# REMOVAL OF LIGNIN IN PULPING WASTEWATER BY HETEROGENEOUS FENTON-LIKE PROCESS USING IRON MOLYBDATE

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# การกำจัดลิกนินในน้ำเสียโรงงานเยื่อกระดาษโดยกระบวนการเฟนตันเสมือนแบบเนื้อผสมโดยใช้ไอรอนโมลิบเดต

นางสาวอภิญญา ศุภรพิพัฒน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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| Thesis Title | REMOVAL OF LIGNIN IN PULPING WASTEWATER BY HETEROGENEOUS FENTON-LIKE PROCESS USING IRON MOLYBDATE |
| By | Miss Apinya Subharaphiphat |
| Field of Study | Environmental Management |
| Thesis Advisor | On-anong Larpparisudthi, Ph.D. |

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อภิญญา ศุภรพิพัฒน์ : การกำจัดลิกนินในน้ำเสียโรงงานเยื่อกระดาษโดยกระบวนการเฟนตันเสมือนแบบเนื้อผสมโดยใช้ไอรอนโมลิบเดต (REMOVAL OF LIGNIN IN PULPING WASTEWATER BY HETEROGENEOUS FENTON-LIKE PROCESS USING IRON MOLYBDATE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร.อรอนงค์ ลาภปริสุทธิ, 122 หน้า.

โรงงานผลิตเยื่อกระดาษมีการใช้วัตถุดิบและสารเคมีเป็นอย่างมากในแต่ละกระบวนการผลิต หนึ่งในปัญหาของน้ำเสียจากโรงงานเยื่อกระดาษนี้คือน้ำที่มีสีดำ ซึ่งมักมีลิกนินเป็นส่วนประกอบหลัก ลิกนินก่อให้เกิดปัญหาสิ่งแวดล้อมเช่น เพิ่มความต้องการใช้ออกซิเจนในน้ำ และ สามารถย่อยสลายกลายเป็นสารมีพิษได้ เช่น ฟีนอล คีโตน คาร์บอกซิลิก แอซิด ดังนั้นกระบวนการบำบัดน้ำเสียจึงเป็นสิ่งจำเป็นก่อนที่จะมีการปล่อยน้ำเสียออกสู่สิ่งแวดล้อม ในงานวิจัยนี้ได้มีการศึกษาถึงการบำบัดน้ำเสียสังเคราะห์โรงงานเยื่อกระดาษด้วยกระบวนการเฟนตันโดยใช้เฟอร์รัสซัลเฟตและกระบวนการเฟนตันเสมือนแบบเนื้อผสมโดยใช้ไอรอนโมลิบเดตเพื่อหาสภาวะที่เหมาะสมในการบำบัดสีและลิกนิน นอกจากนี้ ไอรอนโมลิบเดตยังถูกนำมาใช้ซ้ำเพื่อศึกษาความคงทนของคะตะลิสต์ ความเข้มข้นเริ่มต้นของน้ำเสียสังเคราะห์ที่ใช้มีลิกนินอยู่ 910 มิลลิกรัมต่อลิตร จากผลการทดลองพบว่า ในกระบวนการเฟนตันเมื่อใช้ความเข้มข้นเฟอร์รัสไอออน 400 มิลลิกรัมต่อลิตร ค่าพีเอชเริ่มต้นที่ 3 และอัตราส่วนเหล็กเฟอร์รัสต่อไฮโดรเจนเปอร์ออกไซด์ที่ 1 ต่อ 2.5 ให้ประสิทธิภาพในการบำบัดลิกนิน สี และซีโอดี 92%, 90% และ 92% ตามลำดับ จากการทดลองเมื่อใช้ไอรอนโมลิบเดตเป็นตัวเร่งปฏิกิริยาในกระบวนการเฟนตันเสมือนแบบเนื้อผสมพบว่า เมื่อใช้ความเข้มข้นเฟอร์ริกไอออน 2 กรัมต่อลิตร ค่าพีเอชเริ่มต้นที่ 8 และอัตราส่วนเหล็กเฟอร์ริกต่อไฮโดรเจนเปอร์ออกไซด์ 1 ต่อ 10 ให้ประสิทธิภาพในการบำบัดลิกนิน สี และซีโอดี 71%, 67% และ 67% ตามลำดับ นอกจากนี้ไอรอนโมลิบเดตยังสามารถรักษาความสามารถในการบำบัดได้ดีเมื่อมีการใช้ซ้ำ 4 ครั้ง แม้ว่าการใช้ไอรอนโมลิบเดตในกระบวนการเฟนตันเสมือนแบบเนื้อผสมจะให้ประสิทธิภาพในการบำบัดต่ำกว่าการใช้เฟอร์รัสซัลเฟตในกระบวนการเฟนตัน แต่ก็สามารถลดข้อเสียของกระบวนการเฟนตันได้แก่ ไม่มีการก่อให้เกิดกากตะกอนเหล็ก สามารถประยุกต์ใช้ได้ในช่วงพีเอชกว้าง และยังรักษาประสิทธิภาพได้ดีเมื่อมีการใช้ซ้ำไปแล้วหลายครั้ง

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KEYWORDS: FENTON / HETEROGENEOUS FENTON-LIKE PROCESS / IRON MOLYBDATE / PULPING WASTEWATER / DECOLORIZATION / LIGNIN

APINYA SUBHARAPHIPHAT: REMOVAL OF LIGNIN IN PULPING WASTEWATER BY HETEROGENEOUS FENTON-LIKE PROCESS USING IRON MOLYBDATE. ADVISOR: ON-ANONG LARPPARISUDTHI, Ph.D., 122 pp.

Pulping industry consumes high amount of raw materials and chemical reagents in each process and wastewater problem from Pulp industries is one of the most concern. One of concerned wastes is black liquor which contains high lignin content. Lignin causes environmental problems such as increase oxygen demand and can be changed to be toxic by-products such as phenols, ketone and carboxylic acids. Therefore, wastewater treatments are required before discharge to environment. This research studied on the treatment of synthetic pulping wastewater. The treatment of synthetic pulping wastewater was carried out by Fenton process using ferrous sulfate and heterogeneous Fenton-like process using iron molybdate to find the optimum conditions for color and lignin removal. Furthermore, iron molybdate was reused to find its durability. The initial lignin concentration of synthetic pulping wastewater was 910 mg/l. The result of Fenton process showed that at pH of 3, $Fe^{2+}$:$H_2O_2$ ratio of 1:2.5 and $Fe^{2+}$ dosage was 400 mg/l achieved 92%, 90% and 92% for lignin, color and COD removal efficiencies, respectively. The result of heterogeneous Fenton-like process showed that at pH of 8, $Fe^{3+}$:$H_2O_2$ ratio of 1:10 and 2 g/l $Fe^{3+}$ dosage, lignin, color and COD removal efficiency were achieved 71%, 67% and 67%, respectively. Moreover, iron molybdate could maintain its durability after four times reuse. Although using of iron molybdate in heterogeneous Fenton-like process showed lower performance than using of ferrous sulfate in Fenton process, it could overcome several drawbacks of Fenton process e.g. no sludge iron, could be applied in wide range of pH, and maintain its performance after several times reused.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

In recent year, industries in Thailand are growing including pulping industry. Pulping industry consumes a lot of materials and chemical reagents in order to produce pulp. Pulping produces high amount of wastewater pollutants (Pokhrel and Viraraghavan, 2004). The wastewater from pulp industry contains high amount of organic and inorganic compounds. One of concerned waste is called black liquor. Which contains high level of lignin. Black liquor causes environmental problems, such as bad smell, increase of oxygen demand, toxicity, and aesthetics problem. Therefore, wastewater treatment is required before discharge to the environment. Wastewater treatment methods such as biological treatment, physical treatment and physico-chemical treatment are applied (Pokhrel and Viraraghavan, 2004; Thompson et al., 2001).

This dissertation focused on removal of lignin in pulping wastewater by heterogeneous Fenton-like process using iron molybdate. This method is an advance oxidation process (AOPs) using iron (Fe) as a catalyst to react with hydrogen peroxide ($H_2O_2$) in acidic condition to form hydroxyl radical (OH•), which is a strong oxidizing agent. The experiment ran under room temperature and atmospheric pressure. Ferrous sulfate ($FeSO_4$) and iron molybdate ($Fe_2(MoO_4)_3$ were used as catalysts in homogeneous and heterogeneous Fenton-like processes, respectively. The factors of Fenton processes for removal of lignin in pulping wastewater were pH, ratio of iron (Fe) to hydrogen peroxide ($H_2O_2$) and concentration of iron (Fe) and hydrogen peroxide ($H_2O_2$).

The optimum ratio of ferrous ion ($Fe^{2+}$) to hydrogen peroxide and ferric ion ($Fe^{3+}$) to hydrogen peroxide and the repeat time of iron molybdate use in heterogeneous Fenton-like process were investigated in this study.

## 1.2 Hypothesis

1. Heterogeneous Fenton-like reaction was able to treat color and lignin in wastewater from pulp industry efficiently.
2. The efficiency of heterogeneous Fenton-like process was comparable to that of homogeneous Fenton process.

## 1.3 Objective

1. To investigate the removal efficiency of color and lignin by homogeneous and heterogeneous Fenton-like processes and to compare the results of removal efficiency
2. To find the optimum ratio of ferrous ion to hydrogen peroxide and ferric ion to hydrogen peroxide.
3. To find the removal efficiency of reused catalyst in heterogeneous Fenton-like process

## 1.4 Scope of Study

All experiment was conducted at Department of Environmental Engineering, Faculty of Engineering Chulalongkorn University. The scopes of this study were stated as follows:

1. All experiment was conducted at room temperature and atmospheric pressure. pH was monitored,
2. This study used synthesis wastewater generated by mixing tap water with lignin at the concentration of 910 mg/l. The volume of reactor was 1 liter,
3. This experiment focused on wastewater treatment by homogeneous and heterogeneous Fenton-like processes using iron (II) sulfate and iron molybdate as catalyst, respectively,
4. Iron molybdate was synthesized and analyzed its characteristics before use in the experiment.

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Overview

Pulp and Paper industry is in the third rank of fresh water consumption in the world (Thompson et al., 2001) after metal and chemical industries and is a major source of industrial pollution (Tunay et al., 2010). To reduce the consumption of fresh water, recovery units are equipped within pulp and paper industry. However, one of the environmental problems from the Pulp industry, especially in most developing countries, is high amount of residual black liquor which is hardly disposed (Araujo, E. et al., 2002). This problem is from non-fully or non-equipped with recovery units.

Black liquor is an intermediate product from the pulping process. Black liquor contains high amount of lignin content (Araujo, E. et al., 2002; Torrades et al., 2011).

## 2.2 The pulp and paper making process

Pulp mills separate the fiber of wood or the other materials to produce pulp. Either chemical, Semi-chemical, or mechanical processes is used in pulp mills (Tunay et al., 2010).

### 2.2.1 Pulping

*1. Fiber furnish preparation and handling*

Furnish is the mixture of fibrous materials for pulp making. Wood is a major source of fiber for paper production as it has high fiber yield. Cellulose fiber, a component of cell wall, is a component of fibrous particles. The cellulose fiber has to be separated from chemical matrix such as lignin, hemicellulose, and resins to form pure fiber mixture.

In this process, logs are debarked. The bark from logs is incinerated in bark-burning furnaces. Debarked logs are chipped using blades mounted on a rotating disk. Then, wood chips are screened to select the size. Wood chips are stored outside as piles and moved to next operations.

*2. Pulping process*

Pulping processes change raw materials to fiber and to form a sheet. There are three types of pulping processes which are:

Chemical pulping: Raw materials are mixed with cooking chemicals under controlled temperature and pressure conditions to separate fibers from wood. Lignin bond is dissolved. Chemical pulping can be separated into three types depending on chemical solutions and chemical recovery processes used.

*Kraft pulping process*: Sodium sulfide ($Na_2S$) and sodium hydroxide (NaOH) (known as white liquor) are mixed with wood chips (in pulp) and black liquor. The black liquor is sent to recovery process to regenerate white liquor again.

*Sulfite pulping process*: Lignin bonding between wood fibers is degraded by the mixture of sulfurous acid ($H_2SO_3$) and bisulfite ion ($HSO_3^-$).

*The soda process*: Use only NaOH in the Kraft process to improve reaction rates.

Semi-chemical pulping: Using soft chemical solution for fiber separation. Sodium sulfite and sodium carbonate are usually used.

Mechanical pulping: This technique uses physical pressure instead of chemicals to separate furnish fibers. Pulp from mechanical pulping has low strength and quality such as newsprint.

Secondary fiber pulping: All operations are included for secondary re-pulping and contaminant removal.

*3. Chemical recovery processes*

Chemical recovery is an important process of chemical pulping process. The spent cooking liquor will be reused by this process.

*4. Pulp process*

Pulp process removes impurities (e.g. uncooked chips) and recycles residual cooking liquor by a washing process. The efficiency of washing process is necessary to maximize the cooking liquor return for chemical recovery and to minimize excess cooking liquor to be carried to the bleach process. The bleaching chemicals can react with lignin and hemicellulose (are classified as dissolved organic compounds) leads to more chemicals consumption and these compounds as precursors to causes chlorinated organic compounds such as dioxins and furans.

*5. Bleaching*

Bleaching is a process that uses chemicals to increase brightness of the pulp. Bleached pulps are whiter and softer than unbleached pulps. The type of pulp bleaching depends on required quality, pulping process, fiber furnish and end use of final product. Therefore, bleaching process for each pulp type are as follow:

*Chemical pulp*: Pulps pass through stages of chemical bleaching and washing. The important characteristics of chemical used for efficiency in bleaching process are high lignin reactivity and selectivity. Bleaching chemicals are, for example, chlorine dioxide ($ClO_2$), hypochlorites (HOCl, NaOCl, and $Ca(OCl)_2$).

*Semi-chemical pulps*: Hydrogen peroxide ($H_2O_2$) is used in a bleach tower.

*Mechanical pulps*: Hydrogen peroxide ($H_2O_2$) or sodium hydrosulfite ($Na_2S_2O_4$) is used.

*Deinking secondary fibers*: Bleaching chemicals such as hypochlorites (HOCl, NaOCl, and $Ca(OCl)_2$), $Na_2S_2O_4$ and $H_2O_2$ can be added in a bleach tower, during the re-pulping process or direct to the pulper.

*6. Stock preparation*

The pulp is transferred into the stock used for paper making. Pulp is dried and bundled, then added wet additives to increase density and strength. Additives are used to improve special properties paper products or simply make paper in papermaking process.

### 2.2.2 Papermaking

*7. Paper and paperboard making processes*

This process consists of wet and dry end operations. In wet end operations, a paper production machine changed the pulp to a paper product. In dry end operations, paper fibers are held together and paper sheet is pressed by heavy rolls to reduce the thickness and to make a smooth surface.

## 2.3 Lignin

Lignin $(C_{10}H_{12}O_4)_n$ is the second most content founded in plant cells and wood tissues after cellulose (Lisperguer et al., 2009). Lignin is a complex and high molecular weight, non-carbohydrate phenolic hetero-polymer, which is formed by polymerization (photosynthetic pathway and de-hydrogenation) of three types of monolignols, i.e., p-hydroxyl-cinnamyl alcohols (phenyl propane units) (Xia et al., 2014). The phenylpropane units consist of p-coumaryl, coniferyl, and sinapyl alcohols. The phenyl propane units in the lignin polymer are related to p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively. The structures of the primary lignin polymers and their related lignin monomer units are shown in Figure2.1 and the structures of lignin precursors are in Figure 2.2.

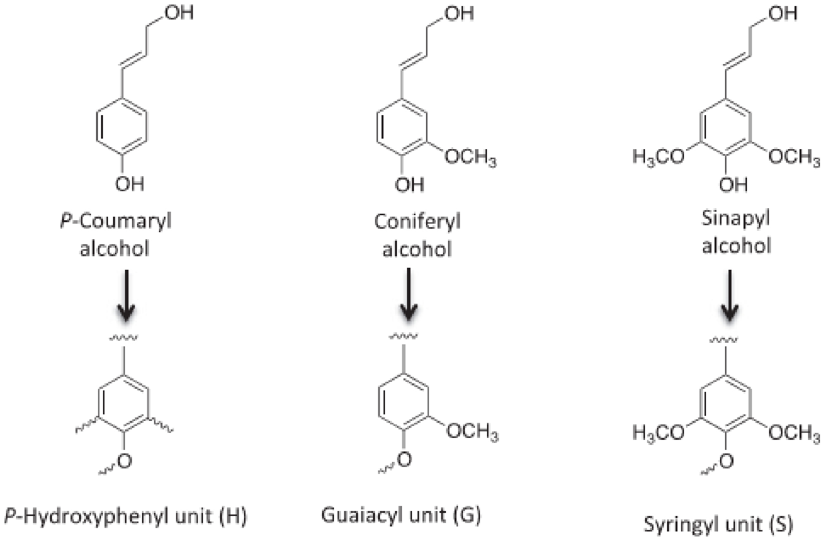


*Figure 2.1 The structure of the primary lignin polymer and their related lignin monomer units (Abdel-Hamid et al., 2013)*

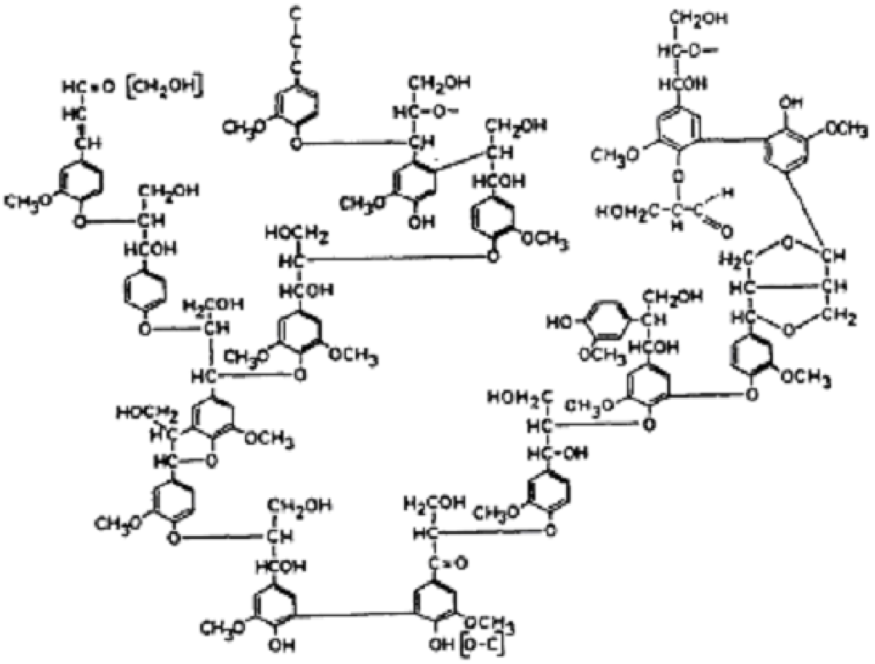


*Figure 2.2 Structure of lignin precursors*

Lignin in nature is characterized into several types based on plant species and plant tissues such as hardwood, softwood, and grasses (Abdel-Hamid et al., 2013). Lignin in hardwood (angiosperm) consists of the binding of the guaiacyl propane unit (G) and the syringyl propane unit (S). The mainly composition of softwood lignin is guaiacyl propane unit (G). Lignin from grasses composes of three monomeric units (G, S, and H) (Fitigau et al., 2013).The molecular structures of softwood lignin are shown in Figure 2.3.

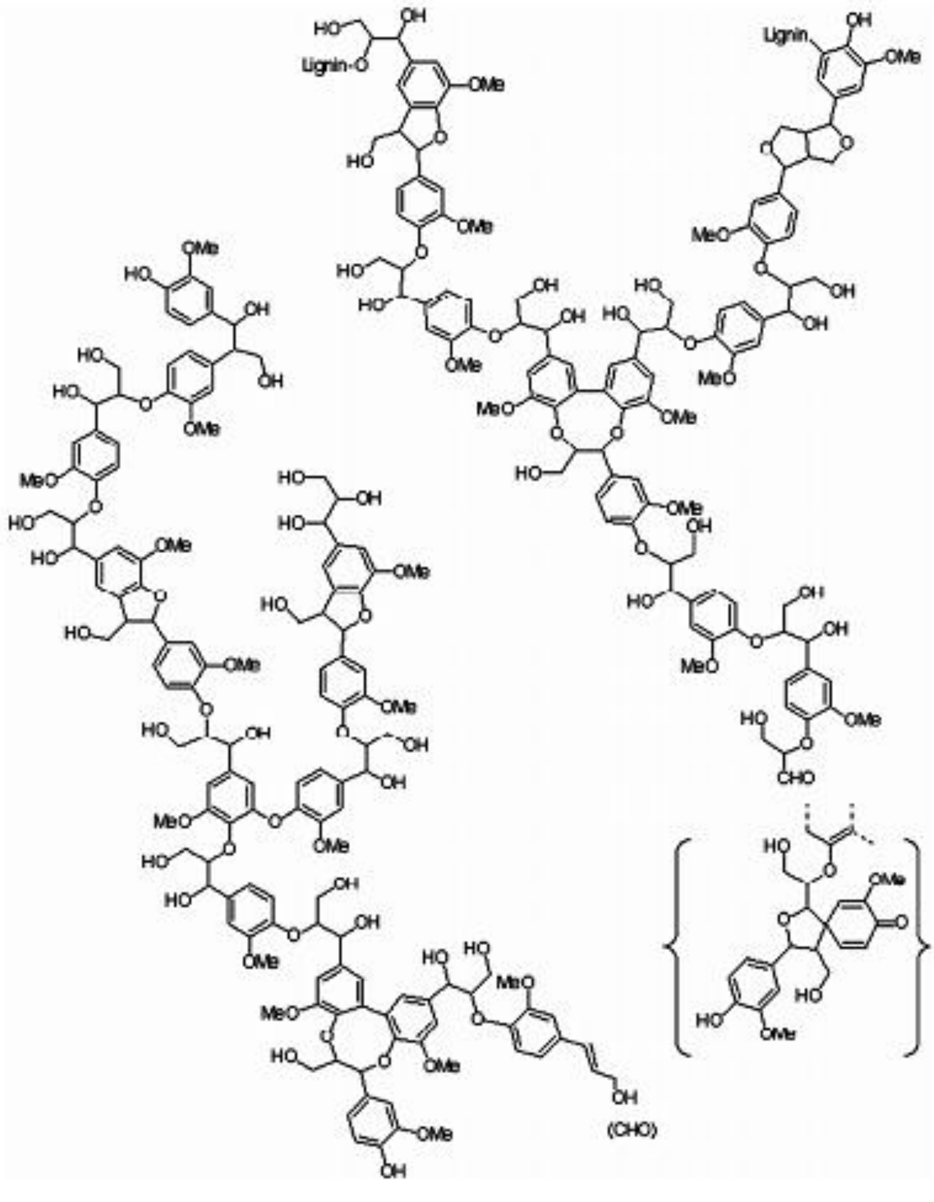


*Figure 2.3 Structure of soft wood lignin*

The main source of lignin in pulping wastewater is the black liquor from the pulping process (Lisperguer et al., 2009). Lignin is separated from fibers and disposed with wastewater as a main compound responsible for color and chemical oxygen demand (COD) in wastewater. Lignin is a problem due to its decomposition to form toxic by-products such as phenols, ketone and carboxylic acids. Lignin decomposition takes long time and has an effect on the ecosystem (Makhotkina et al., 2008).

Acid and base catalyst can de-polymerize lignin. Moreover, oxidation reaction, for example, Fenton's reagent is high effective to de-polymerize lignin. Hydrogen peroxide can be used to degrade and solubilize lignin as well (Xia et al., 2014).

## 2.4 Color

Color of water comes from organics and inorganics both dissolved and non-dissolved solids and may come from human beings or nature. Color from industrial wastewater need to be treated, if its quality does not comply with the standards.

### 2.4.1 Types of colors:

**True color**: Color that can be seen by eyes or can be measured after suspended solids, colloids and turbidity are separated from water

**Apparent color:** Color that can be seen by eyes or can be measured without separation of any suspended solids, colloids and turbidity from water. Therefore, the color that can be measured involves dissolved and non-dissolved solids in water

### 2.4.2 Color Unit

A general unit of color is as Platinum-cobalt unit. A color unit of platinum-cobalt standard is equivalent to platinum solution at the concentration of 1 mg/l in the form of chloroplatinate.

### 2.4.3 Color measurement

There are many kinds of color measurement such as visual eyes, spectrophotometric technique, Tristimulus Filter method and ADMI Tristimulus Filter method.

#### 1.4.3.1 Visual eyes

Compare with the standard color or the color of standard solutions.

1.4.3.2 Spectrophotometric technique

Measure color in the form of light absorption at a specific wavelength. This method can be applied to drinking water, groundwater including municipal and industrial wastewater.

1.4.3.3 ADMI Tristimulus Filter method

The method use Adums-Nickerson equation for color measurement which measure a deviation from colorless.

Color measurement in Platinum Cobalt unit can be performed either comparing water sample with standard color by visual eyes, or UV-visible spectrophotometric method.

## 2.5 Treatment of pulp and paper mill wastewater

Selection of the most effective and the cheapest treatment technique is essential (Ali et al., 2013). Wastewater treatment of pulp and paper mill typically includes:

(1) Primary treatment: Physical treatment is usually the first unit of wastewater treatment processes. High amount of suspended solids (more than 80%) can be removed by a sedimentation tank (Thompson et al., 2001), and applying of activated carbon efficiently to treat Chemical Oxygen Demand (COD) more than 90%.

(2) Secondary treatment: The effluent of paper mill is treated by biological treatment process. There are several processes such as activated sludge, anaerobic process, phosphorus removal and the combination of nitrification-denitrification (Oppenländer, 2002). Biological treatment aims to reduce organic content and destroy toxic organics in wastewater (Tunay et al., 2010). Among these process, the mostly used process is activated sludge process, which is an aerobic process. Activated sludge process can remove about 80% of COD but not efficiently remove toxicity of effluent. An anaerobic process has been suggested as an alternative technique for wastewater

treatment due to low amount of produced sludge and required less nutrient than aerobic process (Ali et al., 2013).

(3) Tertiary treatment: The combination of two or more treatment units (e.g. physico-chemical treatment) is more effective than a single unit such as a combination of coagulation and wet-oxidation achieved 50% of COD remove and 75% of lignin removal (Ali et al., 2013). Ozonation and adsorption are another example of tertiary treatment unit that is widely used (Ali et al., 2013). The tertiary treatment process is needed for further treatment or if there is some more stringent legislation (Thompson et al., 2001).

## 2.6 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) have been widely used in treatment of industrial wastewater because this process produces high potential oxidizing agents for organic removal or pollutant removal at high or low concentrations (Parsons and Williams, 2004; Wan et al., 2011). AOPs have used in groundwater treatment, municipal wastewater treatment, sludge destruction and volatile organic compounds (VOCs) treatment (Parsons and Williams, 2004). Examples of applying AOPs in industries are Chemical Industry, Food and Beverage Industry (Heponiemi and Lassi, 2012), Petrochemical Industry (Gunukula and Tittlebaum, 2001), Textile and Dying Industry (Al-Kdasi et al., 2004) and Pulp and Paper Industry (Covinich et al., 2014).

There are many types of organic compounds such as phenol, hydrocarbon, aliphatic and aromatic hydrocarbon which can be degraded by AOPs (Machulek et al., 2012). AOPs typically use chemical agents such as iron (Fe), ozone ($O_3$), $TiO_2$ as a catalyst usually combined with hydrogen peroxide ($H_2O_2$) or UV. The examples of AOPs are $O_3/H_2O_2$ (Peroxone reaction), $O_3$/UV, $O_3/H_2O_2$/UV, Fe (II)/$H_2O_2$ (Fenton reaction), Fe (III)/$H_2O_2$ (Fenton-like reaction), Fe (II)/$H_2O_2$/UV (photo-Fenton reaction) and $TiO_2$/UV (Catalkaya and Kargi, 2007).

The purpose of AOPs is to produce hydroxyl radical (OH•) in water. Hydroxyl radical is one of very reactive species, having short lived and is a non-selective oxidizing agent (Oppenländer, 2002). Hydroxyl radical is the second rank strong oxidizing agent after fluorine as show in Table 2.1. Hydroxyl radical can oxidize various types of organic compounds or toxic substances in wastewater to simple organic compounds which have less toxic and biodegradable (Chu et al., 2012; Lucking et al., 1998) or to remove color and odor (Araujo, E. et al., 2002). Carbon dioxide ($CO_2$) and water ($H_2O$) may be generated as final products.

