/m^2)**								
	150			**200**			**250**		
	Color	**Lignin**	**COD**	**Color**	**Lignin**	**COD**	**Color**	**Lignin**	**COD**
0	10.00	21.00	23.00	24.00	30.00	52.00	65.00	56.00	72.00
0.083	14.00	22.99	24.00	31.26	39.67	55.76	72.00	64.63	76.08
0.25	17.00	25.62	26.00	37.56	44.00	56.21	75.00	72.41	80.43
1	15.00	31.00	26.00	36.97	45.24	62.76	83.00	76.17	78.25
2	22.00	28.47	32.00	45.79	55.40	66.21	87.00	77.91	84.78
5	23.00	40.08	29.00	53.31	61.85	89.65	87.00	74.36	90.58
10	20.00	40.03	42.00	84.62	92.14	93.65	93.00	93.63	93.48
20	29.00	43.04	44.00	95.37	91.16	95.98	94.00	90.76	92.61
30	34.00	47.85	46.00	93.76	91.91	97.70	93.90	92.14	93.48
45	36.00	43.36	52.00	92.94	90.32	97.13	94.50	95.09	95.22
60	43.00	45.54	54.00	94.89	90.68	90.55	95.00	95.64	95.22

Note: initial lignin concentration = 910 mg/l, initial pH = 3

Table C. 28 Effect of current density on oxidation efficiency of color, lignin and COD removal by electro-Fenton process

Time (min)	**Current density (A/m^2)**								
	150			**200**			**250**		
	Color	**Lignin**	**COD**	**Color**	**Lignin**	**COD**	**Color**	**Lignin**	**COD**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.083	4.00	1.99	1.00	7.26	9.67	3.76	7.00	8.63	4.08
0.25	7.00	4.62	3.00	13.56	14.00	4.21	10.00	12.41	8.43
1	5.00	10.00	3.00	12.97	15.24	10.76	18.00	16.17	6.25
2	12.00	7.47	9.00	15.79	15.40	14.21	22.00	17.91	9.78
5	12.00	19.08	6.00	13.31	13.85	17.65	22.00	9.36	15.58
10	8.00	19.03	14.00	27.62	22.14	20.65	19.00	21.63	18.48
20	18.00	22.04	13.00	28.37	25.16	18.98	22.00	18.76	17.61
30	12.00	26.85	13.00	26.76	25.91	22.70	24.90	20.14	18.48
45	14.00	22.36	19.00	25.94	23.32	19.13	24.50	23.09	20.22
60	21.00	21.54	21.00	27.89	21.68	23.00	25.00	23.64	20.22

Note: initial lignin concentration = 910 mg/l, initial pH = 3

Table C. 29 Effect of step feeding operation on overall efficiency of color, lignin and COD removal by electro-Fenton process

Time	**Step feeding at initial**			**Time**	**Step feeding at 20 minutes**		
	Color	**Lignin**	**COD**		**Color**	**Lignin**	**COD**
0	0	0	0	0	0	0	0
0.083	12.07	12.91	0.00	5	3.00	0.70	15.90
5	3.45	11.14	7.40	15	14.00	8.10	24.20
10	10.34	23.64	11.11	20	24.00	30.00	52.00
15	31.03	39.95	37.04	20.083	25.43	36.79	52.15
20	60.34	50.14	68.11	21	31.14	31.15	58.58
25	93.91	88.97	92.41	25	65.71	57.56	92.15
30	94.77	91.24	93.33	30	91.43	92.31	95.72
40	96.21	91.17	90.96	35	91.43	94.87	95.72
50	92.51	92.16	92.89	40	94.14	92.95	92.15
60	93.64	91.87	91.81	45	94.29	90.90	89.29
80	93.12	93.12	92.12	50	97.14	93.85	90.72
-	-	-	-	65	90.00	86.03	92.15
-	-	-	-	80	94.29	86.41	92.15

Note: initial lignin concentration = 910 mg/l, initial pH = 3, total H_2O_2 concentration = 400 mg/l