*Table 2.1 Oxidation potential of common species. (Karat, 2013; Rodríguez, 2003)*

| Oxidant Species | | Oxidation Potential (Volts) |
|---|---|---|
| Fluorine | $F_2 + 2e^- \rightarrow 2F^-$ | 3.03 |
| Hydroxyl radical | $OH\bullet + H^+ + e^- \rightarrow H_2O$ | 2.80 |
| Atomic Qxygen | $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | 2.42 |
| Ozone | $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ | 2.07 |
| Hydrogen peroxide | $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | 1.78 |
| Perhydroxyl radical | $HO_2\bullet \rightarrow H+ + O_2^-\bullet$ | 1.70 |
| Permanganate | $MnO_4 + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ | 1.68 |
| Hypobromous acid | $OBr^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$ | 1.59 |
| Chlorine dioxide | $ClO_2(g) + e^- \rightarrow ClO_2^-$ | 1.57 |
| Hypochlorous acid | $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ | 1.49 |
| Chlorine | $Cl_2 + 2e^- \rightarrow 2Cl^-$ | 1.36 |

Hydroxyl radical can oxidize organic and inorganic substances by different types of reactions as follows: (Oppenländer, 2002; Torrades et al., 2011)

$OH\bullet + M^n \rightarrow M^{n+1} + (OH^-)_{aq}$ (Electron transfer) …. (1)

$OH\bullet + R\text{-}H \rightarrow R\bullet + H_2O$ (Hydrogen abstraction) …. (2)

$OH\bullet + R_2C{=}CR_2 \rightarrow \bullet CR_2\text{-}C(OH)R_2$ (Electrophilic addition) …. (3)

For AOPs, Fenton reaction has been widely used for wastewater treatment (Benatti and Tavares, 2012).

## 2.7 The Fenton Reaction

The Fenton reaction is the reaction of iron (Fe) and hydrogen peroxide ($H_2O_2$) based on an electron transfer between iron (Fe) ions and hydrogen peroxide ($H_2O_2$) (Lucking et al., 1998). The oxidation process for Fenton process mainly occurs in acidic condition. Iron act as catalyst in the reactions and the reactions generate hydroxyl radical (OH•). The related chemical reactions are defined by (Barbusinski, 2009; Catalkaya and Kargi, 2007) as shown in equations (1)-(6).

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^-$ (chain initiation) $k_1 \approx 70\ M^{-1}\ s^{-1}$…….. (1)
$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^-$ (chain termination) $k_2 = 3.2 \times 10^8\ M^{-1}\ s^{-1}$ …….. (2)
$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet$ $k_3 = 0.001–0.01\ M^{-1}\ s^{-1}$…….(3)
$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^-$ $k_5 = 1.3 \times 10^6\ M^{-1}\ s^{-1}$ at pH = 3…… (4)
$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2$ $k_6 = 1.2 \times 10^6\ M^{-1}\ s^{-1}$ at pH = 3…… (5)
$H_2O_2 + OH\bullet \rightarrow H_2O + HO_2^\bullet$ $k_7 = 3.3 \times 10^7\ M^{-1}\ s^{-1}$ …….. (6)

The overall of Fenton reaction as follow:
$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$

From the series of equations, the presence of $H^+$ is required in the decomposition of $H_2O_2$, indicating the need of an acid environment to produce the maximum amount of hydroxyl radicals (Neyens and Baeyens, 2003). Thus, Fenton's reagent in acid solutions is an efficient source of hydroxyl radicals (Haung and Flaherty, 1992).

In case of very high concentration of ferrous iron ($Fe^{2+}$) condition, the reaction will follow equations (1) and hydroxyl radical can be scavenged reaction with $Fe^{2+}$ (2) (Hunter, 1997). In high concentration of hydrogen peroxide ($H_2O_2$), under acidic condition, the reaction will follow equations (1), (4) and (6) due to the scavenging effect of $H_2O_2$ react with OH•. Therefore, equations (2), (3) and (5) will not occur (Neyens and Baeyens, 2003; Torrades et al., 2011).

Fenton reaction is also combined with biological treatment process either as pre-treatment to change non-biodegradable compounds to biodegradable compounds or high toxic to low toxic compounds, or as post-treatment to improve the efficiency of wastewater treatment (Benatti and Tavares, 2012). The advantages of Fenton process are not required an external energy (such as light), not expensive, easy to operate and high oxidation performance (Chu et al., 2012). However, a disadvantage is the remaining of the iron sludge after treatment process (Lucking et al., 1998).

### 2.7.1 Oxidation of organic compounds by Fenton’s reagent

The reaction between Fenton process and organics in wastewater can proceed as chain mechanism or non-chain mechanism as follows: (Haung and Flaherty, 1992)

| | |
|---|---|
| $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet$ | Chain initiation |
| $R\text{-}H + OH\bullet \rightarrow R\bullet + H_2O$ | Chain propagation |
| $R\bullet + H_2O \rightarrow R\text{-}OH + OH\bullet$ | Chain propagation |
| $Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^-$ | Chain termination |
| $R\bullet + OH\bullet \rightarrow R\text{-}OH$ | Non-chain termination |
| $2R\bullet \rightarrow$ Products | Non-chain termination |

### 2.7.2 Factors that affect the oxidation efficiency of Fenton reaction: (Pérez et al., 2002; Torrades et al., 2011)

1. pH: The reaction between iron (Fe) and hydrogen peroxide ($H_2O_2$) generates hydroxyl radical ($OH\bullet$) in acidic condition at pH range 2-4 (Dantas et al., 2006). Higher pH leads to decompose of hydrogen peroxide ($H_2O_2$), lower oxidation potential of $OH\bullet$, and deactivate catalyst (Chu et al., 2012).

The formation and precipitation of ferric hydroxide ($Fe(OH)_3$) obstructs the Fenton reaction and $H_2O_2$ will break down to $O_2$ and $H_2O$ at higher pH. Lower pH value than optimal level results in formation of Fe(III) different complex species in solution (Torrades et al., 2011).

2. Temperature: When temperature increases, oxidation rate increases. However, hydrogen peroxide ($H_2O_2$) will change to carbon dioxide ($CO_2$) and water ($H_2O$) when temperature is more than 40°C (Karat, 2013).

TOC removal rate increases when temperature increases. The temperature seems to assist alternative ways of $H_2O_2$ cleavage and $OH\bullet$ formation, or Fe(II) recovery (Pérez et al., 2002).

3. Ratio of iron to hydrogen peroxide: Optimum ratio of iron to hydrogen peroxide for wastewater treatment process depending on characteristic of wastewater.

For the treatment of color, TOC, and AOX from pulp mill effluents, Catalkaya and Kargi (2007) suggested the ratio of Fe(II):$H_2O_2$ to be 2.5:50 (1:20). From the study of using Fenton and photo-Fenton for removal of organic contaminants in pulp treatment effluents, it was showed that TOC reached to 60% removal when applied 450 ppm of Fe (II) and 7500 ppm of $H_2O_2$ (ratio of Fe(II): $H_2O_2$ was 1:16) (Pérez et al., 2002). According to above researches above, different types of wastewaters needed different Fe: $H_2O_2$ ratio in Fenton process.

4. Concentration of iron and hydrogen peroxide: The degradation rate of organic compounds in oxidation reaction increases when concentration of iron (Fe) and hydrogen peroxide ($H_2O_2$) increases. If too much hydrogen peroxide concentration, the remaining hydrogen peroxide can act as an OH• scavenger (Catalkaya and Kargi, 2007; Neyens and Baeyens, 2003; Tian, S. H. et al., 2011). Chu et al. (2012) also reported that overdosed of hydrogen peroxide ($H_2O_2$) reacted with the hydroxyl radical (OH•) and inhibited the oxidation reaction. Large excess of hydrogen peroxide ($H_2O_2$) or $Fe^{2+}$ might be detrimental because their can react with OH• (Pérez et al., 2002).

5. Time: Depending on characteristic and concentration of wastewater. After 30 min of treatment, TOC removal in pulp effluents using of Fenton and photo-Fenton reached 60% (Pérez et al., 2002). 94.8% COD removal was observed after 90 minutes of reaction time in the treatment of black liquor by Fenton reaction (Torrades et al., 2011). For the treatment of coking wastewater by iron powder and hydrogen peroxide, COD removal was 44-50 % and total phenol removal was 95% at reaction time of 1 h. (Chu et al., 2012)

## 2.8 Heterogeneous Fenton- like reaction

There are 2 types of Fenton: homogeneous and heterogeneous Fenton reaction. The homogeneous Fenton reaction uses iron and hydrogen peroxide sources in liquid form. While, heterogeneous Fenton reaction uses immobilized iron compounds on different media (e.g. $Fe_2O_3/\gamma\text{-}Al_2O_3$, Activated carbon, zeolite (FeZSM-5)) or use insoluble iron oxides (e.g. goethite ($\alpha$-FeOOH) and magnetite ($Fe_3O_4$)) to simplify iron separation (Araujo, F. V. F. et al., 2011; Nogueira et al., 2014; Wang, W. et al., 2013; Zhou et al., 2009).

Moreover, the Fenton reaction that uses other catalysts instead of ferrous ion ($Fe^{2+}$) in the reaction also called Fenton-like reaction. The reaction can be used either homogeneous or heterogeneous reaction. The catalyst can be ferric ion ($Fe^{3+}$), iron powder, compounds of iron oxide (such as hematite ($Fe_2O_3$)), or iron oxychloride ($FeOCl$) (Yang et al., 2013). These catalysts can react with $H_2O_2$ in the reaction similar to ferrous ion ($Fe^{2+}$).

The Fenton-like reaction is the use of ferric ion ($Fe^{3+}$) as catalyst to react with $H_2O_2$. At the beginning, ferric ion ($Fe^{3+}$) changes to ferrous ion ($Fe^{2+}$) and, then the reaction produces hydroxyl radical ($OH\bullet$) the same as Fenton reaction as follows:

| Homogeneous Fenton-like reaction (Hasan et al., 2012) | Heterogeneous Fenton-like reaction (Bayat et al., 2012) |
|---|---|
| $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet}$ …. (7)<br>$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^-$ …. (8) | $S\text{-}Fe^{3+} + H_2O_2 \rightarrow S\text{-}Fe^{2+} + H^+ + HO_2^{\bullet}$ …. (9)<br>$S\text{-}Fe^{2+} + H_2O_2 \rightarrow S\text{-}Fe^{3+} + OH\bullet + OH^-$ …. (10) |
| $R + OH\bullet \rightarrow R\bullet + H_2O$ …. (11) | |

A heterogeneous Fenton-like process is interesting due to no sludge separation step required compared to homogeneous Fenton process. Thus, heterogeneous Fenton-like process is another alternative for treatment of wastewater (Karthikeyan et al., 2011).

## 2.9 Literature Review

### 2.9.1 Color and lignin removal in pulp mill wastewater

- Catalkaya and Kargi (2007) investigated the efficiency of color, TOC, and AOX removals from pulp mill effluents by different oxidation processes.

For Fenton process, the suitable conditions for COD and TOC removals were 2.5 mM of ferrous concentration, 50 mM of $H_2O_2$ concentration with initial pH 5 and

30 minutes of reaction time. Concentration of Fe(II) higher than 2.5 mM showed the inhibition effect of iron due to percent color removal decrease when Fe(II) concentration increased from 2.5 mM to 10 mM.

Direct UV photolysis alone showed no effective for color and TOC removal. Therefore, it was combined with $H_2O_2$, iron salt ($Fe^{2+}$) and ozone to improve the efficiency.

In the experiment of UV/$H_2O_2$, the results showed suitable pH of 11 and 50 mM $H_2O_2$ concentration with 30 minutes reaction time. Addition of $H_2O_2$ improved the treatment efficiency when compared to UV treatment alone, but high concentration of $H_2O_2$ might act as free-radical scavenger.

For photo-Fenton treatment, the optimum condition were at pH 5, 2.5 mM of $Fe^{2+}$ concentration and 50 mM of $H_2O_2$ concentration with the reaction time of 30 minutes. 85% TOC removal and 82.5% color removal were achieved after 5 minutes of irradiation which was much faster than that of UV/$H_2O_2$ treatment. Therefore, Photo-Fenton treatment improved the removal efficiency of UV/$H_2O_2$.

Another oxidizing agent was ozone. Applying ozone treatment had a major drawback which was high operation cost. The results showed that at pH 7, 91% color removal, 29% TOC removal and 62.4 % AOX removals were achieved at the end of 30 minutes with ozone feeding rate of 4.7 g/h. TOC removal with ozonation was not effective compared to the photo-Fenton treatment.

The treatment by peroxone ($O_3$/$H_2O_2$) showed the results that at pH 11, 5mM dose of $H_2O_2$ was suitable for peroxone treatment at ozone feeding rate of 4.7 g/h.

From the study, the suitable ratio of Fe(II) to $H_2O_2$ was 2.5mM of Fe(II) to 50 mM of $H_2O_2$ (or ratio of 1:20). Either Fenton process or photo-Fenton process was effective for removal of color, TOC or AOX from pulp mill wastewater.

- Makhotkina et al. (2008) investigated the use of $H_2O_2$/ UV photolysis, homogeneous, heterogeneous Fenton, and UV-assisted heterogeneous Fenton reactions for delignification in water. Initial lignin concentration was varied in the range of 50-650 mg/l and $H_2O_2$ concentration was varied in the range of 0.25-3 M. FeZSM-5 zeolite was 16 g/l in heterogeneous Fenton. $Fe(NO_3)_3$ was 5mM in homogeneous Fenton system and pH 4. For photo-assisted oxidation, UV lamp at 254 nm was used.

The results of $H_2O_2$/UV system showed that lignin mineralization about 80% at initial lignin concentration of 340 mg/l, 0.25 M of $H_2O_2$ concentration and pH of 4 in 5 hours of reaction time.

Lignin adsorption on the FeZSM-5 zeolite depended on pH. Lignin adsorption on zeolite surface was not observed in alkaline solution due to the negative charge of both FeZSM-5 zeolite surface and lignin-$OH^-$.

According to the results of homogeneous and heterogeneous Fenton, lignin oxidation proceed slower and lower mineralization in heterogeneous system than in homogeneous system.

At initial $H_2O_2$ concentration of 1 M and lignin concentration of 340 mg/l with 16 g/l of zeolite, lignin mineralization was 25% at pH of 3-4. Oxidation rate decreased at slightly alkaline condition (pH 8), and at pH 10 lignin oxidation was not observed.

According to the results of UV-assisted heterogeneous Fenton system, the oxidation rate of FeZSM-5/$H_2O_2$/UV depended on pH. The lignin oxidation efficiency at pH 3 of FeZSM-5/$H_2O_2$/UV was higher than that of FeZSM-5/$H_2O_2$ and $H_2O_2$/UV.

From the results, lignin oxidation were more effective in homogeneous Fenton and $H_2O_2$/UV. However, UV-assisted heterogeneous Fenton system showed the performance close to $H_2O_2$/UV.

- Ramos et al. (2009) investigated the degradation of lignin and its derivatives in residual water of paper industry by combining chemical precipitation and ozonation. Initial COD concentration of 70,000 mg/l was diluted 10 times for experiment. Lignin in diluted sample was pre-treated by precipitation with concentrated sulfuric acid at the initial pH 1 and 3. Color decreased 96% from initial color and 77% COD was removed in precipitation step.

The samples precipitate at pH 1 were ozonated at pH 1, 8 and 12. The samples precipitate at pH 3 were ozonated at pH 3, 8 and 12. Initial ozone concentration was 30 mg/l and reaction time was 60 minutes. Lignin decomposition in ozonation at different pH of ozonation was the same after end of 60 minutes of ozonation time. Moreover, ozonation increased the biodegradability of residual water and achieved more than 50% of lignin decolorization.

### 2.9.2 Fenton Process

- Pérez et al. (2002) studied the use of Fenton and photo-Fenton for removal of organic contaminants in pulp treatment effluents at pH 2.8. The concentration of Fe(II) was in the range of 0-800 mg/l and the concentration of $H_2O_2$ was in the range of 0-10,000 mg/l.

The results showed that TOC reached 60% removal when applied 450 ppm of Fe (II) and 7500 ppm of $H_2O_2$ (ratio of Fe(II): $H_2O_2$ was 1:16) after 30 min of irradiation. Color removal at the end of the experiment was more than 90%. Fenton reaction occurred firstly in a few seconds then photo-Fenton would occur after several minute passed.

- Araujo, E. et al. (2002) investigated the effect of Fenton’s reagent on the degradation of residual Kraft black liquor. $FeCl_2$ at the concentration of 1 mM, $H_2O_2$ at 60 mM, pH at 5.5 were used with 20 minutes reaction time at room temperature. $H_2O_2$ caused the fragmentation of lignin molecule. The reaction in the presence of iron ions (with Fenton’ reagent) could induced an initial fragmentation of lignin molecule faster than $H_2O_2$ alone and could rapidly degrade lignin completely in the black liquor. From the results, Fenton’s reaction could efficiently treat black liquor under acidic condition.

- Torrades et al. (2011) investigated the treatment of black liquor by Fenton reaction using central composite experimental statistical design. The initial concentration of COD was 628 mg/l as $O_2$. Four parameters were considered, i.e. pH, temperature, $H_2O_2$ and Fe (II) concentrations. The experiment was at the initial pH of 3 and room temperature (298 K).

The equation of the factorial design showed that the most important parameters for removal of COD, $UV_{254}$ (aromatics content) and $UV_{280}$ (lignin content) were $H_2O_2$ and Fe (II) concentration. The optimum conditions for removal of COD, $UV_{254}$ and $UV_{280}$ were 4.655mM Fe (II) and 44.1mM $H_2O_2$ at pH 3, 298 K. The ratio of Fe (II): $H_2O_2$ was 1:9.5. 94.8% of COD removal, 80.9% of $UV_{254}$ reduction and 85.6% of $UV_{280}$ reduction were observed after 90 minutes of reaction time.

### 2.9.3 Heterogeneous Fenton-like reaction

- Chu et al. (2012) investigated the use of iron powder and hydrogen peroxide to treat coking wastewater. The experiment was run at the initial pH less than 6.5, 3.0 g/l of iron powder and 0.3 M of hydrogen peroxide. The ratio of iron to hydrogen peroxide was 1:6.

COD removal was 44-50 % and total phenol removal was 95% at reaction time of 1 hour. After reaction time of 1 hour, Specific Oxygen Uptake Rate of the wastewater increased to 64.9%, meaning that it could be treated by biological degradation.

- Wan et al. (2011) studied the use of $Fe_2O_3/\gamma$-$Al_2O_3$ as a catalyst in heterogeneous Fenton reaction for phenol degradation. The initial phenol concentration was 250 mg/l at pH 3. The catalysts were prepared by impregnation method and used $Fe(NO_3)_3$ as precursors and $\gamma$-$Al_2O_3$ as a carrier. From the result showed that small size $Fe_2O_3$ crystal can be achieved on $\gamma$-$Al_2O_3$. The use of 0.1 mol/L $Fe(NO_3)_3$ concentration, 4 ml. of $H_2O_2$ in $Fe_2O_3/\gamma$-$Al_2O_3/H_2O_2$ process could reach 91.1% of phenol removal after 2 hours treatment. The use of 0.05 mol/L $Fe(NO_3)_3$ concentration, 4 ml. of $H_2O_2$ in $Fe_2O_3/\gamma$-$Al_2O_3/H_2O_2$/UV process could reach 94.7% after 2 hours treatment. Catalyst dose of 0.4 g $Fe_2O_3/\gamma$-$Al_2O_3$ was suitable to form Fenton reaction. Higher dose of catalyst showed similar results of phenol removal.

- Tian, S. H. et al. (2011) studied the using of $Fe_2(MoO_4)_3$ as a heterogeneous Fenton-like catalyst to degrade Acid Orange II at neutral pH. The initial concentration of Acid Orange II (AOII) was 100 mg/l at pH 6.7. The result showed that AOII removal reached 94.1% in 1 hour of the treatment with $Fe_2(MoO_4)_3$ of 0.8-1.6 g/l and 6-18mM of $H_2O_2$ concentration. The suitable ratio of Fe: $H_2O_2$ is 1.4g/l of $Fe_2(MoO_4)_3$: 18 mM $H_2O_2$ (or 1:7.6). The catalytic activity is slightly affected by pH at the range of 3.0-9.0. This showed that $Fe_2(MoO_4)_3$ could be applied at neutral and alkaline conditions. $Fe_2(MoO_4)_3$ showed low iron leaching and good structural stability. After five times reused, it still could maintain its performance.

According to several works, wastewater from pulp and paper industry contains mostly lignin. Lignin cause color in wastewater and as a precursors of toxic by-products that have to be treated before discharge to the environment. Homogeneous Fenton and heterogeneous Fenton-like reaction were applied to treat wastewater from many industries. With high efficiency of treatment. From several researches showed the advantages of heterogeneous Fenton-like reaction due to low amount of sludge and can be applied in wide range of pH (e.g. iron molybdate). However, the use of heterogeneous Fenton-like reaction have not widely applied in treatment of pulping wastewater. Therefore, this research studied on the applying of heterogeneous Fenton-like reaction for treatment of pulping wastewater using of iron molybdate as heterogeneous Fenton-like catalyst.

# CHAPTER 3

# METHODOLOGY

This research applied homogeneous Fenton and heterogeneous-Fenton-like processes to treat color and lignin in pulping wastewater. The experiment used synthetic wastewater to find the optimum conditions for color and lignin removal. Then, the optimum condition from synthetic wastewater was used to treat real pulping wastewater.

## 3.1 Chemicals and equipments

Chemicals:

1. Ferrous Sulfate heptahydrate ($FeSO_4.7H_2O$)
2. Hydrogen peroxide ($H_2O_2$) 30%
3. Sodium hydroxide ($NaOH$)
4. Lignin Alkaline
5. Sulfuric acid ($H_2SO_4$)
6. Manganese dioxide ($MnO_2$)
7. Silver sulfate ($AgSO_4$)
8. Mercury (II) sulfate ($HgSO_4$)
9. 1, 10-Phenanthroline Monohydrate ($C_{12}H_8N_2.H_2O$)
10. Ferrous Ammonium Sulfate (FAS) ($Fe (NH_4)_2(SO_4)_2.6H_2O$)
11. Ferroin Indicator
12. Potassium Dichromate ($K_2Cr_2O_7$)
13. Hydrochloric ($HCl$)
14. Hydroxylamine ($NH_2OH.HCl$)
15. Ammonium Acetate ($NH_4C_2H_3O_2$)
16. Glacial Acetic acid ($CH_3COOH$)
17. Potassium Permanganate ($KMnO_4$)
18. Ammonium Molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$
19. Ammonium Hydroxide ($NH_4OH$)

20. Iron Nitrate ($Fe(NO_3)_3$)
21. Potassium Chloroplatinate ($K_2PtCl_6$)
22. Crystalline cobaltous chloride ($CoCl_2.6H_2O$)

Equipments:

1. Magnetic stirrer
2. pH meter
3. Stopwatch
4. Spectrophotometer
5. Hot air oven
6. Volumetric Flask 1000 ml.
7. Test tube 20 x 150 mm.
8. Micro pipet
9. Centrifuge
10. Centrifuge tube

## 3.2 Experimental procedure

This experiment conducted at Department of Environmental Engineering, Faculty of Engineering Chulalongkorn University. The experiment was able to be separated into 4 parts:

### 3.2.1. Part 1. Experimental Preparation

Real wastewater was analyzed its characteristic as described in 3.2.1.1. Synthetic pulping wastewater was generated by mixing lignin with tap water to use for the experiment. Catalyst for heterogeneous Fenton-like reaction is iron molybdate. Iron molybdate was synthesized by using of chemicals and methods as described in 3.2.1.2 and analyzed to find its characteristic as describe in 3.2.1.3. The analytical method of this research show in Table 3.1

*Table 3.1 Analytical method*

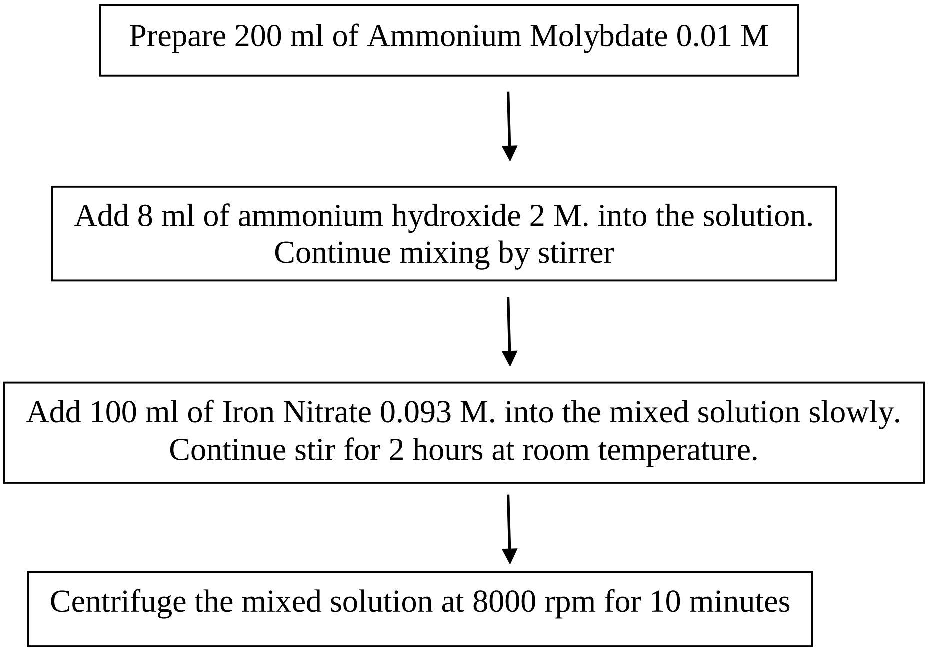
| Parameter | Analytical method |
|---|---|
| **pH** | pH meter |
| **Color** | Platinum-cobalt standard method |
| **Lignin concentration** | Spectrophotometer at 280 nm |
| **COD** | Closed reflux titrimetric method |

#### 3.2.1.1 Wastewater analysis

Wastewater from pulping process was analyzed for COD and pH. Wastewater was filtered through 0.45 µm of filter paper. Then the filtrated wastewater was analyzed for lignin content at 280 nm with spectrophotometer. Synthetic pulping wastewater was synthesized at lignin concentration from pulping wastewater. Lignin standard curve was prepared at lignin concentration 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/l. Lignin concentration (X-axis) and absorbance at 280 nm (Y-axis) were plotted. Absorbance of wastewater at 280 nm was converted to concentration of lignin by this standard curve (see in Appendix A2).

#### 3.2.1.2 Iron Molybdate ($Fe_2(MoO_4)_3$) synthesis

Iron molybdate ($Fe_2(MoO_4)_3$) was prepared followed Tian, S. H. et al. (2011)



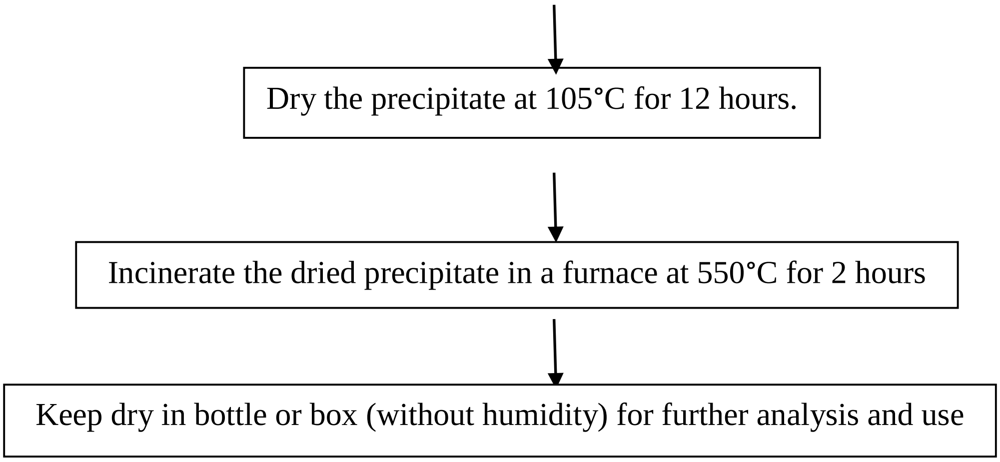


*Figure 3.1 Diagram for Iron Molybdate synthesis*

Iron molybdate was selected size by using sieve size mesh NO.20, aperture 850 nm for the same size of catalyst before used in the experiment.

### 3.2.1.3 Iron Molybdate analysis

Iron Molybdate was analyzed crystal lattice, particle size distribution, surface characteristics and quantity of component, and surface analysis and porosity analyzer (BET)

(1.) Crystal lattice analysis was measured by X-ray diffractometer (XRD) at the Science and Technology Service Center, Chulalongkorn University.

(2.) Particle size distribution, surface characteristics and quantity of component were analyzed by Scanning Electron Microscope with EDS (SEM-EDS) at the Science and Technology Service Center, Chulalongkorn University.

(3.) Surface analysis and Porosity Analyzer (BET) was analyzed by Surface Area Analyzer operated at Department of Chemical Technology, Faculty of Science, Chulalongkorn University.

### 3.2.2. Part 2. Control experiment

The experiment in this part studied the effect of pH change, iron alone and hydrogen peroxide alone for color and lignin removal of synthetic pulping wastewater.

#### 3.2.2.1 Control experiment for pH

This experiment aims to find the effect of pH variation for color and lignin removal. The experimental procedure was given in Figure 3.2.

The first control experiment was fixed pH at 2 by adding sulfuric acid to adjust pH to 2.

The second control experiment was fixed pH at 7 by adding sulfuric acid to adjust pH to 7.

The third control experiment was fixed pH at 9 by adding sodium hydroxide to adjust pH to 9.

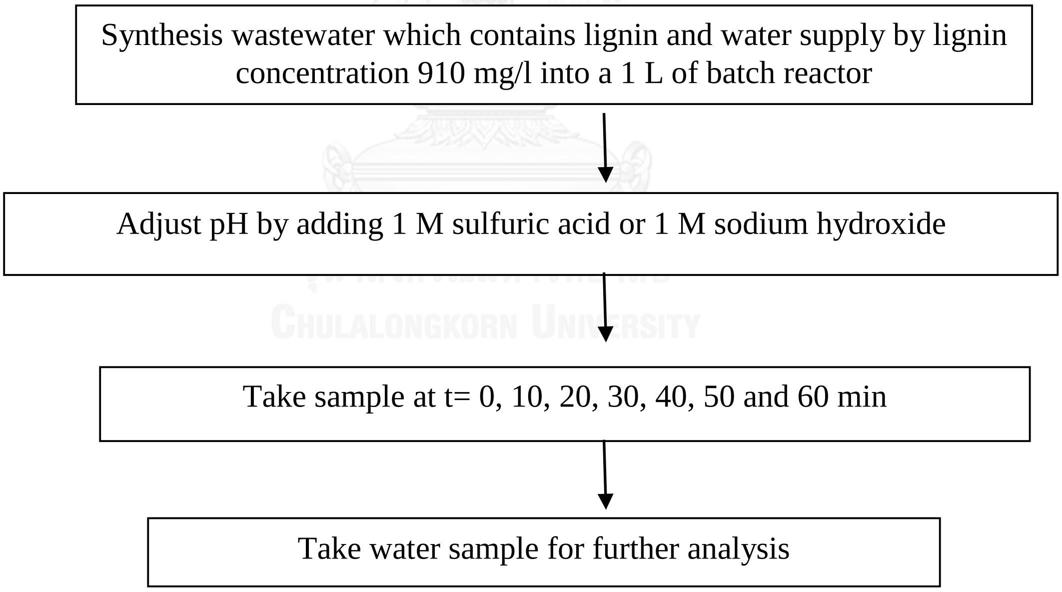


*Figure 3.2 Diagram of control experiment for pH*

#### 3.2.2.2 Control experiment for iron coagulation

This experiment aims to find the effect of iron alone on chemical reaction and coagulation for color and lignin removal. The experimental procedure was given in

Figure 3.3. Synthetic wastewater was added ferrous sulfate heptahydrate at concentration of ferrous ion 400 mg/l.

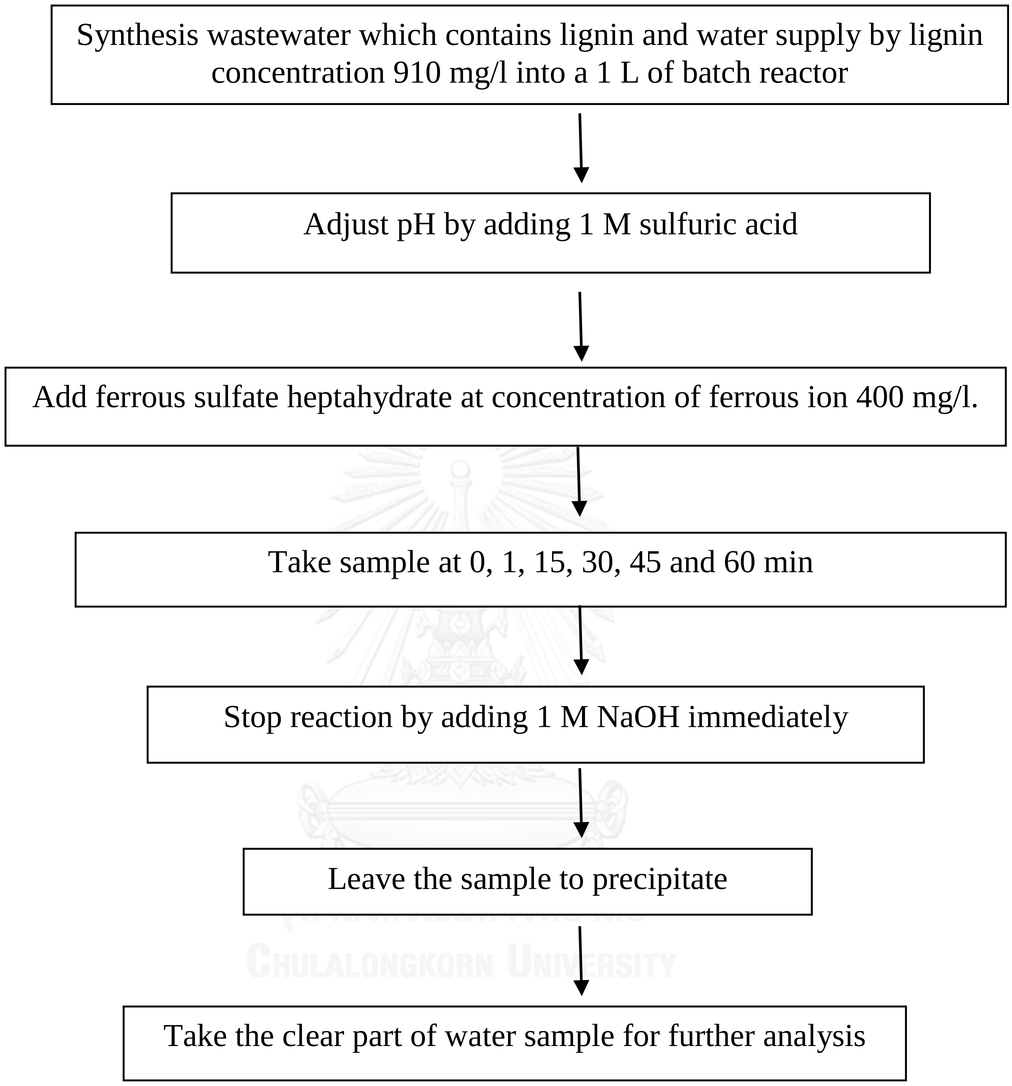


*Figure 3.3 Diagram of control experiment for iron*

3.2.2.3 Control experiment for hydrogen peroxide

This experiment aims to find the effect of direct oxidation by hydrogen peroxide. The experimental procedure was given in Figure 3.4.

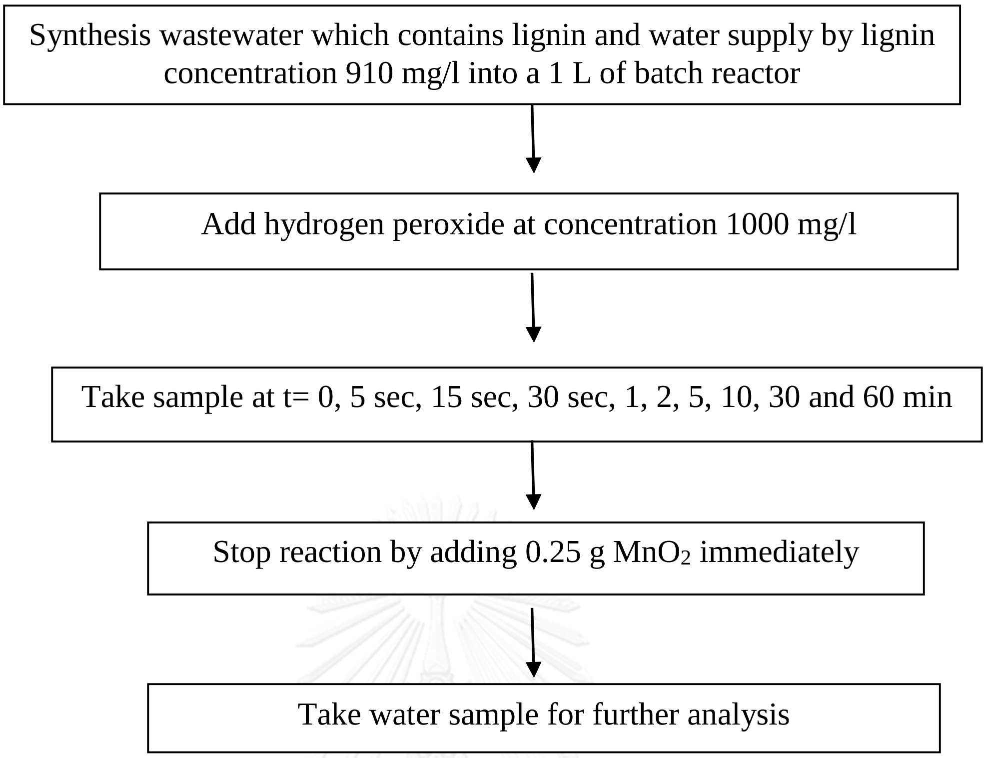


*Figure 3.4 Diagram of control experiment for hydrogen peroxide*

3.2.3. Part 3. De-colorization and lignin removal of synthetic pulping wastewater in a batch reactor with homogeneous Fenton and heterogeneous Fenton-like reaction.

pH, ratio and concentration of iron were varied to find the optimum conditions for color and lignin removal of synthetic pulping wastewater in a batch reactor. Moreover, iron molybdate was found the number of times for reuse in heterogeneous Fenton-like process.

3.2.3.1 Homogeneous Fenton reaction.

This experiment aims to find optimum conditions for treating synthetic pulping wastewater by homogeneous Fenton reaction.

The first, pH was fixed at 3 and ferrous ion dosage at 400 mg/l, then ferrous ion to hydrogen peroxide ratio was varied at 1:0.6, 1:1, 1:2.5, 1:5, 1:10, 1:15 and 1:20 by mass, respectively.

The second, ferrous ion dosage at 400 mg/l and optimum ratio of ferrous ion to hydrogen peroxide which obtain from previous experiment were fixed, pH was varied at 2, 3 and 4 respectively.

The third, pH and ratio of ferrous ion to hydrogen peroxide were fixed under optimum condition from previous experiment. Ferrous ion dosage was varied at 300, 400 and 500 mg/l respectively.

Reaction of all experiment was stopped by adding NaOH to neutralization and adding $MnO_2$ to stop $H_2O_2$ (Catalkaya et al., 2006).

In all operating condition, the experiment was run as shown in Figure 3.5.

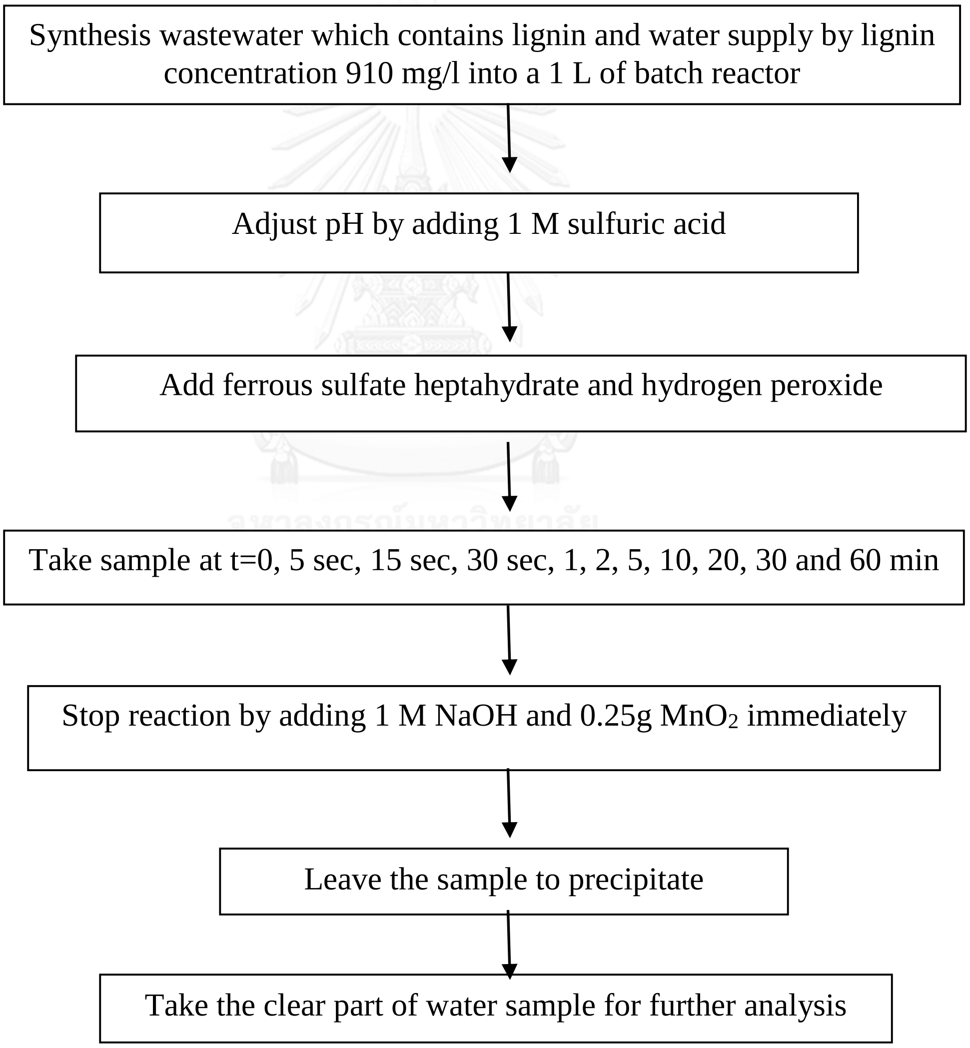


*Figure 3.5 Diagram for find the optimum condition of homogeneous Fenton process*

3.2.3.2 Heterogeneous Fenton-like reaction.

This experiment aims to find optimum conditions for treating synthetic pulping wastewater by heterogeneous Fenton-like reaction.

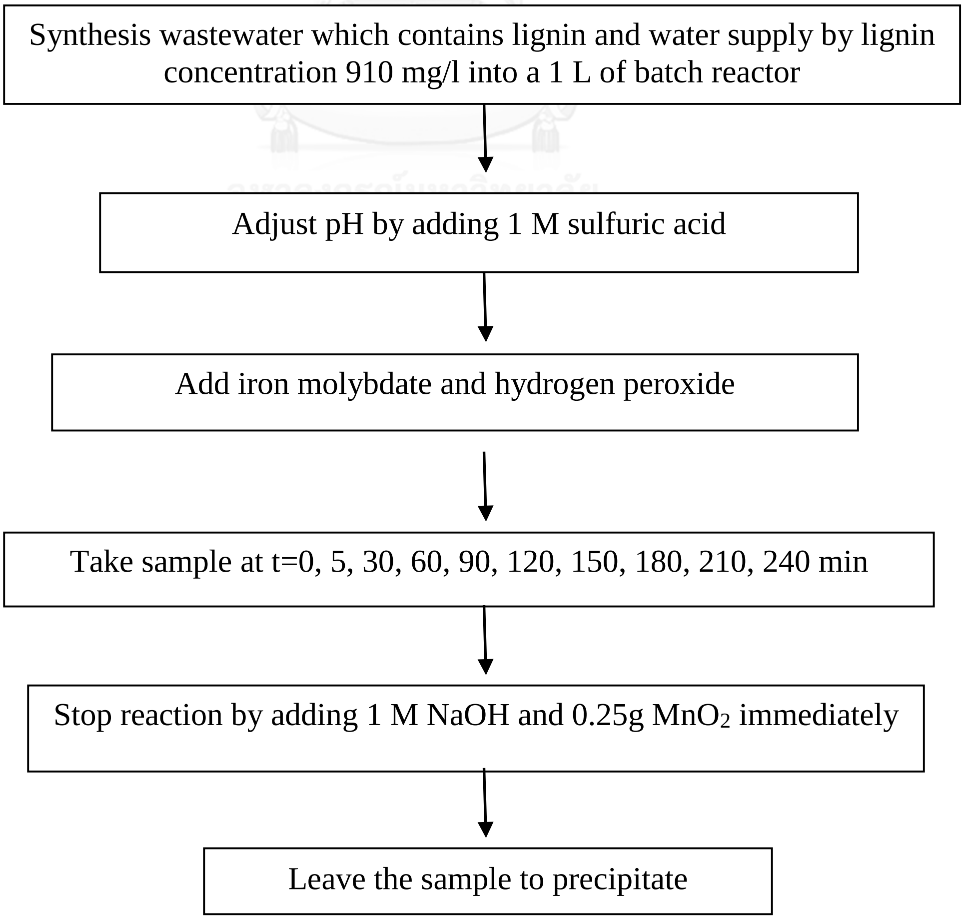
The first, pH was fixed at 8 and ferric ion dosage at 2 g/l, then ferric ion to hydrogen peroxide ratio was varied at 1:2.5, 1:5, 1:10, 1:15 and 1:20 by mass, respectively.

The second, ferric ion dosage at 2 g/l and optimum ratio of ferric ion to hydrogen peroxide which obtain from previous experiment were fixed, pH was varied at 4, 6 and 8 respectively.

The third, pH and ratio of ferric ion to hydrogen peroxide were fixed under optimum condition from previous experiment. Ferric ion dosage was varied at 0.5, 1, 2, 2.5 and 3 g/l respectively.

Reaction of all experiment was stopped by adding NaOH to neutralization and adding $MnO_2$ to stop $H_2O_2$ (Catalkaya and Kargi, 2007).

In all operating condition, the experiment was run as shown in Figure 3.6.



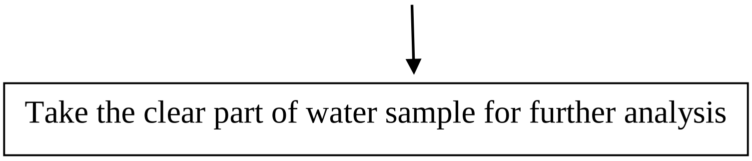


*Figure 3.6 Diagram for find the optimum condition of heterogeneous Fenton-like process*

3.2.3.2.1 Recovery iron molybdate

This experiment aims to determine the number of recycling times of iron molybdate.

After end of reaction time, iron molybdate was separated from previous synthetic wastewater and reused in the next experiment.

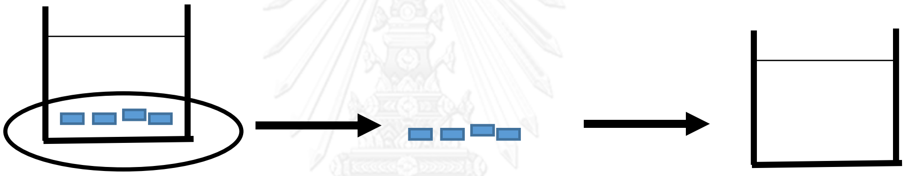


*Figure 3.7 Reuse of iron molybdate*

3.2.4. Part 4. De-colorization and lignin removal of real pulping wastewater in a batch reactor with homogeneous Fenton and heterogeneous Fenton-like reaction.

The experiment used optimum condition from part 3.2.3 for treatment of real pulping wastewater. The experiment could separate into 2 parts as follows:

3.2.4.1 Homogeneous Fenton reaction

This experiment aims to study the performance of homogeneous Fenton reaction using optimum condition from part 3.2.3.1 for color and lignin removal of real pulping wastewater.

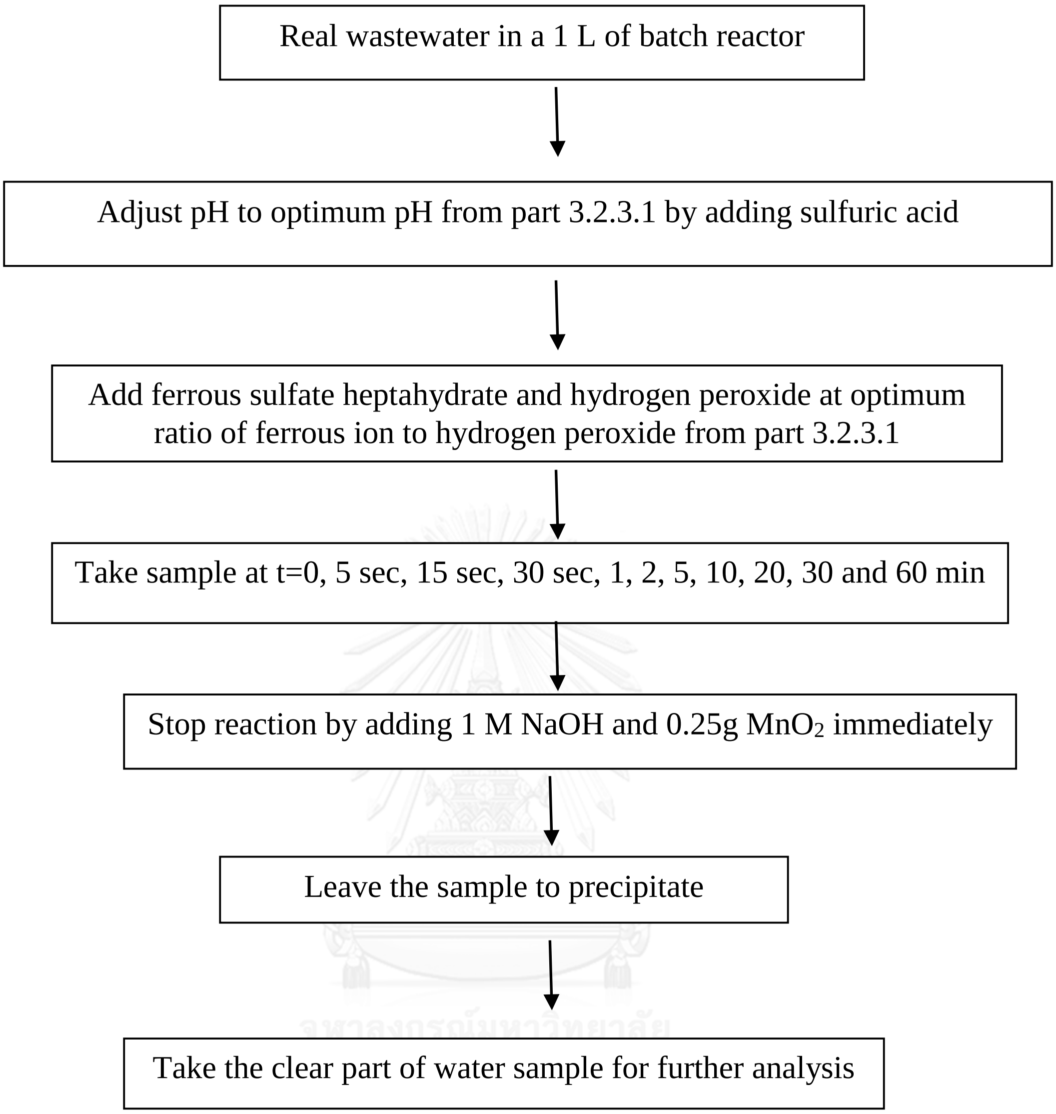


*Figure 3.8 Diagram for treatment of wastewater by homogeneous Fenton process*

### 3.2.4.2 Heterogeneous Fenton-like reaction

This experiment aims to study the performance of heterogeneous Fenton-like reaction using optimum condition from part 3.2.3.2 for color and lignin removal of real pulping wastewater.

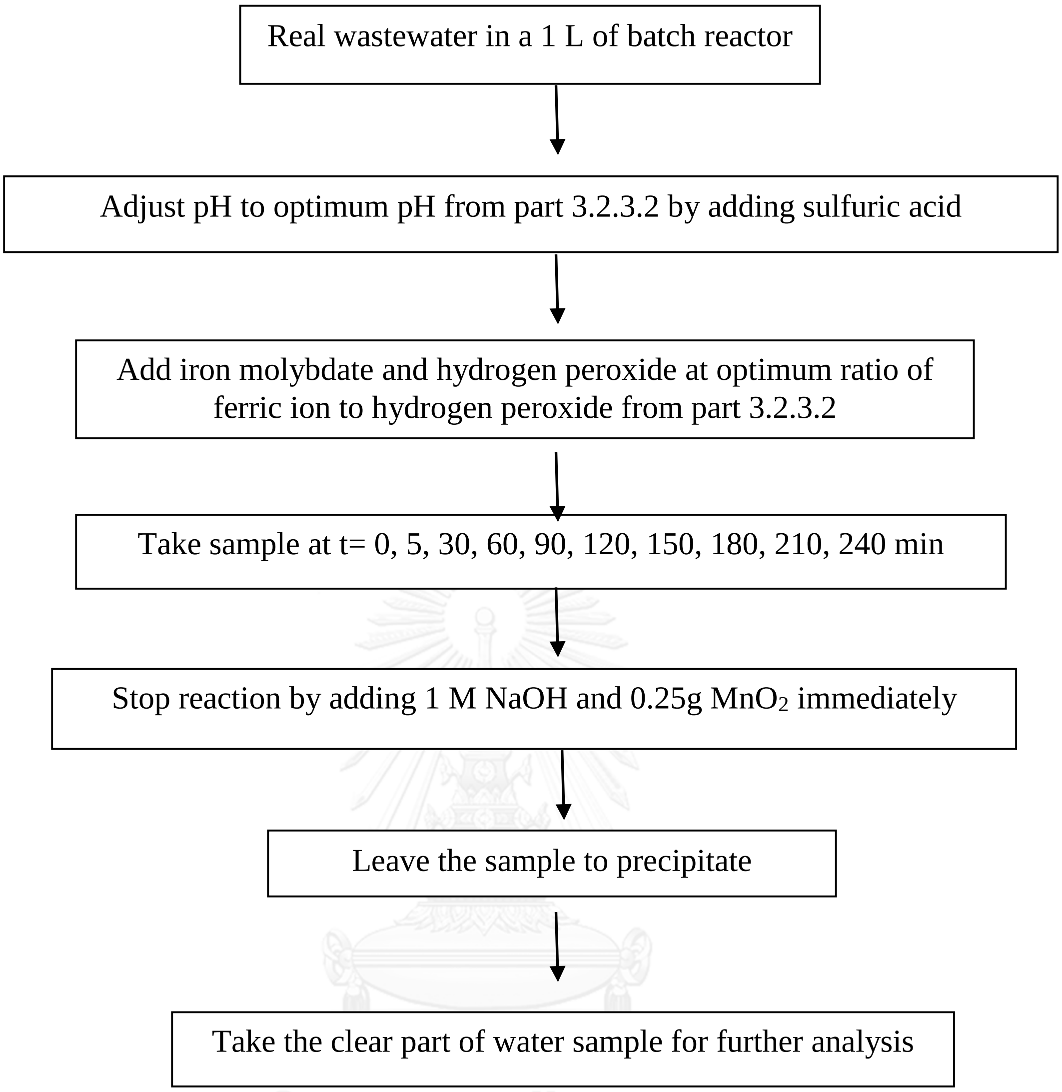


*Figure 3.9 Diagram for treatment of wastewater by heterogeneous Fenton-like process*

# CHAPTER 4

# RESULTS AND DISCUSSIONS

This research studied on removal of phenolic compound in pulping wastewater by heterogeneous Fenton-like process using iron molybdate by compare the results of using iron molybdate in heterogeneous Fenton-like process with using of ferrous in Fenton process. Moreover, study the recovery of iron molybdate catalyst after the first time used to determine the number of recycling times of iron molybdate. Iron molybdate was synthesized and found its characteristics before used by SEM-EDS, XRD and BET.

## 4.1 Wastewater analysis

This research used synthetic wastewater containing lignin and water supply. Lignin concentration was characterized from pulping wastewater. The concentration of lignin was about 0.91 g/l. Synthetic wastewater was used to find the optimum condition for lignin and color removal by Fenton and heterogeneous Fenton-like processes. The optimum condition obtained from synthetic wastewater was used for treating pulping wastewater.