Table C. 30 Real wastewater treatment on color, lignin and COD removal

Time	Conventional Fenton			Time	Step feeding of H_2O_2			Time	Step feeding of Fe^{2+} and H_2O_2		
	Color	Lignin	COD		Color	Lignin	COD		Color	Lignin	COD
0	0	0	0	0	0	0	0	0	0	0	0
0.083333	67.86	81.65	74.42	0.083333	24.32	5.42	17.06	0.0833333	4.35	2.88	12.23
0.25	71.43	81.84	74.03	5	39.19	63.79	36.58	5	40.58	57.65	42.09
0.5	70.00	80.93	75.58	10	32.43	60.44	34.14	10	57.97	60.64	51.15
1	68.57	81.84	75.58	20	29.73	52.07	34.14	20	59.42	68.20	60.33
2	70.71	74.57	78.68	25	25.68	49.88	39.02	30	81.16	73.76	85.92
5	85.71	78.30	77.52	30	18.92	53.49	34.14	35	95.22	88.13	88.64
10	84.29	71.49	77.52	35	16.22	45.37	39.02	40	96.96	87.44	86.28
20	84.29	67.49	76.36	40	22.97	48.59	34.14	45	97.17	85.45	84.44
30	82.86	62.84	77.13	45	24.32	47.82	36.58	50	97.17	83.27	85.94
60	82.14	59.30	75.97	50	22.97	47.04	39.02	60	97.39	84.28	83.05
-	-	-	-	60	28.38	48.46	39.02	-	-	-	-

Note: initial pH =3, total Fe^{2+} concentration = 400 mg/l, total H_2O_2 concentration = 1,000 mg/l

Table C. 31 Calculation of oxidation efficiency at different ratio of Fe^{2+} and H_2O_2 on color, lignin and COD removal

Oxidation efficiency can be calculated from the subtraction of overall efficiency and coagulation efficiency as shown in Table C. 31. Reaction time of 20 min was obtained as optimum reaction time.

Calculation

At ratio of Fe^{2+} and H_2O_2 of 1:0.6
Oxidation efficiency on color removal = overall efficiency – coagulation efficiency
= 87.2% - 65%
= 22.3%
Oxidation efficiency on lignin removal = overall efficiency – coagulation efficiency
= 91.75% - 72%
= 19.76%
Oxidation efficiency on COD removal = 92.6% - 69%
= 23.21%

Ratio	Overall efficiency			Coagulation efficiency			Oxidation efficiency		
	Color	Lignin	COD	Color	Lignin	COD	Color	Lignin	COD
1:0.6	87.3	91.75	92.2	65	72	69	22.3	19.76	23.21
1:1	89.5	94.73	91.5	65	72	69	24.5	22.73	22.50
1:2.5	91	94.82	92.6	65	72	69	26	22.82	23.66
1:5	89.33	90.30	92.6	65	72	69	24.33	18.30	23.63
1:10	89.08	89.76	92.6	65	72	69	24.08	17.76	23.56
1:15	81.04	92.77	92.1	65	72	69	16.04	20.77	23.07
1:20	71.5	85.50	90.4	65	72	69	6.5	13.50	21.37

Note: initial lignin concentration = 910 mg/l, Ferrous concentration = 400 mg/l

Table C. 32 Calculation of oxidation efficiency at Fenton's dosage on color, lignin and COD removal

Dosage	Overall efficiency			Coagulation efficiency			Oxidation efficiency		
	Color	Lignin	COD	Color	Lignin	COD	Color	Lignin	COD
300	46.44	69	84	35	58	65	11.44	10.71	19.08
400	90.99	95	91	65	72	68	25.99	23.66	23.00
500	95.40	93	93	83.5	78.5	81	11.89	14.18	11.92

Note: initial lignin concentration = 910 mg/l, Ferrous concentration = 300-500 mg/l, ratio of Fe^{2+} and H_2O_2 = 1:2.5

Table C. 33 Calculation of oxidation efficiency of Fe^{2+} and H_2O_2 step feeding operation on color, lignin and COD removal