*Table 4.1 Characteristic of synthetic pulping wastewater*

| **Characteristic** | **Value** |
|---|---|
| pH | 8.3 ± 0.2 |
| COD | 1200 mg/l $O_2$ |
| Lignin | 910 mg/l |
| Color | 3000 Pt-co unit |

## 4.2 Iron molybdate analysis

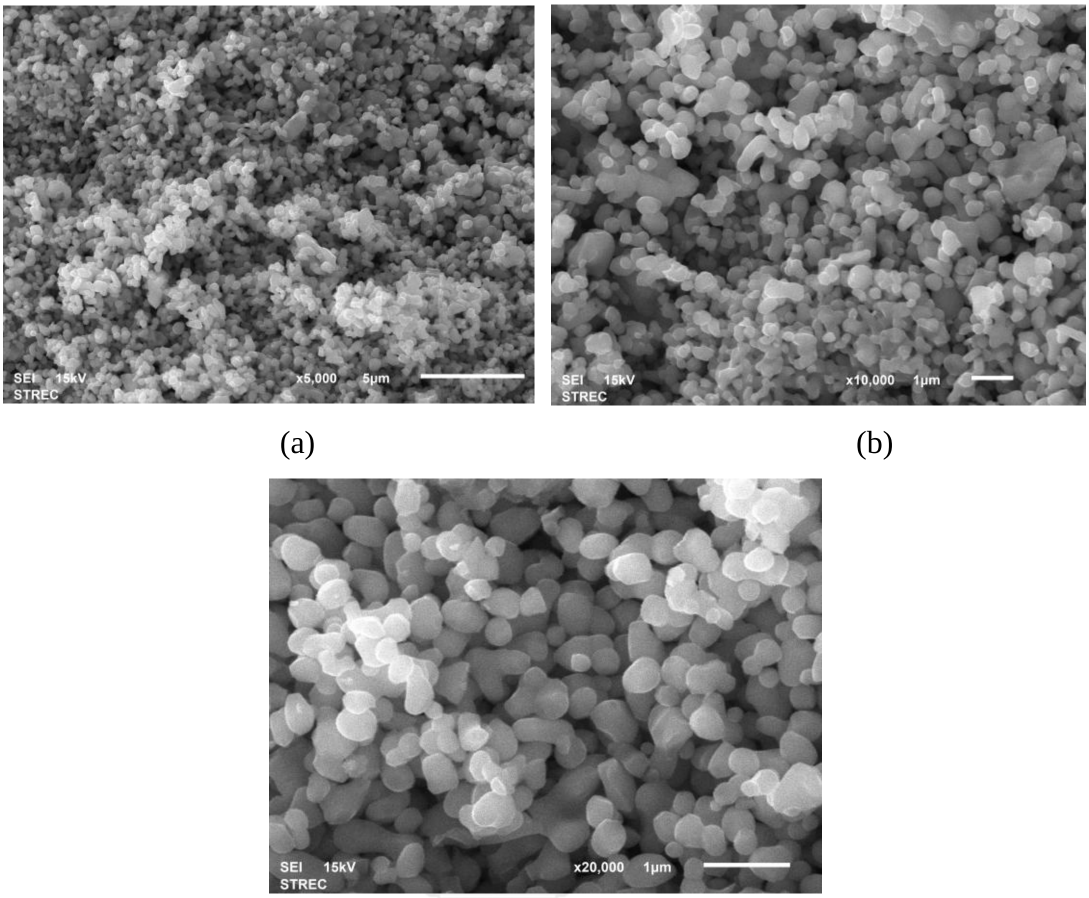
From iron molybdate synthesis followed the method of Tian, S. H. et al. (2011), the iron molybdate was appeared in yellow-green color as show in Figure 4.1.

Synthesized iron molybdate was characterized by SEM-EDS, XRD and BET at the Science and Technology Service Center, Chulalongkorn University and at Department of Chemical Technology, Faculty of Science, Chulalongkorn University. The results of analysis as follows:

*Figure 4.1 synthesized iron molybdate*

### 4.2.1 Particle size distribution, surface characteristics and quantity of component analyzed by Scanning Electron Microscope (SEM)

The morphology analysis of iron molybdate by Scanning Electron Microscope with EDS (SEM-EDS) brand JEOL Model JSM-6610 LV and Inca X-max 50 show in Figure 4.2 at magnifying power 5000x, 10,000x and 20,000x found that the catalyst consist of spherical particles which was agreed with Peng et al. (2008). Diameter of iron molybdate was about 500 nm.



(a) (b)

(c)

*Figure 4.2 Photo of iron molybdate by using SEM at magnifying power (a) 5000x, (b) 10,000x and (c) 20,000x.*

### 4.2.2 Quantity of component analyzed by Energy Dispersive Spectroscopy (EDS)

Figure 4.3 show the result of component analysis of iron molybdate by Energy Dispersive Spectroscopy (EDS) and Table 4.2 show % of each component in iron molybdate. The spectrum was agreed with Zhang et al. (2010). The main peak were iron (Fe), molybdenum (Mo) and oxygen (O). The atomic ratio of Mo/Fe component from Table 4.2 was about 1.7 which was favorable catalyst (Routray et al., 2010). The Fe: Mo: O weight ratio of stoichiometric iron molybdate (Table 4.2) was 1: 2.57: 1.72. The Fe: Mo: O weight ratio from the result of component analysis by EDS (Table 4.2) was 1: 2.97: 1.94 show the value closed to the stoichiometric of $Fe_2(MoO_4)_3$.

*Table 4.2 Quantity of component of iron molybdate*

| **Element** | **Weight%** | **Atomic%** | **Weight % from stoichiometric $Fe_2(MoO_4)_3$** |
|---|---|---|---|
| O | 32.84 | 71.29 | 32.47 |
| Fe | 16.88 | 10.50 | 18.87 |
| Mo | 50.28 | 18.20 | 48.66 |
| Totals | 100.00 | | 100.00 |

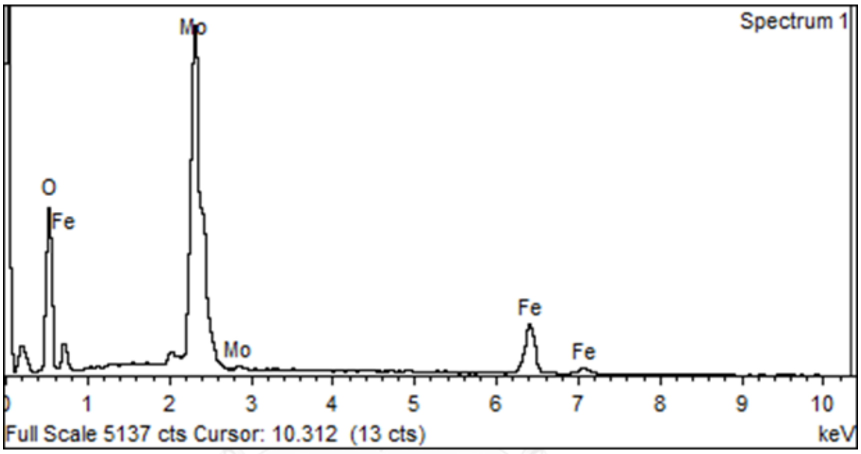


*Figure 4.3 Spectrum EDS of iron molybdate*

### 4.2.3 Crystal lattice analysis measured by X-ray diffractometer (XRD)

XRD pattern of the iron molybdate catalyst was obtained by using X-ray diffractometer (XRD) brand Bruker AXS Model D8 Discover with a Cu-Kα radiation at wavelength of 1.5406 Å, 40 kV and 40 mA in the angle range of 5°-70° as show in Figure 4.4. The main XRD peaks of iron molybdate were appear at 2θ of 19.4°, 20.4°, 21.7°, 22.9°, 23.6°, 24.9°, 25.7°, 27.5°, 27.8°, 30.2° and 34.1° corresponded to the crystal planes (2 0 0), (0 1 2), (1 1 2), (1 2 0), ($\bar{2}$ 1 4), (1 1 4), (2 2 0), (2 1 2), (1 2 2), ($\bar{1}$ 0 5), ($\bar{2}$ 2 4), ($\bar{5}$ 0 3), (2 2 2), (0 2 4), (0 3 2), ($\bar{1}$ 1 6), ($\bar{5}$ 2 5), ($\bar{6}$ 1 6), (5 1 1), (1 0 6), (4 0 3) and (0 3 5) (Tian, S. et al., 2013). The result was in accordance with the JCPDS file no. 35-0183 (Tian, S. H. et al., 2011). They are attributed to monoclinic with the parameters a=15.65 Å, b=9.2 Å, c=18.2 Å, α=90.0°, β=125.6° and γ=90.0° (Hicham, 2015). Moreover, this synthesized catalyst appear some of molybdenum oxide ($MoO_3$)

in their structure with was in accordance with the result from EDS file. The Mo/Fe ratio was 1.7 which this catalyst was $Fe_2(MoO_4)_3$ with excess Mo. $MoO_3$ promote the selectivity of catalyst and $Fe_2(MoO_4)_3$ promote the activity of catalyst (Hummadi et al., 2009). Thus, the presence of excess $MoO_3$ in $Fe_2(MoO_4)_3$ is the favorable catalyst (Routray et al., 2010). The catalyst which presence of $MoO_3$ in $Fe_2(MoO_4)_3$ is active and selective catalyst (Söderhjelm et al., 2008).

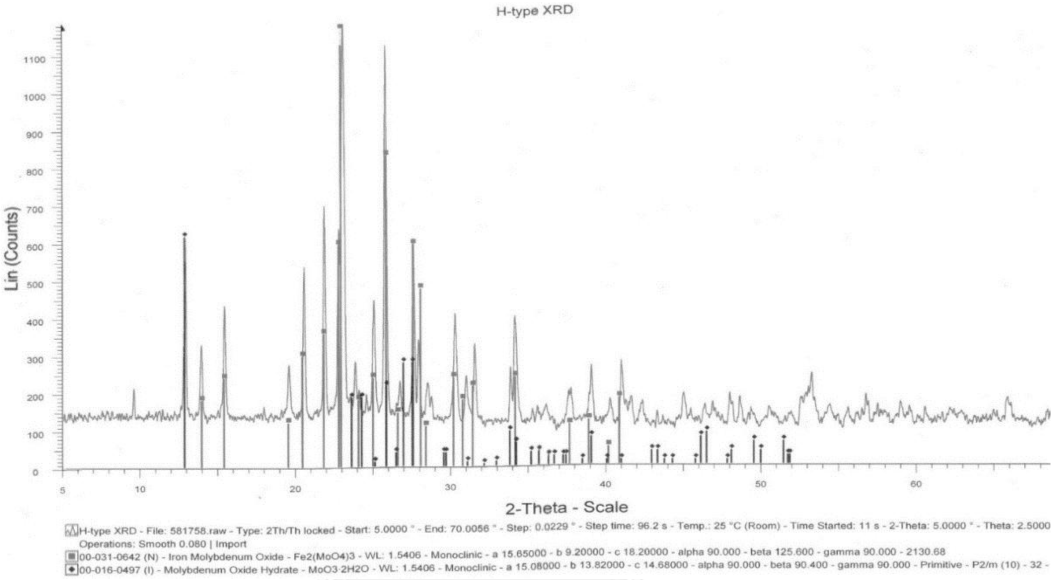


*Figure 4.4 XRD analysis of iron molybdate*

### 4.2.4 Surface analysis and Porosity Analyzer (BET) analyzed by Surface Area Analyzer

The BET surface area was determined with a Surface Area and Porosity Analyzer (Chemisorption Analyzer) brand Micromeritic Model ASAP2020 with $N_2$ adsorption at 300˚C. The BET surface area was 4.11 $m^2/g$ which was in accordance with the BET value of Tian, S. H. et al. (2011).

The pattern from the XRD analysis confirmed that this is iron molybdate. The peak appear at 2θ compared with JCPDS file no. 35-0183 was monoclinic. The ratio of Mo:Fe component was 1.7 which was favorable catalyst (Routray et al., 2010). The BET surface area was 4.11 $m^2/g$ which was in accordance with the BET value of Tian, S. H. et al. (2011).

## 4.3 Control experiment

Control Experiments were carried out by considered the effect of initial pH, iron coagulation and direct oxidation by $H_2O_2$ on color, lignin and COD removal for synthetic wastewater.

### 4.3.1. Control experiment for pH

To study the effect of pH on lignin, color and COD removal, initial pH was adjusted to acidic (pH 2), neutral (pH 7) and basic (pH 9) conditions and samples were taken at various times. The results showed that lignin, color and COD removal of synthetic wastewater at different initial pH did not change (data in Appendix B1-2). Therefore, pH alone was not effect on the change of color or lignin in the solution and not effect to COD removal of wastewater.

### 4.3.2. Control experiment for iron precipitation

Precipitation of iron has been considered since iron could dissolve at low pH value and iron precipitate under alkaline condition. The initial pH was adjusted to 3 and $Fe^{2+}$ dosage of 300, 400 and 500 mg/l. The results for iron precipitation show in Figure 4.5 and Appendix B4-2. These results indicated that iron precipitation could reduce lignin, color and COD in wastewater.

The highest removal efficiency was obtained using $Fe^{2+}$ concentration of 400 mg/l. Increasing dosage beyond this value led to reduce the removal efficiency due to the charge reversal effect that was commonly occur under excess of coagulant dosage.

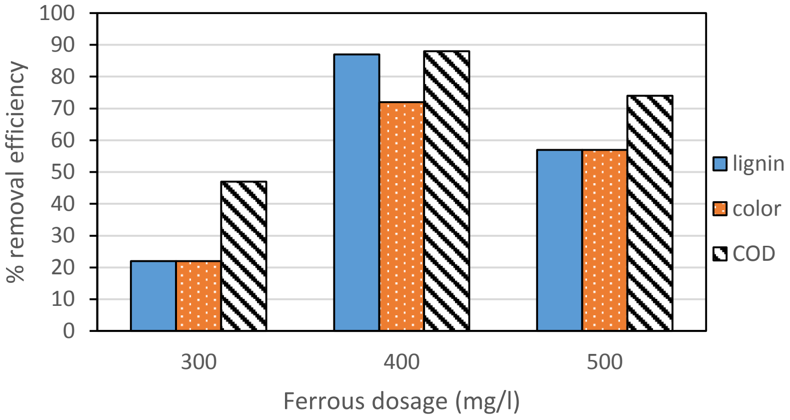


*Figure 4.5 Removal efficiencies of lignin, color and COD at Fe$^{2+}$ dosage of 300, 400 and 500 mg/l by iron precipitation*

### 4.3.3. Control experiment for $H_2O_2$

To study the direct oxidation by $H_2O_2$ at $H_2O_2$ concentration of 240, 400, 1,000, 2,000, 4,000, 6,000 and 8,000 mg/l (from $H_2O_2$ concentration that used in varied ratio of Fe$^{2+}$:$H_2O_2$) was added into the synthetic wastewater under initial pH of 3. The results in Table 4.3 and Appendix B4-1 show lignin, color and COD removal efficiency of each $H_2O_2$ concentration.

*Table 4.3 Lignin, color and COD removal efficiency by $H_2O_2$*

| $H_2O_2$ (mg/l) | % lignin removal efficiency | % color removal efficiency | % COD removal efficiency |
|---|---|---|---|
| 240 | 0.7 | 0.0 | 0.0 |
| 400 | 1.0 | 0.0 | 3.0 |
| 1000 | 1.6 | 4.1 | 1.1 |
| 2000 | 3.0 | 8.3 | 8.0 |
| 4000 | 0.4 | 4.3 | 5.0 |
| 6000 | 1.4 | 4.3 | 9.2 |
| 8000 | 5.2 | 12.0 | 16.1 |

The direct oxidation by $H_2O_2$ at $H_2O_2$ concentration of 1000 mg/l which obtained from optimum Fe$^{2+}$:$H_2O_2$ ratio of 1:2.5. The results of direct oxidation at time interval by $H_2O_2$ show in Appendix B1-2. Under $H_2O_2$ direct oxidation, the efficiencies of lignin, color and COD removal were 1.6%, 4.1%, and 1.1%, respectively after 60 minutes of reaction time. This result indicated that direct oxidation by $H_2O_2$ was not efficient to treat lignin and COD in synthetic wastewater due to the oxidation potential of $H_2O_2$ is lower than OH•. Thus, combination of ferrous salt and $H_2O_2$ in Fenton process would help to improve removal efficiency.

## 4.4 De-colorization and lignin removal of synthetic pulping wastewater in a batch reactor with homogeneous Fenton and heterogeneous Fenton-like reaction.

This research studied on Fenton process and heterogeneous Fenton-like process based on different phases of catalyst.

### 4.4.1. Homogeneous Fenton reaction (Conventional Fenton process)

The Fenton reaction is the reaction of iron (Fe) and hydrogen peroxide ($H_2O_2$) and the reactions generate hydroxyl radical (OH•) under acidic condition. The related chemical reactions are as followed Barbusinski (2009);

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^-$ (chain initiation) $k_1 \approx 70\ M^{-1}\ s^{-1}$……..(1)

Treatment methods in this part were varied ratio of $Fe^{2+}:H_2O_2$, pH and $Fe^{2+}$ dosage to find optimum condition for lignin and color removal of synthetic pulping wastewater.

#### 4.4.1.1 Different ratio of $Fe^{2+}:H_2O_2$

The experiment used initial lignin concentration of 0.91 g/l characterized from pulping wastewater. Initial pH was adjust to 3 and $Fe^{2+}$ dosage was 400 mg/l. The ratio of $Fe^{2+}:H_2O_2$ was varied at 1:0.6, 1:1, 1:2.5, 1:5, 1:10, 1:15 and 1:20. The results of removal efficiencies at different $Fe^{2+}:H_2O_2$ ratio show in Figure 4.6 and Appendix B1-1. At $Fe^{2+}:H_2O_2$ ratio of 1:2.5 showed high overall lignin, color and COD removal efficiencies. Higher ratio of $Fe^{2+}:H_2O_2$ did not show different on lignin, color and COD removal. Excess of $H_2O_2$ concentration acts as a radical scavenger as show in equation (4.1)-(4.3) (Bautista et al., 2007):

$$H_2O_2 + OH\bullet \rightarrow H_2O + HO_2^{\bullet} \qquad (4.1)$$

$$HO_2\bullet + OH\bullet \rightarrow O_2 + H_2O \qquad (4.2)$$

$$OH\bullet + OH\bullet \rightarrow O_2 + H_2O \qquad (4.3)$$

From the equation (4.1), excess of $H_2O_2$ react with OH• and produce perhydroxyl radical ($HO_2\bullet$). The generated $HO_2\bullet$ has lower oxidative potential than OH•. Moreover, $HO_2\bullet$ can react with OH• (equation (4.2)) and OH• can react together (equation (4.3)). Therefore, the removal efficiency would decrease.

Catalkaya and Kargi (2007) suggested the ratio of $Fe^{2+}$:$H_2O_2$ to be 1:12. While Pérez et al. (2002) showed the ratio of $Fe^{2+}$: $H_2O_2$ was 1:16. Moreover, Torrades et al. (2011) suggested the $Fe^{2+}$: $H_2O_2$ ratio was 1:6. According to these other researches, the optimum ratio in this research was lower than the others due to the different of characteristics of wastewaters. Thus, it is necessary to determine the $Fe^{2+}$: $H_2O_2$ ratio of each wastewater.

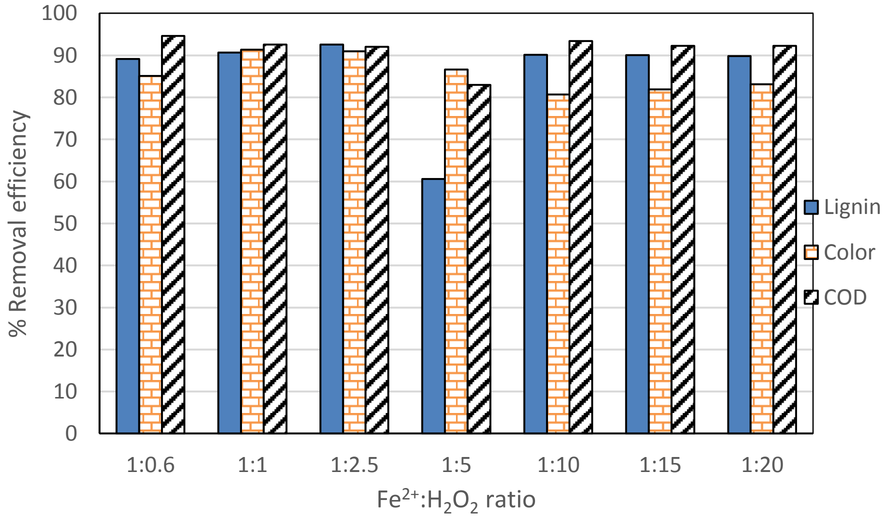


*Figure 4.6 Lignin, color and COD removal efficiency at different ratio of* $Fe^{2+}$*:*$H_2O_2$

The coagulation of iron at $Fe^{2+}$ dosage of 400 mg/l from part 4.3.2 show the result of removal efficiencies by iron coagulation in Figure 4.7 and Appendix B1-2.

The effect of iron coagulation for lignin, color and COD removal were 87%, 72% and 88%, respectively. These results indicated that coagulation could remove lignin, color and COD in wastewater.

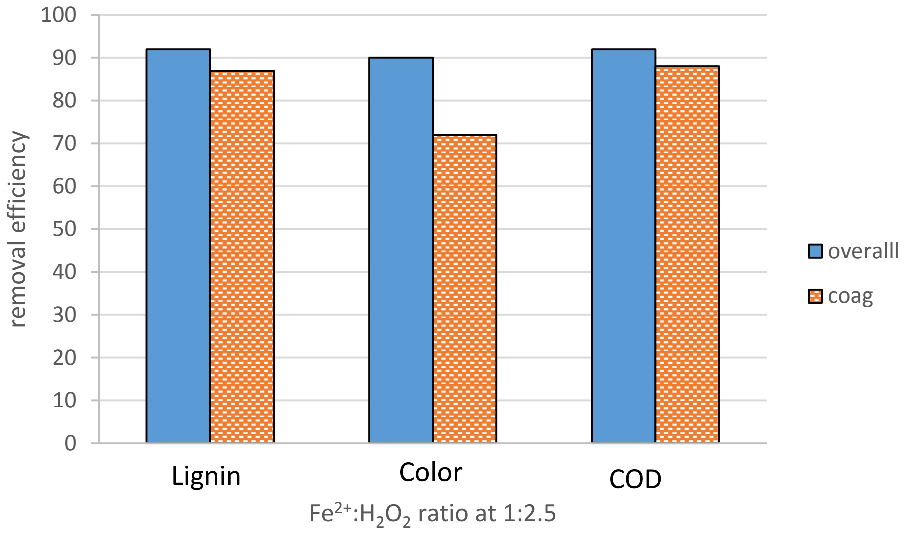


*Figure 4.7 Removal efficiencies of lignin, color and COD by iron coagulation*

The overall removal efficiencies of lignin, color and COD in Fenton process due to the Fenton oxidation and formation of iron sludge. The minimum efficiency from Fenton oxidation was 4% (Appendix B4-3).

4.4.1.2 Different pH

The experiment used ratio of $Fe^{2+}$:$H_2O_2$ at 1:2.5 (obtained from part 4.4.1.1) and $Fe^{2+}$ dosage was 400 mg/l. Initial pH was varied at pH of 2, 3 and 4. The results of removal efficiencies at different initial pH show in Figure 4.8-4.10 and Appendix B1-3. At initial pH of 3 showed high removal efficiencies of lignin, color and COD. Lower pH than optimum value leads to formation of Fe(III) different complex species $(Fe(II)(H_2O)_6)^{2+}$ and OH• is scavenged by $H^+$ (Fan et al., 2009). Higher pH than optimum value leads to decomposition of $H_2O_2$ and formation of $Fe(OH)_3$ (Liu et al., 2011). Therefore, the removal efficiency would decrease.

From the Figure 4.8-4.10, the removal efficiency reached to the maximum and then decreased and reached to the certain value. This due to the effect of $H_2O_2$ would change to oxonium ion ($H_3O_2^+$) under pH value below 3 which is a stable form (equation 4.4). Therefore, low amount of $H_2O_2$ can react with available $Fe^{2+}$ resulting in low OH• production (Hassan and Hameed, 2011; Wang et al., 2015).

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \qquad (4.4)$$

Moreover, the formation of Fe(III) different complex species $(Fe(II)(H_2O)_6)^{2+}$ and $(Fe(H_2O)_6)^{3+}$ at lower pH value (pH 2) would react slowly with $H_2O_2$ (Hassan and Hameed, 2011). Hence, the amount of OH• and $H_2O_2$ would lower than at optimum pH value (pH 3). Moreover, pH of solution become lower than at the initial pH value when the process occurred during reaction time. The NaOH that added in the solution was controlled at the same amount, which would not enough for iron precipitation at low pH. At higher pH, the formation of $Fe(OH)_3$ occurred, which did not participated in the Fenton process. So, the removal efficiency reduced (Mitsika et al., 2013).

Fan et al. (2009) investigated the degradation of crystal violet and the result showed that the optimum pH in Fenton process was about 3. Furthermore, the degradation of reactive black 5 by Fenton process was suggested at initial pH of 3.5 (Liu et al., 2011). While Samet et al. (2012) investigated the removal of chlorpyrifos insecticide in wastewater found that the optimum conditions were obtained at pH of 3. Moreover, Agustina and Ang (2012) suggested the optimum pH was 3 by Fenton process for decolorization and mineralization of C.I. reactive blue 4 and C.I. reactive red 2. From other researches, the optimum pH was found at acidic condition (around 3) which the result in this research was conformed to the others. This could be inferred that Fenton process was limited at acidic condition whether the wastewater has different its characteristics.

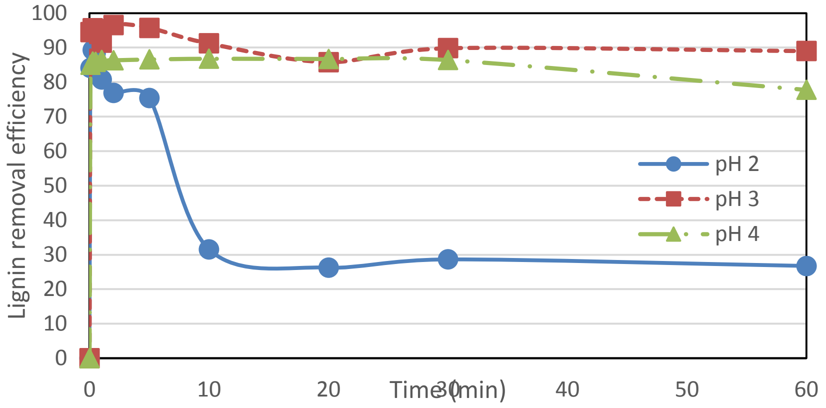


Figure 4.8 Lignin removal efficiency at different pH

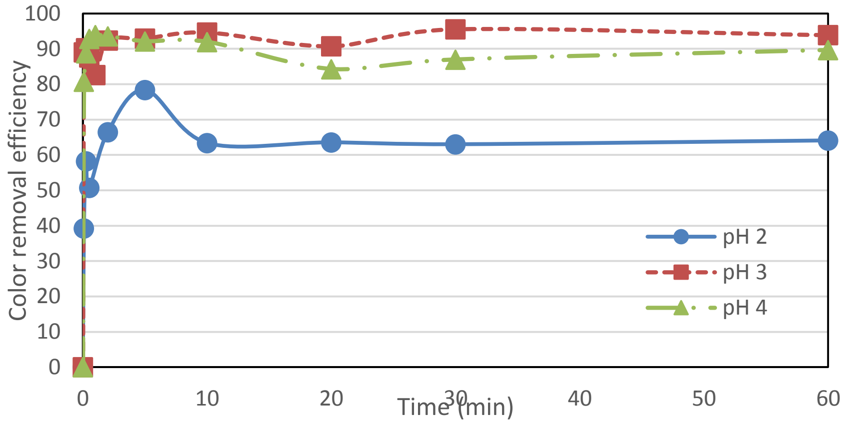


Figure 4.9 Color removal efficiency at different pH

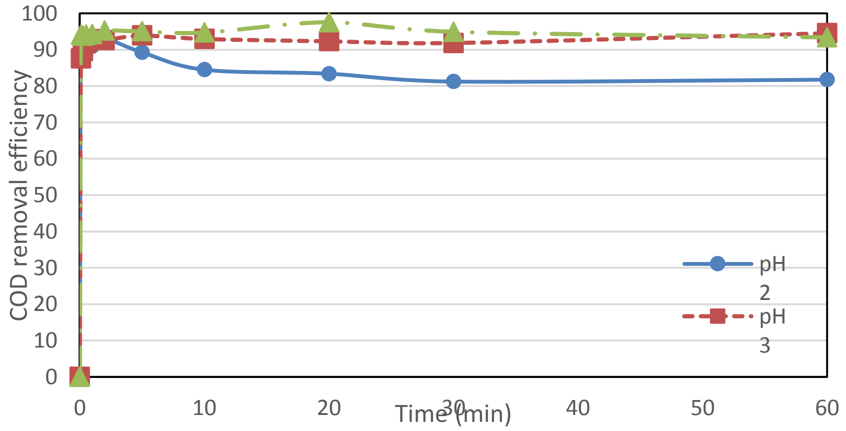


Figure 4.10 COD removal efficiency at different pH

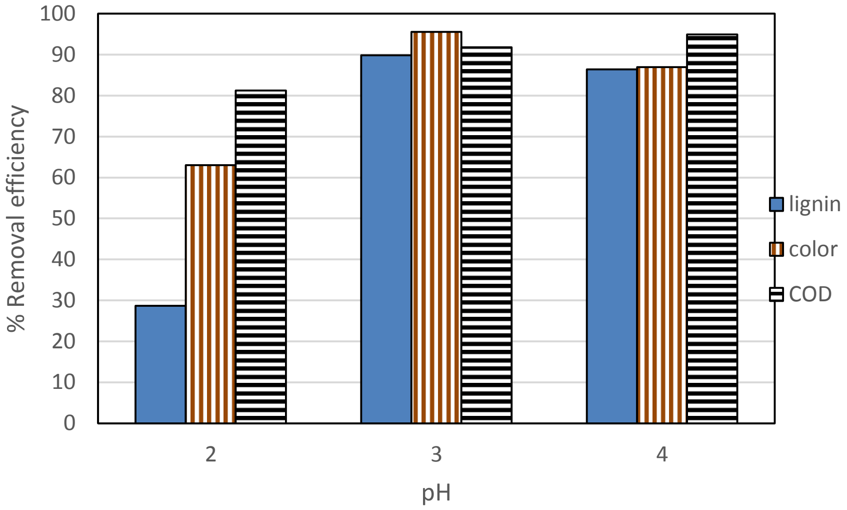


*Figure 4.11 Comparison of overall removal efficiency of lignin, color and COD at pH of 2, 3 and 4 at 30 minutes*

4.4.1.3 Effect of Fenton's reagent dose

The experiment used ratio of $Fe^{2+}$:$H_2O_2$ at 1:2.5 (obtained from part 4.4.1.1). Initial pH was adjusted to 3 (obtained from part 4.4.1.2) and $Fe^{2+}$ dosage was varied at 300, 400 and 500 mg/l. The results of removal efficiencies at different $Fe^{2+}$ dosage show in Figure 4.12-4.14 and Appendix B1-4. At $Fe^{2+}$ dosages of 400 mg/l showed the highest removal efficiencies of lignin, color and COD. Removal efficiency at $Fe^{2+}$ dosage of 400 mg/l and 500 mg/l were not different. Excess of $Fe^{2+}$ dosage may also act as a radical scavenger. The mechanism between $Fe^{2+}$ and OH• when excess of $Fe^{2+}$ dosage as follows (Fan et al., 2009):

$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH-$ (4.4)

Moreover, organic compounds might not be treated efficiently at lower $Fe^{2+}$ dosage due to the lower catalyst than at optimum value. Lower amount of catalyst caused lower generation of OH• which was not enough to treat lignin and color in synthetic wastewater. Therefore, the optimum $Fe^{2+}$ dosage was 400 mg/l.