Operation	Overall efficiency			Coagulation efficiency			Oxidation efficiency		
	Color	Lignin	COD	Color	Lignin	COD	Color	Lignin	COD
initial	91	95	91	65	72	68	26	23	23
6 times	97.8	91.7	96.5	61	66.7	65.6	37	25	31
12 times	99	92.1	97.7	54	53.1	59.7	45	39	38

Note: initial lignin concentration = 910 mg/l, fixed total ferrous concentration = 400 mg/l, ratio of Fe^{2+} and H_2O_2 = 1:2.5

Table C. 34 Calculation of oxidation efficiency of Fe^{2+} and H_2O_2 step feeding operation on color, lignin and COD removal

Ratio	Overall efficiency			Coagulation efficiency			Oxidation efficiency		
	Color	Lignin	COD	Color	Lignin	COD	Color	Lignin	COD
1:0.6	91.3	91.9	93	67	72.5	75	24.3	19.4	18
1:1	94.8	91.2	96	67	69.2	75	27.9	21.9	20.5
1:2.5	92.9	89.6	92	65	72.1	75	27.2	17.4	17.1
1:5	92.9	90.4	88	69	73.5	72	23.2	16.9	16
1:10	83	84.8	90	67	70.1	72	16	14.7	18
1:15	73	77.8	86	62	69	75	11	8.7	11.3

Note: initial lignin concentration = 910 mg/l, electrical current = 1A

Table C. 35 Calculation of oxidation efficiency of current density on color, lignin and COD removal

Current density	Overall efficiency			Coagulation efficiency			Oxidation efficiency		
	Color	Lignin	COD	Color	Lignin	COD	Color	Lignin	COD
150A/m^2	29	43	44	18	28	34	11	15	10
200 A/m^2	95.4	91.2	96	67.4	69.2	76	28	22	20
250 A/m^2	94	91	92.6	75	73.8	78.6	19	17	14

Note: initial lignin concentration = 910 mg/l, current density = 150-250 A/m^2

Appendix D

Cost estimation

Appendix D-1

Cost evaluation for conventional Fenton under optimum operating conditions

At optimum operating conditions, 2 g/l of $FeSO_4$ and 1g of H_2O_2 was used to the treatment of 0.91 g/l of lignin. Cost calculation for removal of lignin are shown below.

1. Chemical cost

1.1 $FeSO_4$ = 2 g x 0.025 THB/g
= 0.05 THB/ 1 litre of wastewater
= 50 THB/ 1 m^3 of wastewater

1.2 H_2O_2 = 1 g x 0.029 THB/g
= 0.029 THB/ 1 litre of wastewater
= 29 THB/ 1 m^3 of wastewater

1.3 H_2SO_4 (98%) = 1 ml x 0.0015 THB/ml
= 0.0015 THB/ 1 litre of wastewater
= 1.5 THB/ 1 m^3 of wastewater

1.4 NaOH = 12.5 ml x 0.003 THB/ml
= 0.045 THB/ 1 litre of wastewater
= 45 THB/ 1 m^3 of wastewater

2. Total cost = 50+29+1.5+45 THB/m^3 of wastewater
= 125.5 THB/m^3 of wastewater

Appendix D-2

Cost evaluation for step feeding of H_2O_2 operation

In this operation, 0.2 g/l of $FeSO_4$ and 1g of H_2O_2 was used to the treatment of 0.91 g/l of lignin. Cost calculation for removal of lignin are shown below.

1. Chemical cost

1.1 $FeSO_4$ = 0.2 g x 0.025 THB/g
= 0.005 THB/ 1 litre of wastewater
= 5 THB/ 1 m^3 of wastewater

1.2 H_2O_2 = 1 g x 0.029 THB/g
= 0.029 THB/ 1 litre of wastewater
= 29 THB/ 1 m^3 of wastewater

1.3 H_2SO_4 = 1 ml x 0.0015 THB/ml
= 0.0015 THB/ 1 litre of wastewater
= 1.5 THB/ 1 m^3 of wastewater

1.4 NaOH = 12.5 ml x 0.003 THB/ml
= 0.045 THB/ 1 litre of wastewater
= 45 THB/ 1 m^3 of wastewater

2. Total cost = 5+29+1.5+45 THB/ 1 m^3 of wastewater
= 80.5 THB/ 1 m^3 of wastewater

Appendix D-3

Cost evaluation for step feeding of Fe^{2+} and H_2O_2 operation

1.5 g/l of $FeSO_4$ and 1g of H_2O_2 was used to the treatment of 0.91 g/l of lignin. Cost calculation for removal of lignin at optimum reaction time are shown below.