From the Figure 4.12-4.14, the removal efficiency of 300 mg/l $Fe^{2+}$ dosage gradually increase to the maximum then decreased and reached to equilibrium. This due to the reaction produced OH• at high concentration at initial stage of reaction and the reaction reach to constant value. The removal efficiency of 300 mg/l of $Fe^{2+}$ concentration was lower than the optimum value. Moreover, lower concentration of 300 mg/l $Fe^{2+}$ might not enough to precipitate for neutralization by NaOH. Thus, the removal efficiency would drop.

Since Ginni et al. (2013) investigated pulp and paper mill wastewater treatment containing high organic loading, they found that using of 1 g/l $Fe^{2+}$ dosage provide the optimum condition in solar-photo Fenton process. While Zahrim et al. (2007) found that optimum concentration of $Fe^{2+}$ was 400 mg/l for pulp and paper mill wastewater with collecting sample at point before biological treatment by photo-Fenton process, in that research found that the efficiency decrease when exceeded of $Fe^{2+}$ concentration. Moreover, $Fe^{2+}$ dosage was used at 2.8 mg/l for degradation of reactive black 5 by Fenton process (Liu et al., 2011). According to other researches, the concentration of $Fe^{2+}$ in each treatment techniques and each characteristic of wastewater was different. For this research, the optimum $Fe^{2+}$ dosage of 400 mg/l was due to suitable for the initial concentration of synthetic wastewater.

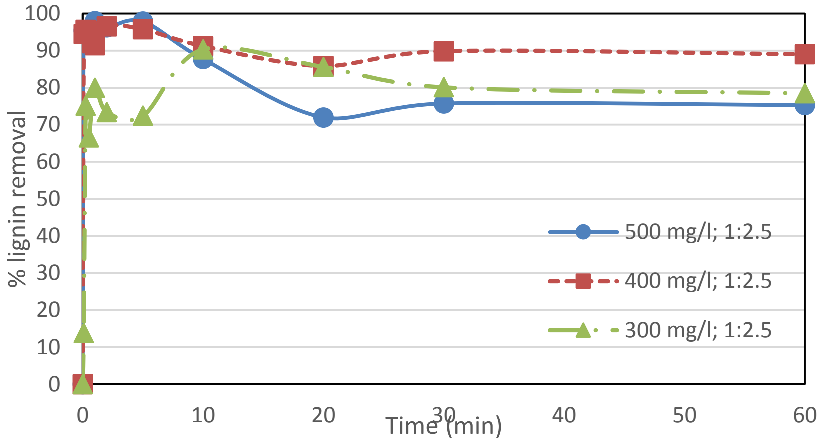


*Figure 4.12 Lignin removal efficiency at different* $Fe^{2+}$ *dosage*

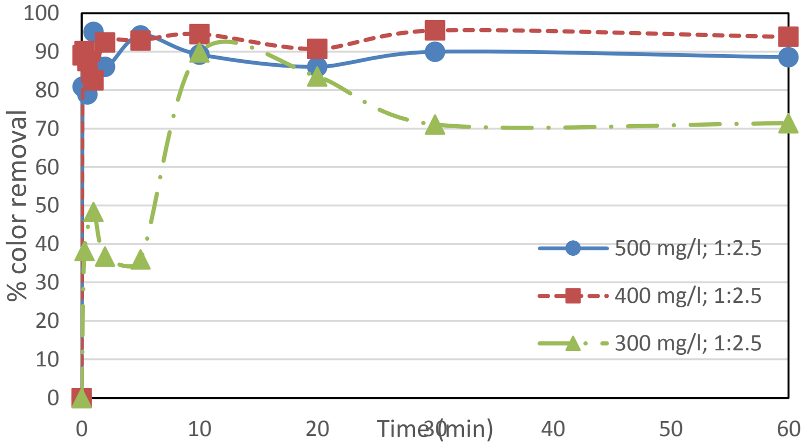


*Figure 4.13 Color removal efficiency at different* $Fe^{2+}$ *dosage*

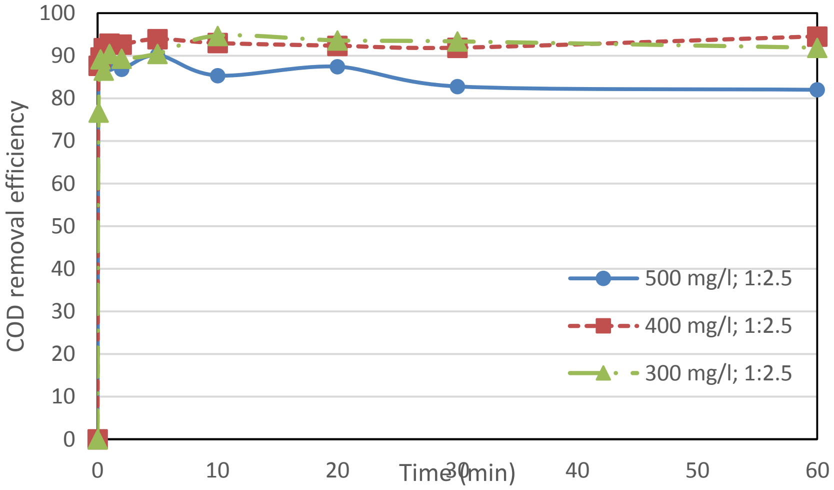


*Figure 4.14 COD removal efficiency at different* $Fe^{2+}$ *dosage*

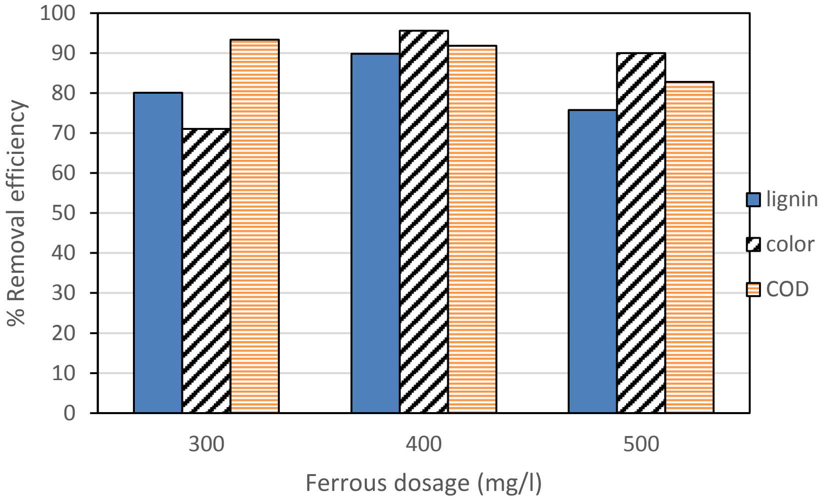


*Figure 4.15 Comparison of overall removal efficiency of lignin, color and COD at $Fe^{2+}$ dosage of 300, 400 and 500 mg/l at 30 minutes*

### 4.4.2. Heterogeneous Fenton-like reaction using iron molybdate ($Fe_2(MoO_4)_3$)

The heterogeneous Fenton-like reaction is the reaction of using ferric ion ($Fe^{3+}$) in solid form or insoluble form react with hydrogen peroxide ($H_2O_2$) at the first step of reaction. After that, ferric ion change to ferrous ion ($Fe^{2+}$) and ferrous ion react with $H_2O_2$ and the reactions generate hydroxyl radical (OH•) the same as Fenton reaction. The related chemical reactions are as followed Bayat et al. (2012);

$$S\text{-}Fe^{3+} + H_2O_2 \rightarrow S\text{-}Fe^{2+} + H^+ + HO_2^{\bullet} \quad \ldots. (4.5)$$

$$S\text{-}Fe^{2+} + H_2O_2 \rightarrow S\text{-}Fe^{3+} + OH\bullet + OH^- \quad \ldots. (4.6)$$

$$OH\bullet + \text{organic compounds} \rightarrow \text{oxidized products} \quad \ldots. (4.7)$$

Since Fenton process has some disadvantages such as require iron sludge separation step and have to be operated in acidic condition (pH of 2-4). Thus, acidification process has to perform as the Fenton pretreatment (Liu et al., 2011; Tian, S. et al., 2013). Moreover, most of catalyst in heterogeneous Fenton-like process e.g. $Fe_2O_3$ (hematite), FeOOH (goethite) (Wang et al., 2015) and $Fe_3O_4$ show favorable catalytic activity in acidic pH range, relatively low activities, or strong iron leaching at low pH value which homogeneous reactions could occur (Moura et al., 2005; Tian, S. et al., 2013).

Iron molybdate ($Fe_2(MoO_4)_3$) is the catalyst that can be synthesized. This catalyst could offer several advantages such as can be applied in wide pH range (3-9), stability of structure, no iron sludge formation and possibility to recycle the catalyst (Tian, S. H. et al., 2011). Since no work has been reported on the using of iron molybdate in heterogeneous Fenton-like process of pulping wastewater, this research was interesting in using iron molybdate as a catalyst for heterogeneous Fenton-like process.

Treatment methods in this part were varied ratio of $Fe^{3+}$:$H_2O_2$, pH and $Fe^{3+}$ dosage to find optimum condition for lignin and color removal of synthetic pulping wastewater. Iron molybdate was studied their ability to recovery without the loss of performance.

At the initial of all experiment, the experiment was performed using $Fe^{3+}$:$H_2O_2$ ratio of 1:2.5 and 1:10 to observe which ratio could provide higher removal efficiency. At this experiment, the $Fe^{3+}$ concentration was used at 0.4 g/l at $Fe^{3+}$:$H_2O_2$ ratio of 1:2.5 and initial pH of 3 but it not successful for synthetic wastewater treatment (result in Appendix B5-2). Later, $Fe^{3+}$ concentration was varied at 1 and 2 g/l at initial pH of 4, 6 and 8 at $Fe^{3+}$:$H_2O_2$ ratio of 1:2.5 and 1:10 to observe which $Fe^{3+}$ concentration and pH could provide high removal efficiency (result in Appendix B5-2).

#### 4.4.2.1 Different ratio of $Fe^{3+}$:$H_2O_2$

The experiment used initial pH of 8 and $Fe^{3+}$ dosage was 2 g/l. The ratio of $Fe^{3+}$:$H_2O_2$ was varied at 1:2.5, 1:5, 1:10, 1:15 and 1:20. The results of removal efficiencies at different $Fe^{3+}$:$H_2O_2$ ratio show in Figure 4.16-4.18 and Appendix B2-1. At $Fe^{3+}$:$H_2O_2$ ratio of 1:10 showed high lignin, color and COD removal efficiencies. Higher ratio of $Fe^{3+}$:$H_2O_2$ did not show different on lignin, color and COD removal, because high amount of $H_2O_2$ can acts as a radical scavenger (equation (4.1)-(4.3)) resulting in slightly higher removal efficiency comparing with $Fe^{3+}$:$H_2O_2$ ratio of 1:10. Therefore, further added of $H_2O_2$ at higher $Fe^{3+}$:$H_2O_2$ ratio (more than 1:10) did not necessary. To get high removal efficiency and use low chemical reagent, the optimum $Fe^{3+}$:$H_2O_2$ ratio should be 1:10.

Tian, S. H. et al. (2011) and Hummadi et al. (2009) demonstrated that there is synergistic catalytic effect between $Fe^{3+}$ and $MoO_4^{2-}$ in the compound for $H_2O_2$ decomposition. Moreover, $MoO_4^{2-}$ is one of catalyst help to treat wastewater by react with $H_2O_2$ and the reaction generate molybdenum peroxo complex ($MoO_2(O_2)_2^{2-}$) to oxidized organic compound in wastewater. $MoO_2(O_2)_2^{2-}$ is one of oxidizing agent that can oxidize the organic compounds by the direct oxygen transfer (equation (4.8)-(4.9)) or by generating the singlet oxygen ($^1O_2$) (equation (4.10)-(4.11)) (Lin and Liu, 2009). Nevertheless, $MoO_2(O_2)_2^{2-}$ and $^1O_2$ are lower oxidation performance than OH•. Thus, the removal efficiency would comparatively low (Tian, S. H. et al., 2011).

$$MoO_4^{2-} + 2H_2O_2 \rightarrow MoO_2(O_2)_2^{2-} + 2H_2O \quad (4.8)$$

$$MoO_2(O_2)_2^{2-} + \text{organic compounds} \rightarrow \text{oxidized products} + MoO_4^{2-} \quad (4.9)$$

$$MoO_2(O_2)_2^{2-} \rightarrow MoO_4^{2-} + {}^1O_2 \quad (4.10)$$

$${}^1O_2 + \text{organic compounds} \rightarrow \text{oxidized products} \quad (4.11)$$

The reaction slowly occurred at the first 60 minutes of reaction time, then the reaction reached to certain value. This due to the mechanism of ferric changed to ferrous at the first stage of reaction (Jiang et al., 2013; Xu et al., 2013a). When the OH• was maximum produced with ferrous already changed to ferric, the removal efficiency increased to the maximum. The faster removal efficiency may attributed to high concentration of $H_2O_2$ producing more oxidation rate. Nevertheless, $H_2O_2$ may automatically decompose during the reaction time proceed which decline the removal efficiency.

Nadejde et al. (2015) suggested the optimum $Fe^{3+}$:$H_2O_2$ ratio was 1:0.47 for the degradation performance of oxidation process. While Blanco et al. (2014) found that the optimum $Fe^{3+}$:$H_2O_2$ ratio was 1:18 for azo dye degradation. The optimum ratio of 5 g of Fe-clay: 0.272 g of $H_2O_2$ was used to decolorize of reactive blue 4 (Hassan and Hameed, 2011). While Xu et al. (2013b) suggested the $Fe^{3+}$:$H_2O_2$ ratio was 1:8 for degradation of methyl orange. While the result from this research was at $Fe^{3+}$:$H_2O_2$ ratio of 1:10 for lignin degradation.

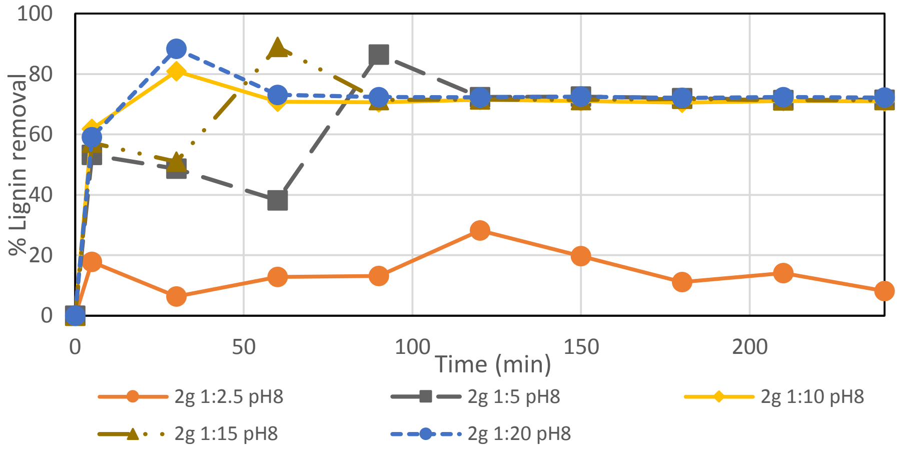


*Figure 4.16 Lignin removal efficiency at different ratio of* $Fe^{3+}:H_2O_2$

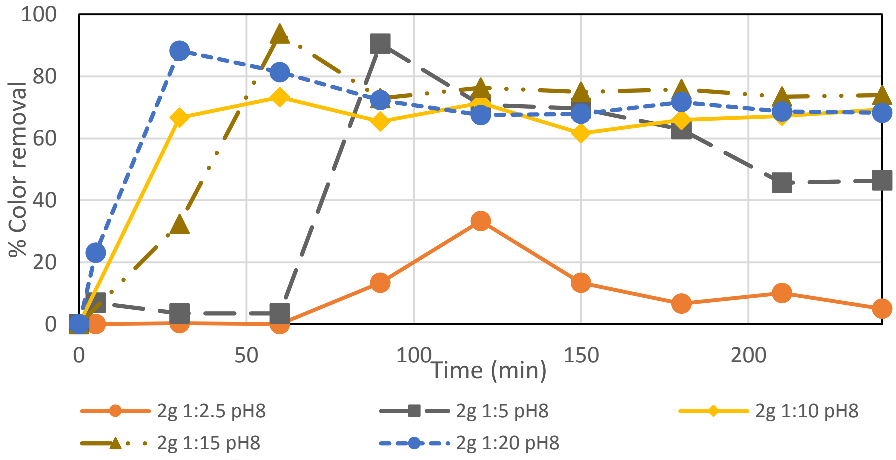


*Figure 4.17 Color removal efficiency at different ratio of* $Fe^{3+}:H_2O_2$

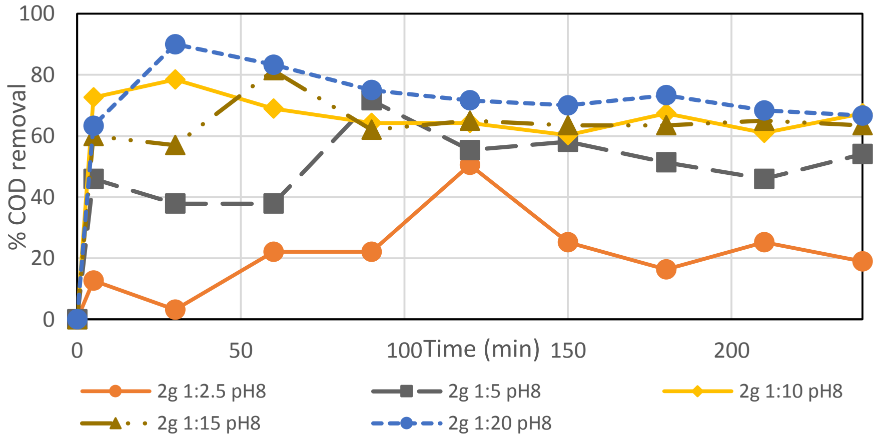


*Figure 4.18 COD removal efficiency at different ratio of* $Fe^{3+}:H_2O_2$

The result of adsorption by catalyst with concentration of $Fe^{3+}$ was 2 g/l at initial pH of 8 show that lignin and color were not adsorbed but COD was treated by the adsorption average of 8% (data in Appendix B2-2). This result indicated that the adsorption of catalyst could be neglected compared with the reaction of heterogeneous Fenton-like process. Therefore, combination with $H_2O_2$ in heterogeneous Fenton-like process would help in wastewater treatment.

The result of direct oxidation by $H_2O_2$ at $H_2O_2$ concentration of 20 g/l which obtained from $Fe^{3+}$:$H_2O_2$ ratio of 1:10 show in Figure 4.19 and Appendix B2-2. The $H_2O_2$ direct oxidation, were achieved 7%, 42%, and 47% of lignin, color and COD removal efficiency, respectively after 240 minutes. This result indicated that direct oxidation by $H_2O_2$ did not efficient to treat lignin compared with the combination of iron catalyst in heterogeneous Fenton-like process due to the oxidation potential of $H_2O_2$ is lower than OH• as compared with the removal efficiencies in heterogeneous Fenton-like process that show in Figure 4.20. Thus, combination with ferric salt in heterogeneous Fenton-like process would help to improve the removal efficiency.

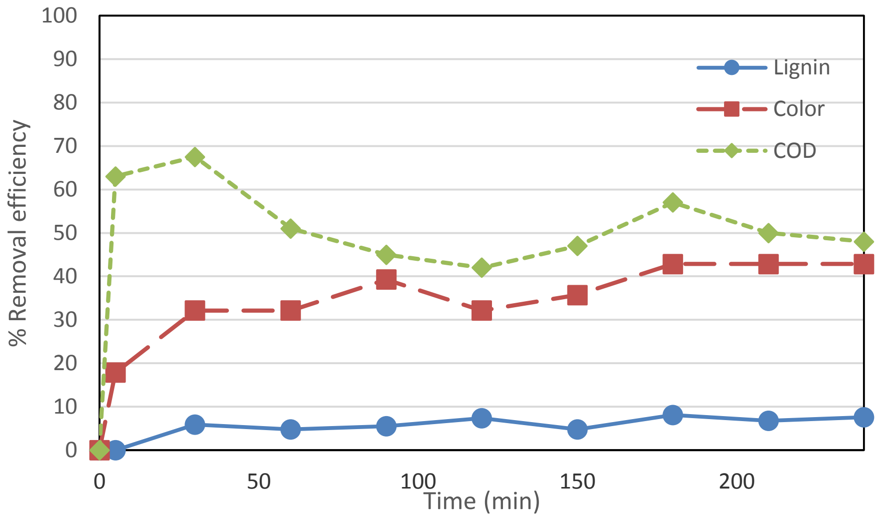


*Figure 4.19 Removal efficiencies of lignin, color and COD by direct oxidation of $H_2O_2$ at 20g/l, initial pH of 8*

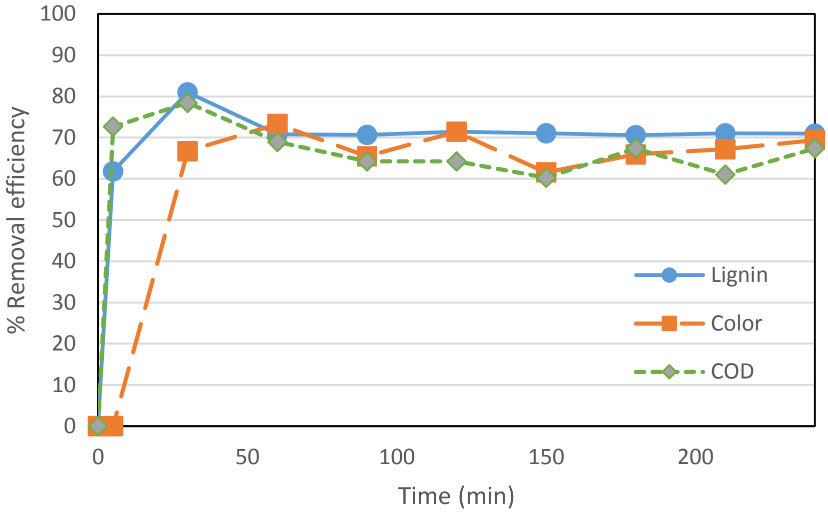


*Figure 4.20 Lignin, color and COD removal efficiency at* $Fe^{3+}$ *2 g/l,* $Fe^{3+}:H_2O_2$ *ratio was 1:10 and initial pH of 8*

The residual $H_2O_2$ after $H_2O_2$ decomposition by $MnO_2$ may interfere COD measurement by consuming potassium dichromate. So, the COD value would higher than actual COD when measure COD. The removal efficiency become lower than actual. Thus, result of COD measurement that showed on graph quite fluctuate.

#### 4.4.2.2 Different pH

The experiment used ratio of $Fe^{3+}:H_2O_2$ at 1:10 (obtained from part 4.4.2.1) and $Fe^{3+}$ dosage was 2 g/l. Initial pH was varied at pH of 4, 6 and 8. The results of removal efficiencies at different initial pH show in Figure 4.21-4.23 and Appendix B2-3. At 30 minutes of reaction time, at initial pH of 8 show lignin, color and COD removal reach to 80%, 66% and 78%, respectively. While at initial pH of 4 could remove 31%, 19% and 40% and at initial pH of 6 could remove 42%, 36% and 55% for lignin, color and COD, respectively. During reaction time, pH of solution decreased from initial pH (4, 6 and 8) to lower pH value of 3 in all experiment (Appendix B5-1). Moreover, after 90 minutes, the removal efficiency at different initial pH show no different value for lignin and COD removal except for color. Color removal at initial pH of 8 was lower than the others but it has a benefit on that no pH adjustment is required. This leads to cost effective of heterogeneous Fenton-like process.

The wide pH operation range can be described to the solid acid property of surface iron molybdate, which can gain or donate protons in the reaction system. Under neutral or alkaline solution, the surface of catalyst is negatively charged and would provide more ion $H^+$ to form an acidic environment near the surface of catalyst. Moreover, $H_2O_2$ acts as an electron-receiver compound react with catalyst due to the electrophilic characteristic of $H_2O_2$, which this phenomenon would favors the generation of OH• (Tian, S. H. et al., 2011). More alkaline solution tends to the decomposition of $H_2O_2$. The decomposition of $H_2O_2$ occur under alkaline pH at over pH 10 (Yazici and Devici, 2010).

According to the result of Tian, S. H. et al. (2011) by using iron molybdate for acid orange degradation found pH from 3 to 9 provided high removal efficiency. This because solid acid characteristic of iron molybdate that could protonate or deprotonate when the pH of solution change below or above than the pH at point of zero charge of catalyst which support the reaction could occur in neutral or alkaline solution. This was an evidence to the result of this research. In addition, Wang, W. M. et al. (2013) investigated the oxidation of phenol by heterogeneous Fenton-like process using schwertmannite as catalyst, the result showed that at pH of 5 provided high removal efficiency. Mammeri et al. (2014) investigated the degradation of 1-naphthol using iron oxide as heterogeneous photo-Fenton-like catalyst, the result showed that at wide pH range of 3-8.3 could provide high efficiency of 1-naphthol degradation. Furthermore, the use of β-FeOOH in photo-Fenton-like process for methyl orange degradation showed high efficiency at wide pH range of 4.5-9.5 (Xu et al., 2013b) because the acid-base properties of surface catalyst with conversion of pH at point of zero charge and pH that can be gained or donated protons when pH of solution below or higher than its $pH_{pzc}$ to maintain the stability of catalyst when pH of solution changed. Moreover, Ameta et al. (2012) investigated the degradation of coomasie brilliant blue R-250 by heterogeneous photo-Fenton process and they found that at pH of 9 provide the maximum reaction rate. According to other several researches, heterogeneous Fenton-like process was able to apply in wide range of pH. This may due to the acid-base properties of surface catalyst. The result from this research was conformed to the others. However, the optimum pH that obtained from the results (pH 8) was formed synthetic pulping wastewater that contain initial lignin concentration approximately 910 mg/l.