1. Chemical cost

1.1 $FeSO_4$ = 1.5 g x 0.025 THB/g
= 0.0375 THB/ 1 litre of wastewater
= 37.5 THB/ 1 m^3 of wastewater

1.2 H_2O_2 = 0.75 g x 0.029 THB/g
= 0.022 THB/ 1 litre of wastewater
= 22 THB/ 1 m^3 of wastewater

1.3 H_2SO_4 (98%) = 1 ml x 0.0015 THB/ml
= 0.0015 THB/ 1 litre of wastewater
= 1.5 THB/ 1 m^3 of wastewater

1.4 NaOH = 12.5 ml x 0.003 THB/ml
= 0.045 THB/ 1 litre of wastewater
= 45 THB/ 1 m^3 of wastewater

2. Total cost = 37.5+22+1.5+45 THB/m^3 of wastewater
= 106 THB/m^3 of wastewater

Appendix D-4

Cost evaluation for initial feeding of electro-Fenton process

Electrical current of 1A and H_2O_2 concentration of 0.2 g was used to the treatment of lignin. The detail of cost estimation is shown below.

1. Chemical cost

1.1 H_2O_2 = 0.2 g x 0.029 THB/g
= 0.0058 THB/ 1 litre of wastewater
= 6 THB/ 1 m^3 of wastewater

1.2 Iron electrode = 0.7 g/l x 21 THB/kg
= 0.015 THB/ 1 litre of wastewater
= 15 THB/ 1 m^3 of wastewater

1.3 H_2SO_4 = 21 ml x 0.0015 THB/ml
= 0.0315 THB/ 1 litre of wastewater
= 31.5 THB/ 1 m^3 of wastewater

1.4 NaOH = 12.5 ml x 0.003 THB/ml
= 0.045 THB/ 1 litre of wastewater
= 45 THB/ 1 m^3 of wastewater

2. Energy cost = Vlt/1,000vol
= (27 x 1 x 0.5)/(1,000 x (1/1,000))
= 13.5 kWh/m^3

Electricity cost = energy cost x unit values x tax
= 13.5 x 2.8095 x 1.07 THB
= 40.6 THB

3. Total cost = 6+15+31.5+45+40.6 THB
= 138.1 THB

Appendix D-5

Cost evaluation for step feeding of electro-Fenton process

Electrical current of 1A and H_2O_2 concentration of 0.18 g was used to the treatment of lignin. The detail of cost estimation is shown below.

1. Chemical cost

1.1 H_2O_2 = 0.18 g x 0.029 THB/g
= 0.0052 THB/ 1 litre of wastewater
= 5 THB/ 1 m^3 of wastewater

1.2 Iron electrode = 0.7 g/l x 21 THB/kg
= 0.015 THB/ 1 litre of wastewater
= 15 THB/ 1 m^3 of wastewater

1.3 H_2SO_4 = 21 ml x 0.0015 THB/ml
= 0.0315 THB/ 1 litre of wastewater
= 31.5 THB/ 1 m^3 of wastewater

1.4 NaOH = 12.5 ml x 0.003 THB/ml
= 0.045 THB/ 1 litre of wastewater
= 45 THB/ 1 m^3 of wastewater

2. Energy cost = Vlt/1,000vol
= (27 x 1 x 0.5)/(1,000 x (1/1,000))
= 13.5 kWh/m^3

Electricity cost = energy cost x unit values x tax
= 13.5 x 2.8095 x 1.07 THB
= 40.6 THB

3. Total cost = 5+15+31.5+45+40.6 THB
= 137.1 TH

VITA

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