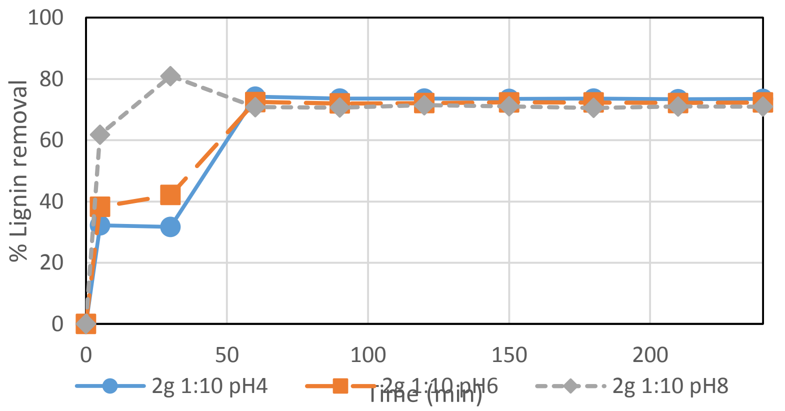


*Figure 4.21 Lignin removal efficiency at different initial pH*

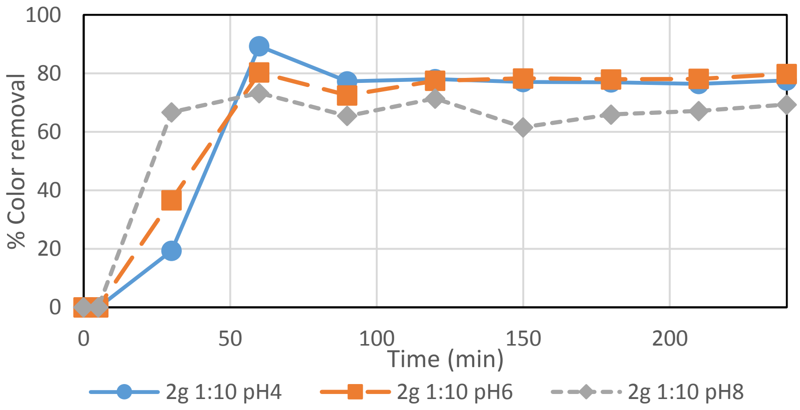


*Figure 4.22 Color removal efficiency at different initial pH*

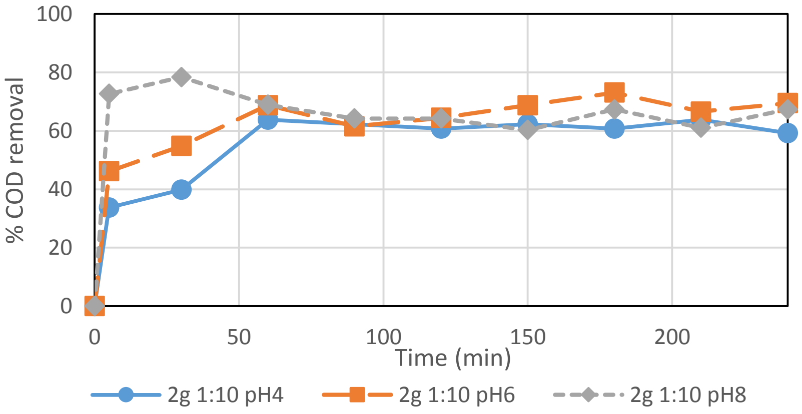


*Figure 4.23 COD removal efficiency at different initial pH*

4.4.2.3 Effect of heterogeneous Fenton-like's reagent dose

The experiment used ratio of $Fe^{3+}$:$H_2O_2$ at 1:10 (obtained from part 4.4.2.1). Initial pH was adjusted to 8 (obtained from part 4.4.2.2) and $Fe^{3+}$ dosage was varied at 0.5, 1, 2, 2.5 and 3 g/l. The results of removal efficiencies at different $Fe^{3+}$ dosage show in Figure 4.24-4.26 and Appendix B2-4. The removal efficiencies increase when the catalyst concentration increase from 0.5 to 2 g/l, mainly due to the increasing amount of active sites leads to more react with $H_2O_2$ and producing more OH• (Tian, S. et al., 2013). Increasing the $Fe^{3+}$ dosage was not different when compared with the efficiency of $Fe^{3+}$ dosage at 2 g/l, attributed to the scavenging effect of OH• when excess of $Fe^{3+}$ dosage. The mechanism between $Fe^{3+}$ and OH• when excess of $Fe^{3+}$ dosage as follows (Watts, 2006):

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH- \qquad (4.4)$$

Thus, the removal efficiency would decrease. However, organic compounds may not be treated efficiently at lower $Fe^{3+}$ dosage due to the lower catalyst than at optimum value. Lower amount of catalyst caused lower generation of OH• which was not enough to treat lignin, color and COD in synthetic wastewater. Therefore, 2 g/l of $Fe^{3+}$ dosage should be the optimum concentration for this work at 90 minutes of reaction time because spend less time while provide high removal efficiency.

The decreasing of removal efficiency was described by inter-conversion of iron in reaction. When the oxidation capacity of Fenton or Fenton-like process was limited, the removal efficiency by Fenton or Fenton-like process would not more increase (Jiang et al., 2013).

Several other researches, Xu et al. (2013b) used 200 mg/l of β-FeOOH for methyl orange degradation, while iron oxide was used 1 g/l investigated by Mammeri et al. (2014) for 1-Naphthol degradation. Moreover, 134 mg/l of Fe in zeolite was the optimum dose for azo dyes degradation (Blanco et al., 2014). Nadejde et al. (2015) suggested the optimum dose of magnetite was 1 g/l for studied the degradation performance of the oxidation process. It can be inferred that iron concentration was determined by the objective of each research. For this research, the optimum Fe concentration was 2 g/l for lignin degradation of pulping wastewater.

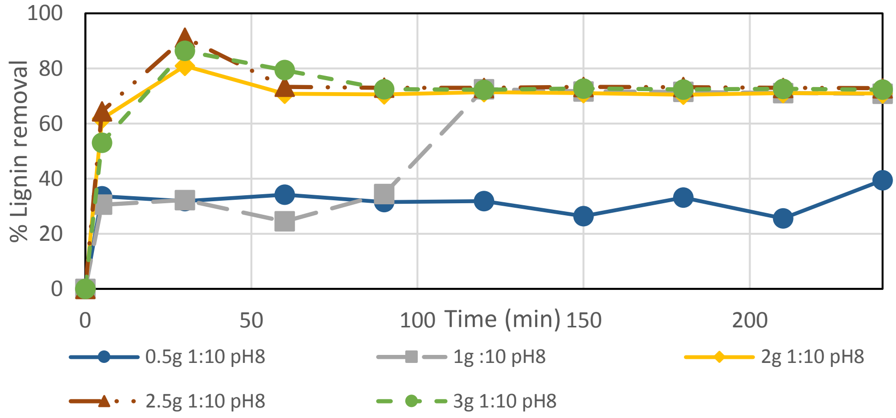


*Figure 4.24 Lignin removal efficiency at different $Fe^{3+}$ dosage*

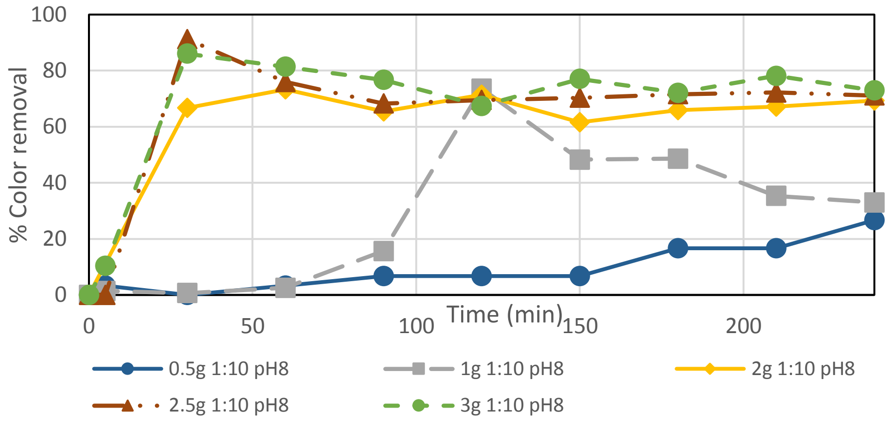


*Figure 4.25 Color removal efficiency at different $Fe^{3+}$ dosage*

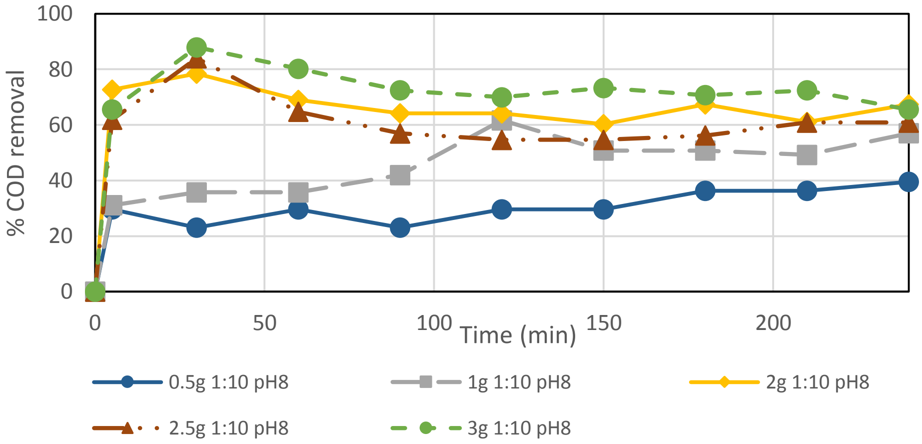


*Figure 4.26 COD removal efficiency at different $Fe^{3+}$ dosage*

#### 4.4.2.4 Amount of leaching iron in heterogeneous Fenton-like process

Leaching iron after treatment of synthetic wastewater was measured since Tian, S. H. et al. (2011) claimed that low iron leaching because of good structure of iron molybdate ($Fe_2(MoO_4)_3$). Phenanthroline method was used to measure the amount of iron (Appendix A3). Figure 4.27 and Appendix B2-5 show iron measurement at $Fe^{3+}$ 2 g/l, $Fe^{3+}$:$H_2O_2$ ratio was 1:10 at initial pH of 8.

From Figure 4.27 total leaching iron after treatment was less than 100 mg/l which was approximately 5% from catalyst. This result confirmed the good structure of iron molybdate. At time before 60 minutes, there was low iron leaching, attributed to the reaction occur at the surface of catalyst but the reaction was slower than in Fenton process as equation (3) (Barbusinski, 2009). After 90 minutes, the amount of ferrous ion maintain constant but the amount of ferric ion increased. This can be inferred that there was iron leaching from the catalyst but in low amount compared to the initial concentration. However, the reaction mainly occur from ferric ion at the surface of catalyst in heterogeneous Fenton-like process that was not from leached iron in the solution due to the low amount of iron in solution could be neglected. This was evidenced that the reaction remained constant after 90 minutes which was accordance with the removal efficiencies of heterogeneous Fenton-like process (show in Figure 4.28).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \qquad k_3 = 0.001\text{–}0.01\ M^{-1}\ s^{-1} \ldots\ldots (3)$$

The increasing of iron leaching after 90 minutes of reaction time was to the decreasing of solution pH from initial pH of 8 to pH of 3 at 90 minute as see in Figure 4.27 and Appendix B5-1. Iron leaching at pH of 3 was observed at 90 minutes. This was evidenced by other researches. Ramirez et al. (2007) demonstrated that iron leaching was obviously observed at pH around 2 and suggested that it would be applied in higher pH value to protect iron lost from the catalyst. The iron lost from catalyst was 7.5% weight catalyst. Also, Feng et al. (2006) demonstrated that strong leaching iron occur at acidic pH of 2. Duan et al. (2014) found that more leaching iron when lower pH value. The iron leached from catalyst at pH of 2, 3, 4 and 5 were 10%, 6% 2% and 0.8% weight of iron in catalyst, respectively. According to these other researches, more leaching iron was attributed to decreasing of pH. Therefore, to protect the iron lost from the catalyst, maintain the pH of solution at neutral condition was suggested. As can see from the result, the reaction maintain constant at 90 minutes reaction time. Applying of the reaction process for 90 minutes is enough for treating of wastewater.

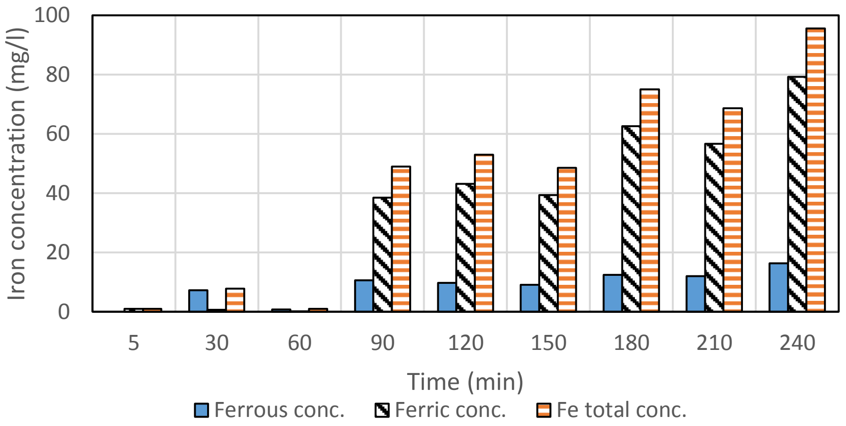


*Figure 4.27 Amount of iron concentration at* $Fe^{3+}$ *2 g/l,* $Fe^{3+}:H_2O_2$ *ratio was 1:10 at initial pH of 8*

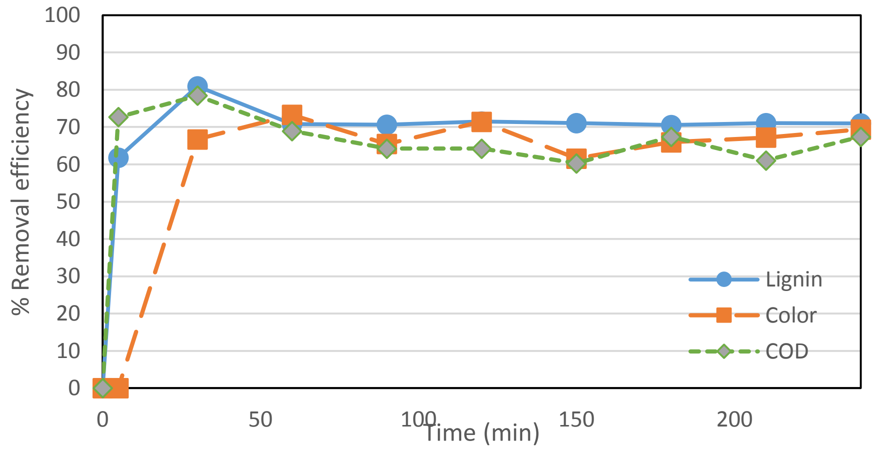


*Figure 4.28 Lignin, color and COD removal efficiency at* $Fe^{3+}$ *2 g/l,* $Fe^{3+}:H_2O_2$ *ratio was 1:10 and initial pH of 8*

### 4.4.3 Reuse of iron molybdate

Since iron molybdate could be reused after the first time used claimed by Tian, S. H. et al. (2011), this research investigated the recovery of catalyst to check its performance. Figure 4.29-4.31 and Appendix B2-6 show removal efficiency of lignin, color and COD of 4 recycling times.

The reuse of catalyst was considered at optimum condition of initial pH of 8, $Fe^{3+}$ dosage of 2 g/l and $Fe^{3+}$:$H_2O_2$ ratio 1:10. The catalyst was reused by separated directly from the previous run and then dried in oven in order to be used in the next batch. From Figure 4.29-4.31, the removal efficiency of lignin did not change much after 4 times of reuse. The lignin removal efficiency after used 4 times was 73%, 70%, 68%, and 68% respectively. Color was treated 77%, 66%, 61% and 62%, respectively. The removal efficiency of COD was 69%, 59%, 61% and 58%, respectively. However, color and COD removal efficiencies after the first time used decreased. In Figure 4.30-4.31, the removal efficiencies was dropped approximately10% from the first time used. At the fourth cycle, the removal efficiencies decreased and reaction rate was slower than the previous batches due to decrease of the catalytic activity. The catalytic activity decreased due to the reduction of active sites as a result of the loss of ferric in component structure or iron leaching after the previous run (Figure 4.32 and Appendix B2-7) (Duan et al., 2014; Pan et al., 2012; Wu et al., 2014). This can be inferred that the catalyst could be recovered but further reused tends to decreased the capability of catalyst. This result was agreed with Tian, S. H. et al. (2011). They reported that the catalyst could be recovered without loss of its performance. It illustrated the durability and stability of catalyst. Moreover, the use of this catalyst was interesting because it could be reused different from ferrous ion in Fenton process which required adding the catalyst every times. The disadvantage of Fenton process tends to be complicated in real practical.

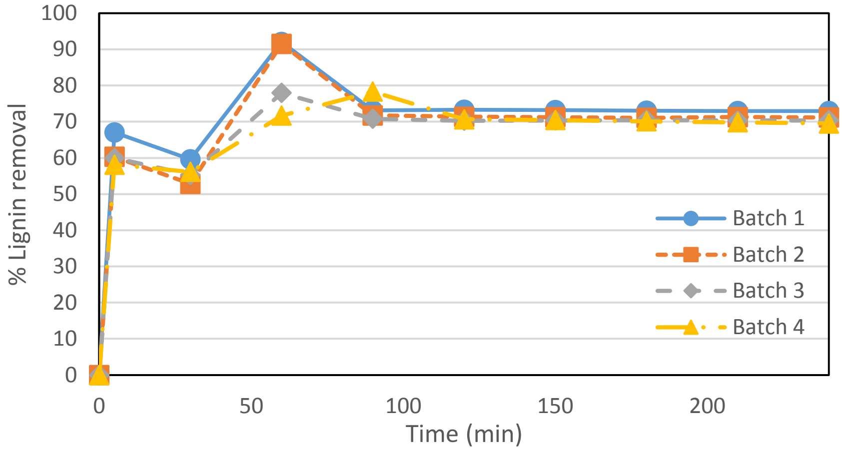


*Figure 4.29 Lignin removal after 4 recycling times of catalyst.*

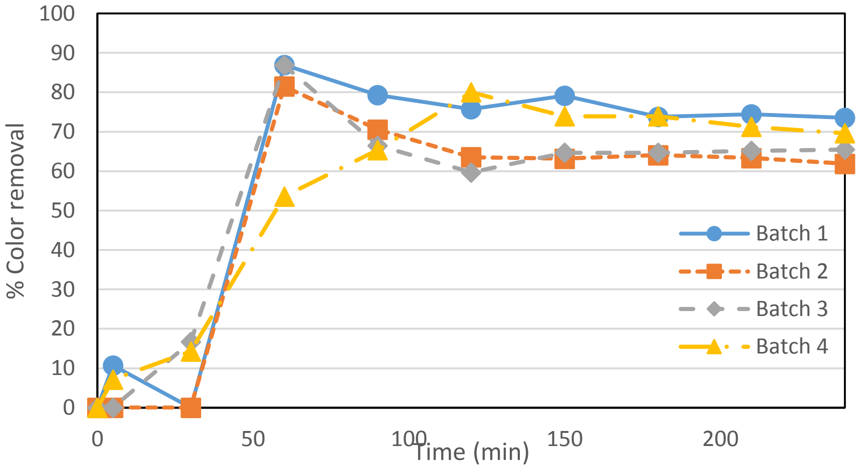


*Figure 4.30 Color removal after 4 recycling times of catalyst*

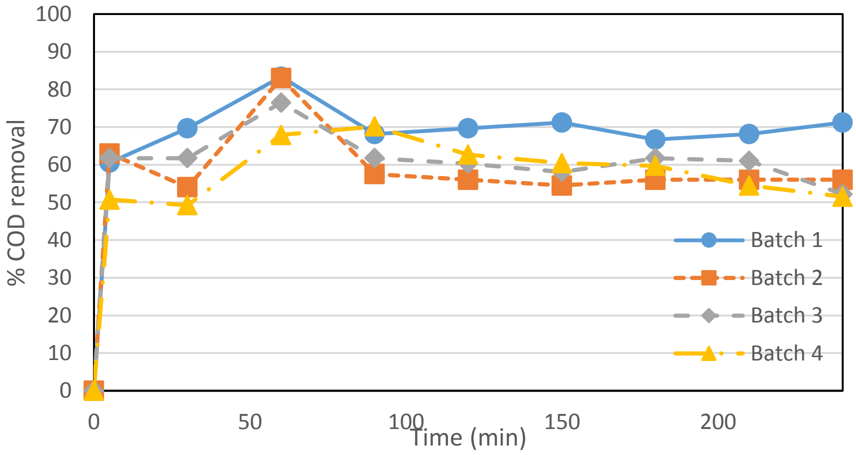
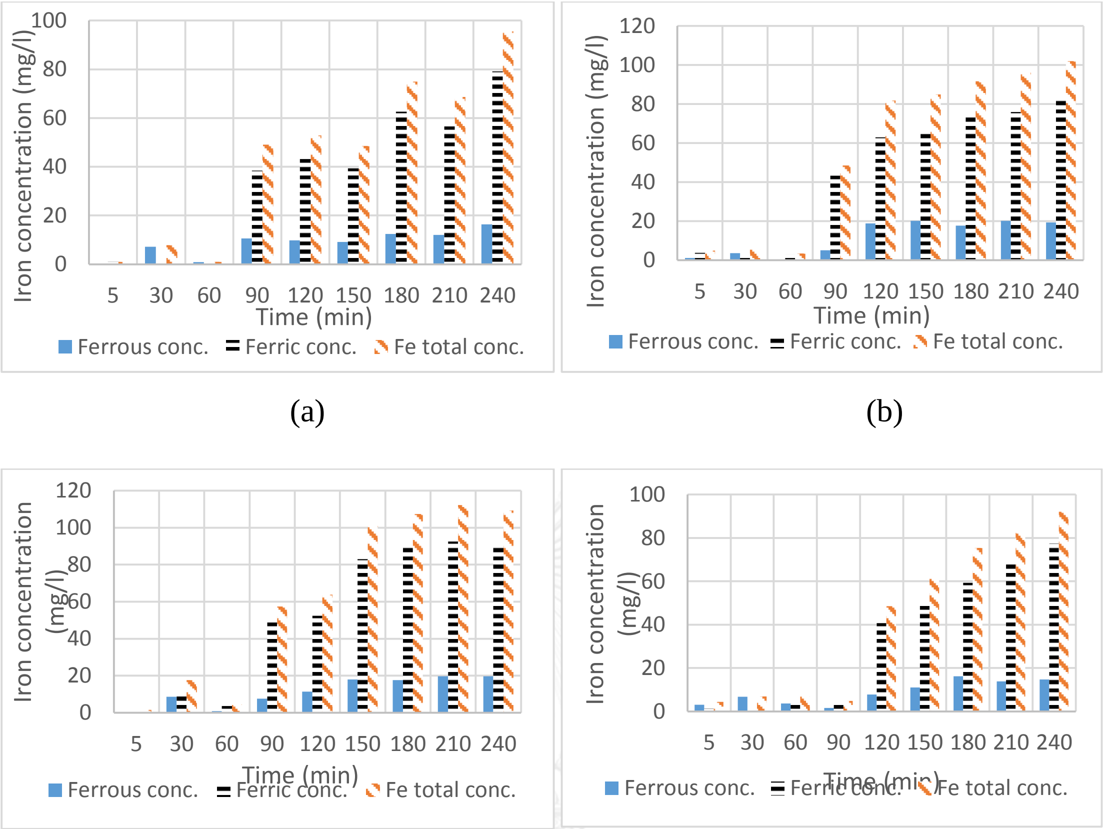


*Figure 4.31 COD removal after 4 recycling times of catalyst*



(a) (b)

(c) (d)

*Figure 4.32 Iron concentration after (a) the first run (b) the second run (c) the third run and (d) the fourth run*

### 4.5. De-colorization and lignin removal of real pulping wastewater in a batch reactor with homogeneous Fenton and heterogeneous Fenton-like reaction.

In this part, the optimum conditions obtained form part 4.4 were used to study the performance of Fenton process and heterogeneous Fenton-like process for treating pulping wastewater.

*Table 4.4 Characteristic of pulping wastewater*

| **Parameter** | **Value** |
|---|---|
| pH | 7.3 |
| COD | 1500-3000 mg/l $O_2$ |
| Color | 6000-7000 Pt-co unit |
| Lignin | 900 mg/l |

### 4.5.1. Homogeneous Fenton reaction

In this part, the optimum condition selected from part 4.4.1.1-4.4.1.3 was used to treat pulping wastewater to study the performance of homogeneous Fenton process for lignin, color and COD removal.

The initial lignin, color and COD concentration as show in Table 4.4. Initial $Fe^{2+}$ dosage was 400 mg/l (from part 4.4.1.3), initial pH was adjusted to 3 (from part 4.4.1.2) and $Fe^{2+}$:$H_2O_2$ ratio of 1:2.5 (from part 4.4.1.1). The results of lignin, color and COD removal efficiencies show in Figure 4.33 and Appendix B3-1. The results show that 81%, 87%, 86% were achieved for lignin, color and COD removal, respectively. This indicated that Fenton process show high performance for wastewater treatment.

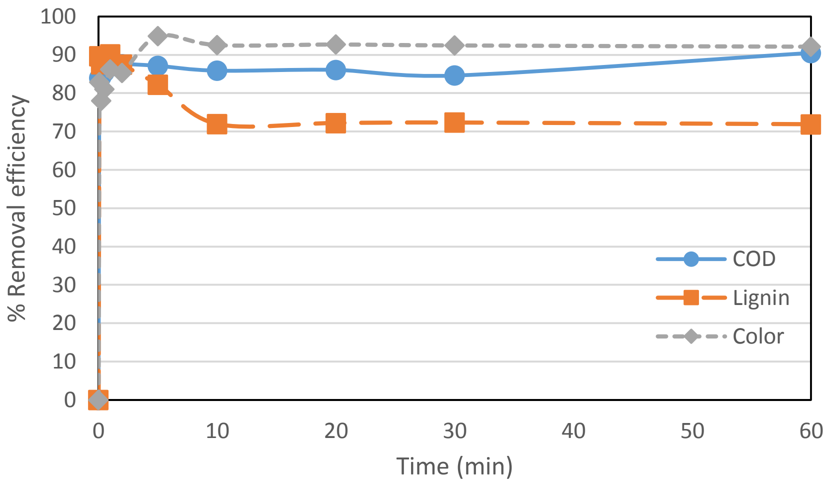


*Figure 4.33 Lignin, color and COD removal of pulping wastewater by Fenton process*

### 4.5.2. Heterogeneous Fenton-like reaction

In this part, the optimum condition selected from part 4.4.2.1-4.4.2.3 was used to treat pulping wastewater to study the performance of heterogeneous Fenton-like process for lignin, color and COD removal.

The initial lignin, color and COD concentration as show in Table 4.4. Initial $Fe^{3+}$ dosage was 2 g/l (from part 4.4.2.3), pH was used at initial pH and $Fe^{3+}$:$H_2O_2$ ratio of 1:10 (from part 4.4.2.1). The results of lignin, color and COD removal efficiencies show in Figure 4.34 and Appendix B3-2. The results show that 73%, 83%, 47% were achieved for lignin, color and COD removal, respectively. This indicated that heterogeneous Fenton-like process show high performance for wastewater treatment.

However, the removal efficiencies was slower and not higher than in Fenton process as at the first stage, ferric ion on solid catalyst has to be changed to ferrous ion to react with $H_2O_2$ and also the limited surface of the solid catalyst. From the graph, the reaction constant after 120 minutes in heterogeneous Fenton-like process while the reaction constant after 20 minutes in Fenton process.

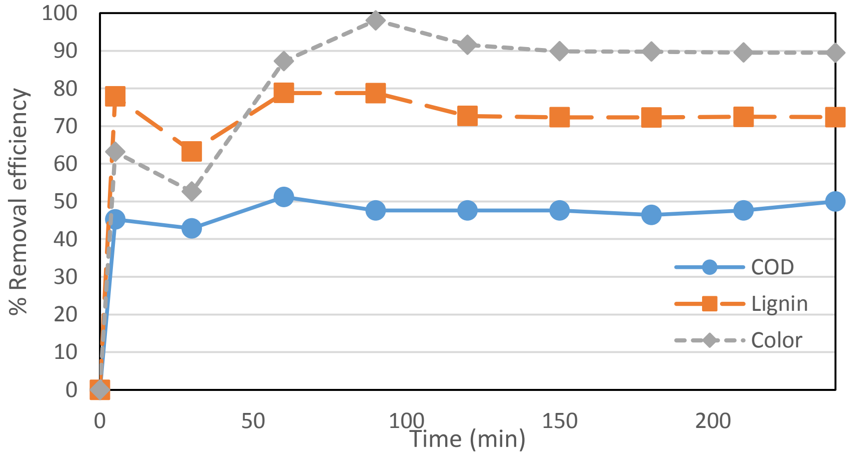


*Figure 4.34 Lignin, color and COD removal of pulping wastewater by heterogeneous Fenton-like process*

Heterogeneous Fenton-like process show several advantages such as not required sludge separation step, could be applied in wide range of pH and was able to reuse several times. However, there was some drawbacks such as require more reaction time than in Fenton process and the reaction occur at the surface of catalyst that may limit the reaction rate. From the results of applying of Fenton process using ferrous sulfate and heterogeneous Fenton-like process using iron molybdate for pulping wastewater treatment, these two treatment techniques show high performance of pulping wastewater treatment. This can be inferred that Fenton process using ferrous sulfate and heterogeneous Fenton-like process using iron molybdate were capable of treating pulping wastewater efficiently.

### 4.6 Comparison of homogeneous and heterogeneous Fenton-like process

All experiment used initial lignin concentration was 910 mg/l. The optimum ratio of Fenton process was initial pH of 3, $Fe^{2+}$:$H_2O_2$ ratio was 1:2.5 and $Fe^{2+}$ dosage of 400 mg/l. The optimum ratio of heterogeneous Fenton-like process was initial pH of 8, $Fe^{3+}$:$H_2O_2$ ratio was 1:10 and $Fe^{3+}$ dosage of 2 g/l. The results of Fenton process and heterogeneous Fenton-like process show in Figure 4.35 that Fenton process using ferrous sulfate could achieve the removal efficiency higher than in heterogeneous Fenton–like process using iron molybdate. When considered the heterogeneous Fenton-like process, the main mechanism was oxidation process. While in Fenton process, it could be seen that the mechanism was oxidation combine with iron coagulation. The optimum Fe:$H_2O_2$ ratio in heterogeneous Fenton-like process (1:10) was higher than in Fenton process (1:2.5) because ferric can change to ferrous by another molecule of $H_2O_2$. Moreover, heterogeneous Fenton-like process produce low sludge after treatment while iron precipitation occur at every Fe:$H_2O_2$ ratio in Fenton process, so, it would produce high amount of iron sludge. The reaction time in heterogeneous Fenton-like process (constant at 90 minutes) was slower than in Fenton process (constant at 20 minutes) because the solid form of ferric ion in solid catalyst and the reaction occur at the surface of catalyst can react slower than the soluble form of ferrous ion in solution.

Liu et al. (2011) have demonstrated that Fenton reaction could reach 92% in 20 minutes while Fenton-like reaction achieve 75% in 20 minutes for decolorization of Reactive Black 5 with 0.05 mmol/l of $Fe^{2+}$ and $Fe^{3+}$. While Fan et al. (2009) showed the molar ratio of $Fe^{2+}$: $H_2O_2$ was 1:25 and $Fe^{3+}$: $H_2O_2$ was 1:50 were achieve 97% and 96%, respectively at pH of 5 in 15 minutes for degradation of crystal violet. According to these other researches, the optimum ratio of $Fe^{3+}$: $H_2O_2$ was higher than $Fe^{2+}$: $H_2O_2$

ratio and the removal efficiency in Fenton-like was lower than in Fenton process. Therefore, the result in this research was agree with the others.

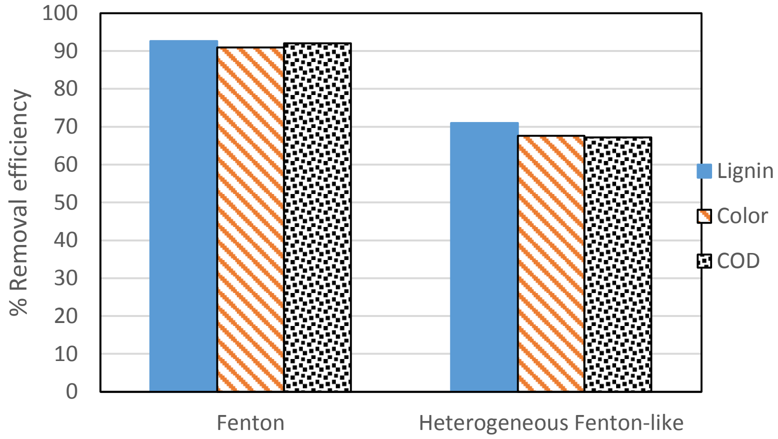


*Figure 4.35 Comparison the removal efficiency of lignin, color and COD by Fenton and heterogeneous Fenton-like process*

Moreover, Fenton and heterogeneous Fenton-like process show the different of initial pH at initial pH of 3 and 8, respectively. The result was in accordance with several researches, Torrades et al. (2011) demonstrated that at pH of 3 was the optimum pH for treatment of black liquor and Pérez et al. (2002) showed more than 90% of color removal was achieved at pH about 2.8 for removal of organic contaminants in pulp effluent. In addition, Chu et al. (2012) investigated the treatment of coking wastewater by iron powder and found that 95% of total phenol was achieved at pH around 6.5. According to these researches, the initial pH in this research was different from the others due to the different of characteristics of wastewaters and the types of catalyst.

From several researches and the results of the experiment, it can be concluded that heterogeneous Fenton-like process was lower removal efficiency than in Fenton process due to the main mechanism in heterogeneous Fenton-like process mostly from oxidation while iron coagulation combine with oxidation in Fenton process can help to treat wastewater. Another is the solid catalyst in heterogeneous Fenton-like process produce low amount of iron sludge while soluble form of catalyst in Fenton process that has to be adjusted pH to neutralize the solution, then iron sludge occur every time.

Moreover, heterogeneous Fenton-like process capable of applying at neutral pH due to the solid characteristic of catalyst which different from soluble iron that have to be apply in acidic condition to protect the change of ferrous to ferric sludge at higher pH. Moreover, solid catalyst in heterogeneous Fenton-like process show capability to be recycling several times. By these reasons, heterogeneous Fenton-like process can overcome Fenton process. Furthermore, the optimum Fe:$H_2O_2$ ratio, initial pH and dose of Fe that obtained from this research was different from others research because of characteristic of wastewater and type of catalyst. Thus, it is necessary to determine the Fe:$H_2O_2$ ratio, initial pH and Fe dosage of each wastewater.

# CHAPTER 5
# CONCLUSION AND SUGGESTION

## 5.1 Conclusion

This research study the used of Fenton process and heterogeneous Fenton-like process for lignin and color removal in synthetic wastewater and real wastewater with initial lignin concentration of 910 mg/l. The catalyst in Fenton process was ferrous sulfate and in heterogeneous Fenton-like process was iron molybdate. However, iron molybdate necessary to be synthesized and found its characteristic before used. Iron molybdate was characterized by SEM-EDS, XRD and BET. Scanning Electron Microscope (SEM) analyzed the morphology of iron molybdate. The quantity of component analyzed by Energy Dispersive Spectroscopy (EDS). The crystal lattice analysis measured by X-ray diffractometer (XRD). The BET surface area was determined with a Surface Area and Porosity Analyzer. This research determined the optimum condition for each of treatment techniques and investigated the removal efficiency of lignin and color. The result of each treatment parts were summarized as follow:

5.1.1 The iron molybdate was synthesized and found its characteristic by SEM-EDS, XRD and BET. The results of iron molybdate analysis can summarize show in table below:

| Analysis | Result |
|---|---|
| SEM | 500 nm |
| EDS | Mo/Fe = 1.7 |
| XRD | Monoclinic $Fe_2(MoO_4)_3$ |
| BET | 4.11 $m^2/g$ |

5.1.2 The treatment of synthetic wastewater by Fenton process can summarize the optimum condition and the removal efficiency at optimum condition in table below:

| **Operating condition** | **Value** | **Parameter** | **% removal** |
|---|---|---|---|
| **pH** | 3 | **Lignin** | 90 |
| **$Fe^{2+}$ dosage** | 400 mg/l | **Color** | 92 |
| **$Fe^{2+}:H_2O_2$ ratio** | 1:2.5 | **COD** | 90 |

The treatment of synthetic wastewater by heterogeneous Fenton-like process can summarize the optimum condition and the removal efficiency at optimum condition in table below:

| **Operating condition** | **Value** | **Parameter** | **% removal** |
|---|---|---|---|
| **pH** | 8 | **Lignin** | 71 |
| **$Fe^{3+}$ dosage** | 2 g/l | **Color** | 67 |
| **$Fe^{3+}:H_2O_2$ ratio** | 1:10 | **COD** | 67 |

It can be concluded that the removal efficiencies of heterogeneous Fenton-like process was comparatively lower than in Fenton process because the main mechanism was oxidation process. The different between heterogeneous Fenton-like process and Fenton process were the phase of catalyst, the mechanism of its reaction and the characteristic of catalyst. Moreover, the advantages of heterogeneous Fenton-like process were capable of applying at neutral pH and low iron sludge produced. From other several researches e.g. Pérez et al. (2002), Torrades et al. (2011), Chu et al. (2012) and Mammeri et al. (2014) showed different Fe:$H_2O_2$ ratio, initial pH and Fe dose because of different characteristics of wastewater, types of catalyst and different treatment techniques. Therefore, it is necessary to determine each of factors.

5.1.3 Iron molybdate could be reused but further reused tend to decrease the durability of catalyst as catalytic activity of catalyst decrease. At this point, this catalyst could overcome the disadvantages of Fenton process.

5.1.4 The important factors for Fenton and heterogeneous Fenton-like process in removal of lignin were pH, Fe:$H_2O_2$ ratio and concentration of iron.

5.1.5 Fenton process and heterogeneous Fenton-like process showed high performance of pulping wastewater treatment. This means that the two treatment techniques could treat wastewater from pulp industry efficiently.

## 5.2 Suggestion

1. Step feed of Fenton and heterogeneous Fenton-like process should be taken into account for improve their performance.
2. Reuse of iron molybdate should be further investigated.
3. The pH of solution should be controlled along with the reaction time in heterogeneous Fenton-like process.

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# APPENDIX

# APPENDIX A-1

## Chemical Oxygen Demand (COD) by Closed reflux, titrimetric method

### Apparatus

1. Digestion tube size 20×150 mm with TFE-lined screw caps.

2. Oven for heat at 150 °C

3. Burette

4. Elemental Flask

### Reagent

1. Standard potassium dichromate digestion solution, 0.0167 M (0.1N): Firstly dried 4.913 g of $K_2Cr_2O_7$ at 150°C for 2 hours then add $K_2Cr_2O_7$ to 500 ml distilled water. Add 167 ml of conc. $H_2SO_4$ and 33.3 g of $HgSO_4$. Dissolve and cool to room temperature. Dilute to 1000 ml.

2. Sulfuric acid reagent: Add 22 g of $Ag_2SO_4$ reagent to 1 liter of conc. $H_2SO_4$. Leave for 1 to 2 day to dissolve.

3. Ferroin indicator solution: Dissolve 1.485 g of 1, 10-phenanthroline monohydrate and 0.695 g of $FeSO_4 \cdot 7H_2O$ in distilled water and dilute to 100 ml or can purchase this solution

4. Standard ferrous ammonium sulfate titrant (FAS), 0.1N: Dissolve 39.2 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 500 ml of distilled water then add 20 ml of conc. $H_2SO_4$. Stir and leave it cool. Dilute to 1000 ml.

For standardize solution: Add 50 ml of distilled water into elemental flask then pipet 5 ml of digestion solution. Add 15 ml of conc. $H_2SO_4$ in to solution. Cool and add 2-3 drops of ferroin indicator and titrate with FAS until color of solution change from green to red-brown.

Normality of FAS solution;

$$\frac{\text{ml of } K_2Cr_2O_7 \text{ solution titrated x 0.1}}{\text{ml of FAS used in titration,}}$$

**Procedure**

Add 5 ml of sample into digestion tube and add 3 ml of $K_2Cr_2O_7$ solution. Then add 7 ml of sulfuric acid reagent into digestion tube. Total volume equals to 15 ml. Seal with screw caps and shake carefully. Put digestion tubes into test tube rack. Put digestion tubes in oven already preheated to 150°C and reflux for 2 hours. Cool to room temperature. Add 0.05-0.10 ml (1 to 2 drops) of ferroin indicator. Shake rapidly while titrating with standardized 0.1N FAS until color change from blue-green to reddish brown. Also, titrate 5 ml of distilled water at the same lot of sample for blank.

$$\text{COD as mg/l } O_2 = \frac{(A-B) \text{ x N x } 8000}{\text{ml. Sample}}$$

Where:

A = ml FAS used for blank,

B = ml FAS used for sample,

N = normality of FAS, and 8000 = milli equivalent weight of oxygen × 1000 ml/l

# APPENDIX A-2

## Platinum Cobalt standard

### Apparatus

Spectrophotometer at wavelength 475 nm.

### Reagent

Standard chloroplatinate solution:

1. Dissolve 0.1246 g of potassium chloroplatinate ($K_2PtCl_6$), 0.1 g of crystalline cobaltous chloride ($CoCl_2.H_2O$) and 10 ml of conc. HCl together.

2. Dilute with distilled water to 100 ml. This standard solution is equal to 500 color unit.

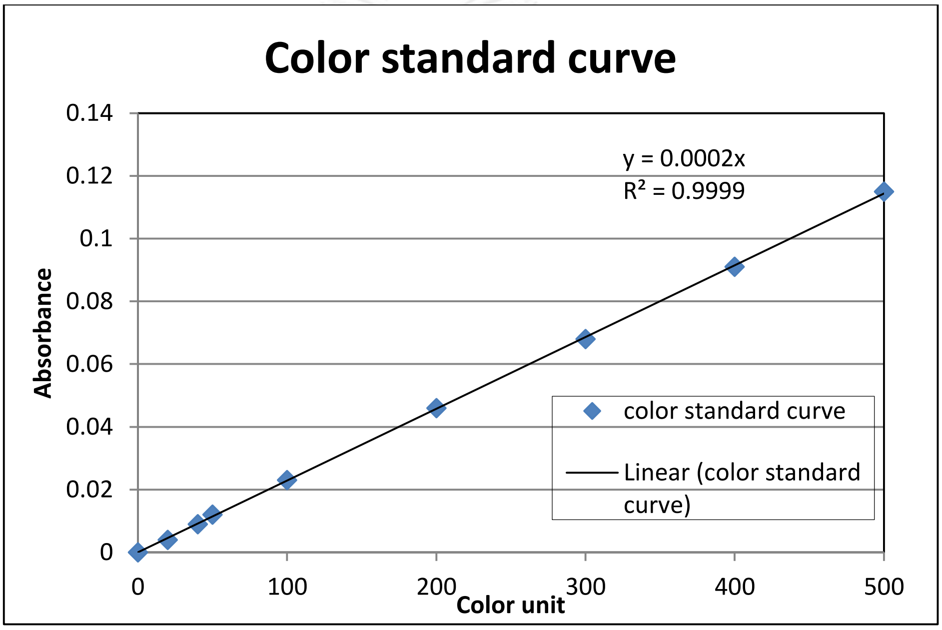
### Preparation of Standard

Preparation of standard color solution concentration of 0-500 color unit.

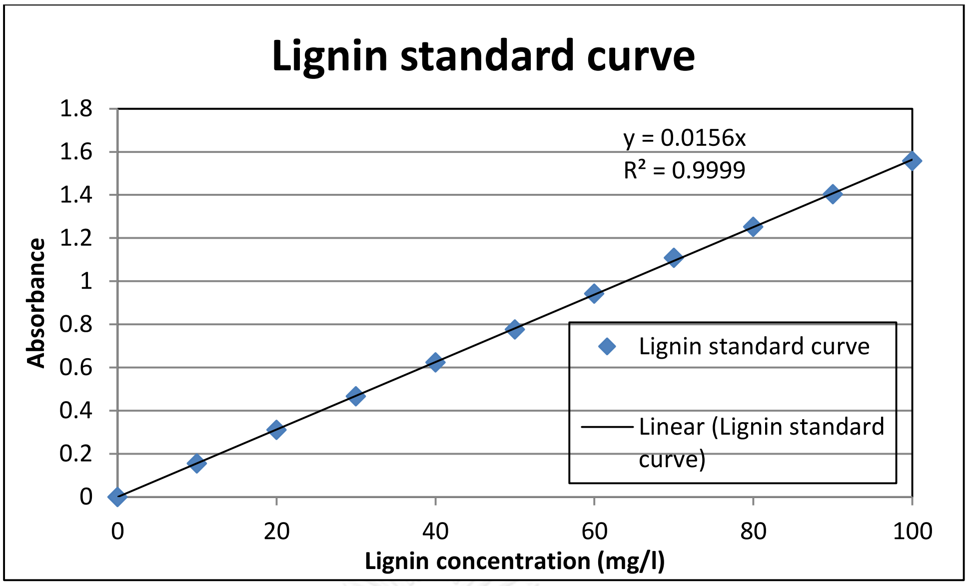
| Standard color solution conc. (color unit) | Volume of standard color solution 500 unit (ml) |
|---|---|
| 0 | - |
| 10 | 0.5 |
| 20 | 1 |
| 30 | 1.5 |
| 40 | 2 |
| 50 | 2.5 |
| 100 | 5 |
| 150 | 7.5 |
| 200 | 10 |
| 250 | 12.5 |
| 300 | 15.0 |

| | |
|---|---|
| 350 | 17.5 |
| 400 | 20.0 |
| 450 | 22.5 |
| 500 | 25.0 |

Prepare standard color solution 0-500 color unit following from Table and pipatte the solution for each concentration, dilute with distilled water to 25 ml. Adsorption measurement at wavelength 475 nm.



Color standard curve derived by Pt-Co method



Lignin standard curve derived at 280 nm with spectrophotometer

# APPENDIX A-3

## Phenanthroline Method

### Apparatus

1. Spectrophotometer use at wavelength 510 nm.

2. Nessler tubes 100 ml.

3. Beaker 250 ml.

4. Hot plate

### Reagents

1. Conc. hydrochloric acid (HCl)

2. Hydroxylamine solution: Dissolve 10 g of hydroxylamine solution ($NH_2OH \cdot HCl$) in 100 ml of distilled water.

3. Ammonium acetate buffer solution: Dissolve 250 g of ammonium acetate solution ($NH_4C_2H_3O_2$) in 150 ml of distilled water. Then add 700 ml of conc. acetic acid (glacial grade).

4. Phenanthroline solution: Dissolve 100 mg of 1, 10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) in 100 ml of distilled water. Stir and heat at 80°C. If the solution appears in dark color, discard it. Or add 2 drops of conc. HCl to the solution. (A 1 ml of this solution is enough for Fe not more than 100 µg)

5. Stock iron solution: add 20 ml of conc. $H_2SO_4$ to 50 ml of distilled water slowly, let it to dissolve 1.404 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$). Dilute

with distilled water to 1000 ml, then mix. A 1.00 ml of this solution is equal to 200 µg Fe.

6. Standard iron solutions: Prepare daily for use by one of these methods;

6.1 Pipet 50.00 ml of stock iron solution into 1000 ml of volumetric flask. Dilute to 1000 ml with distilled water; A 1.00 ml of this solution is equal to 10.0 µg Fe.

Or 6.2 Pipet 5.00 ml of stock iron solution into 1000 ml of volumetric flask. Dilute to 1000 ml with distilled water; A 1.00 ml of this solution is equal to 1.00 µg Fe.

**Procedure**

1. Total iron:

1.1 Measure 50.0 ml of sample into 250 ml of beaker. (If this sample contains more than 200 µg of iron, use a small portion and dilute to 50.0 ml with distilled water).

1.2 Then add 2 ml of conc. HCl and 1 ml of hydroxylamine solution ($NH_2OH{\cdot}HCl$). Add a few glass beads and heat to boiling for sure that all of the iron is dissolved. Continue boiling until volume is reduced to 15 to 20 ml. Cool to room temperature.

1.3 pour to 50 ml of nessler tube, add 10 ml of acetate buffer solution ($NH_4C_2H_3O_2$) and add 4 ml of phenanthroline solution. Dilute to 50 ml with distilled water. Mix and leave for 10-15 minutes for maximum color.

1.4 Measurement at wavelength of 510 nm with spectrophotometer.

1.5 use distilled water as blank instead of sample, follows step 1-3.

1.6 Prepare a standard curve with standard iron solution at concentration of 10, 20, 30, 40, 50 and 60 µg by

1.6.1 Dilution of stock iron solution at 1 ml of this solution is equal to 10.0 µg for 1, 2, 3, 4, 5, and 6 ml.

1.6.2 Measure to 50 ml of nessler tube, dilute with distilled water to 50 ml.

1.6.3 Following step 1-4

1.6.4 Plot standard curve in a relation of Fe concentration (X-axis) and absorbance (Y-axis).

$$\text{Calculation; Fe (mg/l)} = \boxed{\frac{\mu\text{g Fe from graph}}{\text{Volume of sample (ml.)}}}$$

2. Ferrous iron:

2.1 add 2 ml of conc. HCl into 100 ml of bottle. Fill water sample into bottle directly from sampling source and stop.

2.2 Withdraw 50 ml of sample from bottle into 100 ml of nessler tube, add 20 ml of phenanthroline solution and 10 ml of acetate buffer solution ($NH_4C_2H_3O_2$). Stir and dilute to 100 ml.

2.3 Measure color intensity within 5-10 minutes at wavelength of 510 nm. Do not let sample expose to light.

2.4 Use distilled water as blank with adding of 1 ml of conc. HCl per 100 ml of sample, follows step 2-3

2.5 Prepare a standard curve with standard iron solution at concentration of 10, 20, 30, 40 and 50 µg by

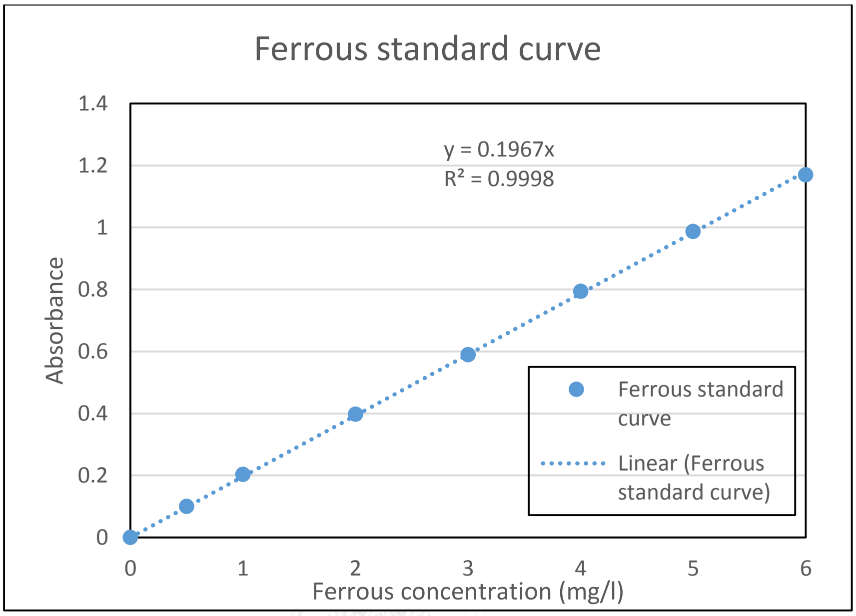
2.5.1 Dilution of stock iron solution at 1 ml of this solution is equal to 10.0 µg for 1, 2, 3, 4 and 5 ml.

2.5.2 Measure to 50 ml of nessler tube, add 1 ml of conc. HCl and dilute with distilled water to 50 ml.

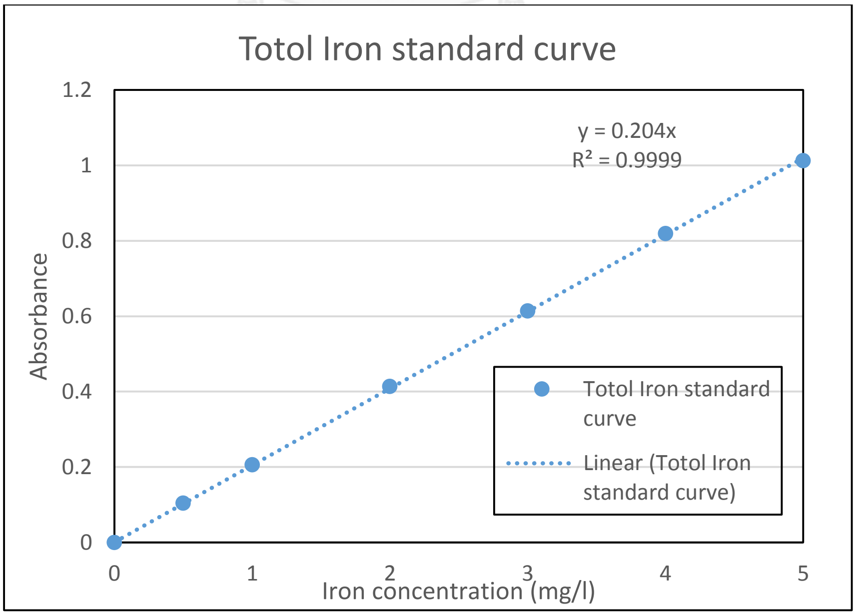
2.5.3 Following step 2-3

2.5.4 Plot standard curve in a relation of Fe concentration (X-axis) and absorbance (Y-axis).

2.6 Calculate ferric iron by $Fe^{3+}$ = Total Fe – $Fe^{2+}$



Ferrous standard curve derived at 510 nm with spectrophotometer



Total iron standard curve derived at 510 nm with spectrophotometer

# APPENDIX B-1

## Results of Fenton process part

Appendix 1-1. The results of removal efficiency in varied $Fe^{2+}$:$H_2O_2$ ratio.

Table 1. Lignin removal at pH of 3 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | Lignin concentration (mg/l) | | | | | | | Lignin removal efficiency (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{2+}$:$H_2O_2$ | | | | | | | $Fe^{2+}$:$H_2O_2$ | | | | | | |
| | 1:0.6 | 1:1 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 | 1:0.6 | 1:1 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 |
| 0 | 917.94 | 930.76 | 908.97 | 916.66 | 900.00 | 916.66 | 907.69 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.083 | 50.64 | 33.54 | 50.51 | - | 121.28 | 90.38 | 47.94 | 94.48 | 96.34 | 94.44 | - | 86.52 | 90.13 | 94.71 |
| 0.25 | 80.76 | 32.26 | 40.06 | - | 69.74 | 121.15 | 58.78 | 91.20 | 96.48 | 95.59 | - | 92.25 | 86.78 | 93.52 |
| 0.5 | 52.99 | 32.90 | 42.88 | 343.58 | 66.85 | 64.87 | 52.37 | 94.22 | 96.41 | 95.28 | 62.51 | 92.57 | 92.92 | 94.23 |
| 1 | 78.84 | 39.52 | 78.14 | 83.58 | 47.88 | 73.91 | 50.51 | 91.41 | 95.69 | 91.40 | 90.88 | 94.67 | 91.93 | 94.43 |
| 2 | 79.27 | 34.82 | 31.53 | 107.94 | 31.02 | 48.58 | 50.89 | 91.36 | 96.20 | 96.53 | 88.22 | 96.55 | 94.69 | 94.39 |
| 5 | 61.32 | 51.70 | 38.84 | 116.98 | 30.32 | 55.57 | 73.84 | 93.31 | 94.36 | 95.72 | 87.23 | 96.63 | 93.93 | 91.86 |
| 10 | 123.50 | 86.32 | 79.93 | 61.79 | 61.28 | 65.44 | 105.64 | 86.54 | 90.59 | 91.20 | 93.25 | 93.19 | 92.86 | 88.36 |
| 20 | 153.52 | 188.88 | 129.10 | 164.67 | 177.05 | 58.26 | 115.89 | 83.27 | 79.42 | 85.79 | 82.03 | 80.32 | 93.64 | 87.23 |
| 30 | 183.54 | 176.92 | 92.43 | 186.92 | 141.92 | 92.43 | 121.79 | 80.00 | 80.72 | 89.83 | 79.60 | 84.23 | 89.91 | 86.58 |
| 60 | 189.10 | 180.12 | 99.87 | 224.67 | 138.07 | 239.35 | 247.30 | 79.39 | 80.37 | 89.01 | 75.48 | 84.65 | 73.88 | 72.75 |

Table 2. Color removal at pH of 3 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | Color (color unit) | | | | | | | Color removal efficiency (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{2+}$:$H_2O_2$ | | | | | | | $Fe^{2+}$:$H_2O_2$ | | | | | | |
| | 1:0.6 | 1:1 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 | 1:0.6 | 1:1 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 |
| 0 | 3000 | 3000 | 2700 | 2800 | 2700 | 2900 | 3100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.083 | 350 | 215 | 295 | 400 | 900 | 720 | 340 | 88 | 92 | 89 | 85 | 66 | 75 | 89 |
| 0.25 | 565 | 220 | 265 | 400 | 490 | 1010 | 390 | 81 | 92 | 90 | 85 | 81 | 65 | 87 |
| 0.5 | 420 | 300 | 335 | 440 | 660 | 505 | 390 | 86 | 90 | 87 | 84 | 75 | 82 | 87 |
| 1 | 580 | 275 | 470 | 335 | 345 | 660 | 365 | 80 | 90 | 82 | 88 | 87 | 77 | 88 |
| 2 | 625 | 240 | 205 | 410 | 175 | 360 | 380 | 79 | 92 | 92 | 85 | 93 | 87 | 87 |
| 5 | 475 | 400 | 190 | 455 | 190 | 410 | 600 | 84 | 86 | 92 | 83 | 92 | 85 | 80 |
| 10 | 370 | 225 | 145 | 350 | 510 | 510 | 915 | 87 | 92.5 | 94 | 87 | 81 | 82 | 70 |
| 20 | 340 | 270 | 250 | 480 | 290 | 385 | 855 | 88 | 91 | 90 | 82 | 89 | 86 | 72 |
| 30 | 305 | 225 | 120 | 200 | 75 | 510 | 710 | 89 | 92 | 95 | 92 | 97 | 82 | 77 |
| 60 | 330 | 235 | 165 | 265 | 60 | 185 | 280 | 89 | 92 | 93 | 90. | 97 | 93 | 90 |

Table 3. COD removal at pH of 3 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | COD (mg/l) | | | | | | | COD removal efficiency (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{2+}$:$H_2O_2$ | | | | | | | $Fe^{2+}$:$H_2O_2$ | | | | | | |
| | 1:0.6 | 1:1 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 | 1:0.6 | 1:1 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 |
| 0 | 1165.0 | 862.8 | 1251.1 | 1205.6 | 1189.1 | 1202.8 | 1228.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 0.083 | 66.8 | 48.2 | 154.8 | 881.9 | 83.6 | 85.3 | 86.6 | 94.2 | 94.4 | 87.6 | 26.8 | 92.9 | 92.9 | 92.9 |
| 0.25 | 46.5 | 50.1 | 130.0 | 444.0 | 82.3 | 108.6 | 91.8 | 96.0 | 94.1 | 89.6 | 63.1 | 93.0 | 90.9 | 92.5 |
| 0.5 | 53.9 | 53.9 | 102.5 | 196.4 | 81.0 | 89.2 | 76.3 | 95.3 | 93.7 | 91.8 | 83.7 | 93.1 | 92.5 | 93.7 |
| 1 | 61.3 | 48.2 | 89.5 | 92.0 | 81.0 | 97 | 89.2 | 94.7 | 94.4 | 92.8 | 92.3 | 93.1 | 91.9 | 92.7 |
| 2 | 61.3 | 52.0 | 92.1 | 86.2 | 83.6 | 89.2 | 95.7 | 94.7 | 93.9 | 92.6 | 92.8 | 92.9 | 92.5 | 92.2 |
| 5 | 64.9 | 78.6 | 76.4 | 82.4 | 78.4 | 89.2 | 100.8 | 94.4 | 90.8 | 93.8 | 93.1 | 93.4 | 92.5 | 91.7 |
| 10 | 68.6 | 63.4 | 88.2 | 55.8 | 77.7 | 93.1 | 85.3 | 94.1 | 92.6 | 92.9 | 95.3 | 93.4 | 92.2 | 93.0 |
| 20 | 72.3 | 74.8 | 96.0 | 63.4 | 43.1 | 81.4 | 118.9 | 93.7 | 91.3 | 92.3 | 94.7 | 96.3 | 93.2 | 90.3 |
| 30 | 64.9 | 74.8 | 101.9 | 67.2 | 70.5 | 93.1 | 95.7 | 94.4 | 91.3 | 91.8 | 94.4 | 94.0 | 92.2 | 92.2 |
| 60 | 68.6 | 93.9 | 68.6 | 86.2 | 101.9 | 100.8 | 108.6 | 94.1 | 89.1 | 94.5 | 92.8 | 91.4 | 91.6 | 91.1 |

Appendix 1-2. The results of removal efficiency in control experiment.

Table 4. Lignin removal at pH of 2, 7 and 9.

| | Lignin concentration (mg/l) | | | Lignin removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| Time (min) | pH 2 | pH 7 | pH 9 | pH 2 | pH 7 | pH 9 |
| 0 | 902.56 | 933.33 | 946.15 | 0 | 0 | 0 |
| 0.25 | 897.44 | 928.03 | 940.78 | 0.56 | 0.5 | 1.62 |
| 10 | 893.53 | 924 | 936.69 | 1 | 0.5 | 0.54 |
| 20 | 893.53 | 924 | 936.69 | 1 | 1.3 | 2.43 |
| 30 | 893.53 | 924 | 936.69 | 1 | 0.2 | 2.43 |
| 40 | 893.53 | 924 | 936.69 | 1 | 0.3 | 1.08 |
| 50 | 900.00 | 930.68 | 943.47 | 0.28 | 0.5 | 1.62 |
| 60 | 893.53 | 924 | 936.69 | 1 | 0.2 | 0 |

Table 5. Color removal at pH of 2, 7 and 9.

| | Color (color unit) | | | Color removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| Time (min) | pH 2 | pH 7 | pH 9 | pH 2 | pH 7 | pH 9 |
| 0 | 227 | 275 | 295 | 0 | 0 | 0 |
| 0.083 | 223 | 270 | 289 | 1.79 | 1.27 | 0.91 |
| 15 | 215 | 261 | 279 | 5.08 | 1.27 | 0.06 |
| 30 | 218 | 264 | 283 | 3.98 | 1.27 | 0.02 |
| 45 | 215 | 261 | 279 | 5.08 | 1.27 | 0.02 |
| 60 | 215 | 261 | 279 | 5.08 | 0.36 | 0.07 |

Table 6. COD removal at pH of 2, 7 and 9.

|  | COD (mg/l) |  |  | COD removal efficiency (%) |  |  |
|---|---|---|---|---|---|---|
| Time (min) | pH 2 | pH 7 | pH 9 | pH 2 | pH 7 | pH 9 |
| 0 | 1213.6 | 1033.6 | 1093.6 | 0 | 0 | 0 |
| 0.25 | 1213.6 | - | 1093.6 | 0 | - | 0 |
| 10 | 1213.6 | 1013.6 | 1080.3 | 0 | 1.934985 | 1.216167 |
| 20 | 1213.6 | 1033.6 | 1093.6 | 0 | 0 | 0 |
| 30 | 1213.6 | 1026.9 | 1073.6 | 0 | 0.64822 | 1.828822 |
| 40 | 1213.6 | 1013.6 | 1093.6 | 0 | 1.934985 | 0 |
| 50 | 1213.6 | 1013.6 | 1093.6 | 0 | 1.934985 | 0 |
| 60 | 1213.6 | 993.6 | 1053.6 | 0 | 3.869969 | 3.657644 |

Table 7. Lignin, color and COD removal at pH of 3 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 916.02 | 3300 | 2652.7 | 0.00 | 0 | 0.0 |
| 1 | 102.56 | 800 | 183.1 | 88.80 | 75 | 93.0 |
| 15 | 100.00 | 650 | 287.7 | 89.08 | 80 | 89.1 |
| 30 | 112.82 | 800 | 366.1 | 87.68 | 75 | 86.1 |
| 45 | 114.10 | 850 | 313.8 | 87.54 | 74 | 88.1 |
| 60 | 122.43 | 1450 | 392.2 | 86.63 | 56 | 85.2 |

Table 8. Lignin, color and COD removal at $H_2O_2$ concentration of 1000 mg/l obtained from $Fe^{2+}$:$H_2O_2$ 1:2.5.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 974.10 | 2400 | 1132.7 | 0.00 | 0 | 0.0 |
| 0.083 | 965.13 | 2300 | 1055.7 | 0.92 | 4.16 | 6.8 |
| 0.5 | 962.82 | 2400 | 1055.7 | 1.16 | 0 | 6.8 |
| 1 | 958.97 | 2400 | 1103.6 | 1.55 | 0 | 2.5 |
| 2 | 961.28 | 2300 | 1117.1 | 1.32 | 4.16 | 1.3 |
| 5 | 958.72 | 2300 | 1055.7 | 1.58 | 4.16 | 6.8 |
| 10 | 970.87 | 2400 | 1055.7 | 0.33 | 0 | 6.8 |
| 20 | 958.72 | 2300 | 1055.7 | 1.58 | 4.16 | 6.8 |
| 30 | 962.31 | 2200 | 1132.7 | 1.21 | 8.33 | 0.0 |
| 60 | 958.46 | 2300 | 1120.1 | 1.61 | 4.16 | 1.1 |

Appendix 1-3. The results of removal efficiency in varied pH.

Table 9. Lignin removal efficiency at $Fe^{2+}$:$H_2O_2$ ratio of 1:2.5 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | Lignin concentration (mg/l) | | | Lignin removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | pH 2 | pH 3 | pH 4 | pH2 | pH 3 | pH 4 |
| 0 | 915.38 | 908.97 | 925.64 | 0.00 | 0.00 | 0.00 |
| 0.083 | 145.51 | 50.51 | 138.40 | 84.10 | 94.44 | 85.04 |
| 0.25 | 98.07 | 40.06 | 130.00 | 89.28 | 95.59 | 85.95 |
| 0.5 | 106.62 | 42.88 | 130.85 | 88.35 | 95.28 | 85.86 |
| 1 | 176.06 | 78.14 | 126.01 | 80.76 | 91.40 | 86.38 |
| 2 | 211.53 | 31.53 | 126.34 | 76.89 | 96.53 | 86.35 |
| 5 | 225.00 | 38.84 | 124.05 | 75.42 | 95.72 | 86.59 |
| 10 | 626.28 | 79.93 | 122.25 | 31.582 | 91.20 | 86.79 |
| 20 | 675.00 | 129.10 | 122.84 | 26.26 | 85.79 | 86.72 |
| 30 | 653.20 | 92.43 | 125.75 | 28.64 | 89.83 | 86.41 |
| 60 | 670.51 | 99.87 | 205.70 | 26.75 | 89.01 | 77.77 |

Table 10. Color removal efficiency at $Fe^{2+}$:$H_2O_2$ ratio of 1:2.5 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | Color (color unit) | | | Color removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | pH 2 | pH 3 | pH 4 | pH2 | pH 3 | pH 4 |
| 0 | 2800 | 2700 | 2800 | 0 | 0 | 0 |
| 0.083 | 1700 | 295 | 540 | 39 | 89 | 80 |
| 0.25 | 1170 | 265 | 315 | 58 | 90 | 88 |
| 0.5 | 1380 | 335 | 200 | 50 | 87 | 92 |
| 1 | 2765 | 470 | 170 | 1.25 | 82 | 93 |
| 2 | 940 | 205 | 180 | 66 | 92 | 93 |
| 5 | 605 | 190 | 220 | 78 | 92 | 92 |
| 10 | 1025 | 145 | 225 | 63 | 94 | 91 |
| 20 | 1020 | 250 | 440 | 63 | 90 | 84 |
| 30 | 1035 | 120 | 365 | 63 | 95 | 86 |
| 60 | 1005 | 165 | 290 | 64 | 93 | 89 |

Table 11. COD removal efficiency at $Fe^{2+}$:$H_2O_2$ ratio of 1:2.5 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | COD (mg/l) | | | COD removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | pH 2 | pH 3 | pH 4 | pH2 | pH 3 | pH 4 |
| 0 | 1215.6 | 1251.1 | 1176.8 | 0.0 | 0.0 | 0.0 |
| 0.083 | 125.3 | 154.8 | 69.8 | 89.6 | 87.6 | 94.0 |
| 0.25 | 102.7 | 130.0 | 72.4 | 91.5 | 89.6 | 93.8 |
| 0.5 | 111.5 | 102.5 | 69.8 | 90.8 | 91.8 | 94.0 |
| 1 | 110.2 | 89.5 | 67.2 | 90.9 | 92.8 | 94.2 |
| 2 | 85.2 | 92.1 | 55.5 | 92.9 | 92.6 | 95.2 |
| 5 | 130.3 | 76.4 | 58.1 | 89.2 | 93.8 | 95.0 |
| 10 | 188.6 | 88.2 | 62.0 | 84.4 | 92.9 | 94.7 |
| 20 | 201.7 | 96.0 | 28.4 | 83.4 | 92.3 | 97.5 |
| 30 | 228.0 | 101.9 | 59.4 | 81.2 | 91.8 | 94.9 |
| 60 | 221.8 | 68.6 | 77.5 | 81.7 | 94.5 | 93.4 |

Appendix 1-4. The results of removal efficiency in varied $Fe^{2+}$ dosage.

Table 12. Lignin removal efficiency at $Fe^{2+}$:$H_2O_2$ at 1:2.5 and initial pH of 3.

| Time (min) | Lignin concentration (mg/l) | | | Lignin removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | $Fe^{2+}$ dosage (mg/l) | | | $Fe^{2+}$ dosage (mg/l) | | |
| | 300 | 400 | 500 | 300 | 400 | 500 |
| 0 | 915.38 | 908.97 | 906.41 | 0.00 | 0.00 | 0.00 |
| 0.083 | 788.46 | 50.51 | 41.45 | 13.86 | 94.44 | 95.42 |
| 0.25 | 227.77 | 40.06 | 41.23 | 75.11 | 95.59 | 95.45 |
| 0.5 | 305.55 | 42.88 | 42.94 | 66.61 | 95.28 | 95.26 |
| 1 | 183.33 | 78.14 | 19.01 | 79.97 | 91.40 | 97.90 |
| 2 | 243.37 | 31.53 | 33.76 | 73.41 | 96.53 | 96.27 |
| 5 | 252.56 | 38.84 | 19.65 | 72.40 | 95.72 | 97.83 |
| 10 | 88.46 | 79.93 | 111.11 | 90.33 | 91.20 | 87.74 |
| 20 | 131.83 | 129.10 | 254.05 | 85.59 | 85.79 | 71.97 |
| 30 | 182.26 | 92.43 | 220.08 | 80.08 | 89.83 | 75.71 |
| 60 | 197.00 | 99.87 | 223.93 | 78.47 | 89.01 | 75.29 |

Table 13. Color removal efficiency at $Fe^{2+}$:$H_2O_2$ at 1:2.5 and initial pH of 3.

| Time (min) | Color (color unit) | | | Color removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | $Fe^{2+}$ dosage (mg/l) | | | $Fe^{2+}$ dosage (mg/l) | | |
| | 300 | 400 | 500 | 300 | 400 | 500 |
| 0 | 2900 | 2700 | 2800 | 0 | 0 | 0 |
| 0.083 | 2900 | 295 | 535 | 0 | 89 | 80 |
| 0.25 | 1730 | 265 | 545 | 38 | 90 | 80 |
| 0.5 | 2330 | 335 | 590 | 16 | 87 | 78 |
| 1 | 1445 | 470 | 135 | 48 | 82 | 95 |
| 2 | 1770 | 205 | 390 | 36 | 92 | 86 |
| 5 | 1790 | 190 | 160 | 36 | 92 | 94 |
| 10 | 285 | 145 | 300 | 89 | 94 | 89 |
| 20 | 460 | 250 | 390 | 83 | 90 | 86 |
| 30 | 810 | 120 | 280 | 71 | 95 | 90 |
| 60 | 800 | 165 | 320 | 71 | 93 | 88 |

Table 14. COD removal efficiency at $Fe^{2+}$:$H_2O_2$ at 1:2.5 and initial pH of 3.

| Time (min) | COD(mg/l) | | | COD removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | $Fe^{2+}$ dosage (mg/l) | | | $Fe^{2+}$ dosage (mg/l) | | |
| | 300 | 400 | 500 | 300 | 400 | 500 |
| 0 | 1110.9 | 1251.1 | 647.2 | 0.0 | 0.0 | 0.0 |
| 0.083 | 259.2 | 154.8 | 84.5 | 76.6 | 87.6 | 86.9 |
| 0.25 | 120.3 | 130.0 | 71.7 | 89.1 | 89.6 | 88.9 |
| 0.5 | 149.9 | 102.5 | 67.9 | 86.5 | 91.8 | 89.5 |
| 1 | 106.1 | 89.5 | 77.5 | 90.4 | 92.8 | 88.0 |
| 2 | 118.5 | 92.1 | 85.2 | 89.3 | 92.6 | 86.8 |
| 5 | 106.1 | 76.4 | 64.0 | 90.4 | 93.8 | 90.1 |
| 10 | 59.2 | 88.2 | 94.8 | 94.6 | 92.9 | 85.3 |
| 20 | 71.5 | 96.0 | 81.3 | 93.5 | 92.3 | 87.4 |
| 30 | 74.0 | 101.9 | 111.4 | 93.3 | 91.8 | 82.7 |
| 60 | 90.7 | 68.6 | 116.6 | 91.8 | 94.5 | 81.9 |

Appendix 1-5. The results of Iron concentration measurement.

Table 15. Total iron, ferrous ion and ferric ion concentration at pH of 3 and $Fe^{2+}$ dosage was 400 mg/l and $Fe^{2+}$:$H_2O_2$ 1:2.5.

| Time (min) | Fe total (mg/l) | Ferrous (mg/l) | Ferric (mg/l) |
|---|---|---|---|
| 0.083 | 330.8 | 14.4 | 316.3 |
| 0.5 | 356.8 | 21.0 | 335.7 |
| 1 | 345.0 | 20.0 | 325.0 |
| 5 | 357.3 | 11.4 | 345.9 |
| 10 | 324.0 | 28.9 | 295.0 |
| 20 | 312.7 | 34.3 | 278.4 |
| 30 | 334.8 | 27.4 | 307.3 |
| 60 | 349.0 | 36.8 | 312.1 |

# APPENDIX B-2

## Results of heterogeneous Fenton-like process part

Appendix 2-1. The results of removal efficiency in varied $Fe^{3+}:H_2O_2$ ratio.

Table 1. Lignin removal at pH of 8 and $Fe^{3+}$ dosage was 2 g/l.

| Time (min) | Lignin concentration (mg/l) | | | | | Lignin removal efficiency (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{3+}:H_2O_2$ | | | | | $Fe^{3+}:H_2O_2$ | | | | |
| | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 |
| 0 | 1007.69 | 906.41 | 896.15 | 923.07 | 917.94 | 0 | 0 | 0 | 0 | 0 |
| 5 | 828.20 | 424.35 | 342.30 | 394.87 | 375.64 | 17.81 | 53.18 | 61.80 | 57.22 | 59.07 |
| 30 | 943.59 | 465.38 | 170.64 | 452.56 | 107.17 | 6.36 | 48.65 | 80.95 | 50.97 | 88.32 |
| 60 | 878.20 | 560.25 | 261.47 | 101.79 | 247.11 | 12.84 | 38.18 | 70.82 | 88.97 | 73.07 |
| 90 | 875.64 | 122.88 | 263.14 | 263.84 | 253.71 | 13.10 | 86.44 | 70.63 | 71.41 | 72.36 |
| 120 | 723.46 | 250.44 | 255.89 | 262.43 | 254.87 | 28.20 | 72.36 | 71.44 | 71.56 | 72.23 |
| 150 | 809.51 | 249.23 | 259.35 | 263.84 | 252.24 | 19.66 | 72.50 | 71.05 | 71.41 | 72.52 |
| 180 | 895.51 | 253.33 | 263.91 | 260.70 | 255.96 | 11.13 | 72.05 | 70.55 | 71.75 | 72.11 |
| 210 | 865.25 | 259.55 | 259.55 | 264.87 | 253.78 | 14.13 | 71.36 | 71.03 | 71.30 | 72.35 |
| 240 | 925.90 | 258.07 | 260.44 | 264.61 | 255.25 | 8.11 | 71.52 | 70.93 | 71.33 | 72.19 |

Table 2. Color removal at pH of 8 and $Fe^{3+}$ dosage was 2 g/l.

| Time (min) | Color (color unit) | | | | | Color removal efficiency (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{3+}$:$H_2O_2$ | | | | | $Fe^{3+}$:$H_2O_2$ | | | | |
| | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 |
| 0 | 3000 | 2900 | 3200 | 2900 | 2600 | 0 | 0 | 0 | 0 | 0 |
| 5 | 3000 | 2700 | 3200 | 2900 | 2000 | 0 | 6 | 0 | 0 | 23 |
| 30 | 2990 | 2800 | 1065 | 1960 | 305 | 0.33 | 3 | 66 | 32 | 88 |
| 60 | 3000 | 2800 | 855 | 180 | 485 | 0 | 3 | 73 | 93 | 81 |
| 90 | 2600 | 275 | 1105 | 785 | 720 | 13.33 | 90 | 65 | 72 | 72 |
| 120 | 2000 | 845 | 915 | 685 | 845 | 33.33 | 70. | 71 | 76 | 67 |
| 150 | 2600 | 880 | 1230 | 725 | 835 | 13.33 | 69 | 61 | 75 | 67 |
| 180 | 2800 | 1075 | 1090 | 700 | 735 | 6.66 | 62 | 65 | 75 | 71 |
| 210 | 2700 | 1575 | 1050 | 770 | 815 | 10 | 45 | 67 | 73 | 68 |
| 240 | 2850 | 1555 | 980 | 755 | 825 | 5 | 46 | 69 | 73 | 68 |

Table 3. COD removal at pH of 8 and $Fe^{3+}$ dosage was 2 g/l.

| Time (min) | COD (mg/l) | | | | | COD removal efficiency (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{3+}:H_2O_2$ | | | | | $Fe^{3+}:H_2O_2$ | | | | |
| | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 | 1:2.5 | 1:5 | 1:10 | 1:15 | 1:20 |
| 0 | 1205.6 | 1370.1 | 1205.6 | 1293.3 | 1176.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5 | 1053.2 | 740.6 | 329.7 | 517.3 | 431.2 | 12.6 | 45.9 | 72.6 | 59.9 | 63.3 |
| 30 | 1167.5 | 851.7 | 260.0 | 556.1 | 117.6 | 3.1 | 37.8 | 78.4 | 56.9 | 90.0 |
| 60 | 939.0 | 851.7 | 374.3 | 239.2 | 196.0 | 22.1 | 37.83 | 68.9 | 81.4 | 83.3 |
| 90 | 939.0 | 388.8 | 431.4 | 491.4 | 294.0 | 22.1 | 71.6 | 64.2 | 61.9 | 75.0 |
| 120 | 596.3 | 611.0 | 431.4 | 452.6 | 333.2 | 50.5 | 55.4 | 64.2 | 64.9 | 71.6 |
| 150 | 900.9 | 573.9 | 479.0 | 472.0 | 352.8 | 25.2 | 58.1 | 60.2 | 63.4 | 70.0 |
| 180 | 1008.8 | 666.5 | 393.3 | 472.0 | 313.6 | 16.3 | 51.3 | 67.3 | 63.4 | 73.3 |
| 210 | 900.9 | 740.6 | 469.5 | 452.6 | 372.4 | 25.2 | 45.9 | 61.0 | 64.9 | 68.3 |
| 240 | 977.1 | 629.5 | 393.3 | 472.0 | 392.0 | 18.9 | 54.0 | 67.3 | 63.4 | 66.6 |

Appendix 2-2. The results of removal efficiency in control experiment.

Table 4. Lignin, color and COD removal by adsorption of catalyst with concentration of $Fe^{3+}$ was 2 g/l at pH of 8.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 906.41 | 2900 | 1370.1 | 0 | 0 | 0 |
| 5 | 906.41 | 2900 | 1259.0 | 0 | 0 | 8.1 |
| 30 | 906.41 | 2900 | 1222.0 | 0 | 0 | 10.8 |
| 60 | 906.41 | 2900 | 1222.0 | 0 | 0 | 10.8 |
| 90 | 906.41 | 2900 | 1259.0 | 0 | 0 | 8.1 |
| 120 | 906.41 | 2900 | 1185.0 | 0 | 0 | 13.5 |
| 150 | 906.41 | 2900 | 1259.0 | 0 | 0 | 8.1 |
| 180 | 906.41 | 2900 | 1259.0 | 0 | 0 | 8.1 |
| 210 | 906.41 | 2900 | 1370.1 | 0 | 0 | 0 |
| 240 | 906.41 | 2900 | 1259.0 | 0 | 0 | 8.1 |

Table 5. Lignin, color and COD removal at $H_2O_2$ concentration of 20 g/l obtained from $Fe^{3+}$:$H_2O_2$ 1:10.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 920.51 | 2800 | 1269.3 | 0.00 | 0 | 0.0 |
| 5 | 920.51 | 2300 | 469.6 | 0.00 | 17 | 62.9 |
| 30 | 1000.00 | 1900 | 412.5 | 5.91 | 32 | 67.4 |
| 60 | 1011.53 | 1900 | 621.9 | 4.82 | 32 | 50.9 |
| 90 | 1003.84 | 1700 | 698.1 | 5.54 | 39 | 44.9 |
| 120 | 984.61 | 1900 | 736.2 | 7.35 | 32 | 41.9 |
| 150 | 1011.53 | 1800 | 926.6 | 4.82 | 35 | 26.9 |
| 180 | 976.92 | 1600 | 545.8 | 8.08 | 42 | 56.9 |
| 210 | 991.02 | 1600 | 888.5 | 6.75 | 42 | 29.9 |
| 240 | 982.05 | 1600 | 660.0 | 7.59 | 42 | 47.9 |

Appendix 2-3. The results of removal efficiency in varied pH.

Table 6. Lignin removal efficiency at $Fe^{3+}$:$H_2O_2$ ratio of 1:10 and $Fe^{3+}$ dosage was 2 g/l.

| Time (min) | Lignin concentration (mg/l) | | | Lignin removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | pH 4 | pH 6 | pH 8 | pH 4 | pH 6 | pH 8 |
| 0 | 975.64 | 925.64 | 896.15 | 0.00 | 0.00 | 0.00 |
| 5 | 661.53 | 571.79 | 342.30 | 32.19 | 38.22 | 61.80 |
| 30 | 666.66 | 535.89 | 170.64 | 31.66 | 42.10 | 80.95 |
| 60 | 251.66 | 254.61 | 261.47 | 74.20 | 72.49 | 70.82 |
| 90 | 257.75 | 258.91 | 263.14 | 73.58 | 72.02 | 70.63 |
| 120 | 257.30 | 258.01 | 255.89 | 73.62 | 72.12 | 71.44 |
| 150 | 258.71 | 255.51 | 259.35 | 73.48 | 72.39 | 71.05 |
| 180 | 257.56 | 256.02 | 263.91 | 73.60 | 72.34 | 70.55 |
| 210 | 259.42 | 257.43 | 259.55 | 73.40 | 72.18 | 71.03 |
| 240 | 258.71 | 256.41 | 260.44 | 73.48 | 72.29 | 70.93 |

Table 7. Color removal efficiency at $Fe^{3+}$:$H_2O_2$ ratio of 1:10 and $Fe^{3+}$ dosage was 2 g/l.

| Time (min) | Color (color unit) | | | Color removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | pH 4 | pH 6 | pH 8 | pH 4 | pH 6 | pH 8 |
| 0 | 3100 | 3000 | 3200 | | 0 | 0 |
| 5 | 3100 | 3000 | 3200 | 0 | 0 | 0 |
| 30 | 2500 | 1900 | 1065 | 19 | 36 | 66 |
| 60 | 330 | 590 | 855 | 89 | 80 | 73 |
| 90 | 705 | 825 | 1105 | 77 | 72 | 65 |
| 120 | 680 | 675 | 915 | 78 | 77 | 71 |
| 150 | 710 | 650 | 1230 | 77 | 78 | 61 |
| 180 | 715 | 660 | 1090 | 76 | 78 | 65 |
| 210 | 730 | 655 | 1050 | 76 | 78 | 67 |
| 240 | 695 | 605 | 980 | 77 | 79 | 69 |

Table 8. COD removal efficiency at $Fe^{3+}$:$H_2O_2$ ratio of 1:10 and $Fe^{3+}$ dosage was 2 g/l.

| Time (min) | COD (color unit) | | | COD removal efficiency (%) | | |
|---|---|---|---|---|---|---|
| | pH 4 | pH 6 | pH 8 | pH 4 | pH 6 | pH 8 |
| 0 | 1304 | 1294.8 | 1205.6 | 0.0 | 0.0 | 0.0 |
| 5 | 864 | 697.1 | 329.7 | 33.7 | 46.1 | 72.6 |
| 30 | 784 | 585.0 | 260.0 | 39.8 | 54.8 | 78.4 |
| 60 | 472 | 404.6 | 374.3 | 63.8 | 68.7 | 68.9 |
| 90 | 492 | 498.0 | 431.4 | 62.2 | 61.5 | 64.2 |
| 120 | 512 | 460.6 | 431.4 | 60.7 | 64.4 | 64.2 |
| 150 | 492 | 404.6 | 479.0 | 62.2 | 68.7 | 60.2 |
| 180 | 512 | 348.5 | 393.3 | 60.7 | 73.0 | 67.3 |
| 210 | 472 | 432.6 | 469.5 | 63.8 | 66.5 | 61.0 |
| 240 | 532 | 395.2 | 393.3 | 59.2 | 69.4 | 67.3 |

Appendix 2-4. The results of removal efficiency in varied $Fe^{3+}$ dosage.

Table 9. Lignin removal efficiency at $Fe^{3+}$:$H_2O_2$ at 1:10 and initial pH of 8.

| Time (min) | Lignin concentration (mg/l) | | | | | Lignin removal efficiency (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{3+}$ dosage (g/l) | | | | | $Fe^{3+}$ dosage (g/l) | | | | |
| | 0.5 | 1 | 2 | 2.5 | 3 | 0.5 | 1 | 2 | 2.5 | 3 |
| 0 | 905.12 | 929.48 | 896.15 | 934.61 | 924.35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5 | 600.00 | 644.87 | 342.30 | 335.89 | 433.33 | 33.71 | 30.62 | 61.80 | 64.41 | 53.12 |
| 30 | 616.66 | 629.48 | 170.64 | 86.47 | 125.83 | 31.86 | 32.27 | 80.95 | 91.24 | 86.38 |
| 60 | 594.87 | 701.28 | 261.47 | 252.30 | 190.03 | 34.27 | 24.55 | 70.82 | 73.40 | 79.44 |
| 90 | 619.23 | 608.97 | 263.14 | 255.83 | 254.23 | 31.58 | 34.48 | 70.63 | 73.02 | 72.49 |
| 120 | 616.66 | 255.70 | 255.89 | 256.21 | 256.02 | 31.86 | 72.48 | 71.44 | 72.98 | 72.30 |
| 150 | 665.38 | 263.14 | 259.35 | 253.01 | 252.11 | 26.48 | 71.68 | 71.05 | 73.33 | 72.72 |
| 180 | 605.12 | 264.80 | 263.91 | 253.46 | 255.12 | 33.14 | 71.51 | 70.55 | 73.28 | 72.39 |
| 210 | 673.07 | 268.58 | 259.55 | 256.28 | 253.20 | 25.63 | 71.10 | 71.03 | 72.97 | 72.60 |
| 240 | 547.43 | 270.89 | 260.44 | 257.37 | 255.64 | 39.51 | 70.85 | 70.93 | 72.86 | 72.34 |

Table 10. Color removal efficiency at $Fe^{3+}$:$H_2O_2$ at 1:10 and initial pH of 8.

| Time (min) | Color (color unit) | | | | | Color removal efficiency (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{3+}$ dosage (g/l) | | | | | $Fe^{3+}$ dosage (g/l) | | | | |
| | 0.5 | 1 | 2 | 2.5 | 3 | 0.5 | 1 | 2 | 2.5 | 3 |
| 0 | 3000 | 3200 | 3200 | 3200 | 2900 | 0 | 0 | 0 | 0 | 0 |
| 5 | 2900 | 3156 | 3200 | 3200 | 2600 | 3 | 1.37 | 0 | 0 | 10 |
| 30 | 3000 | 3180 | 1065 | 280 | 405 | 0 | 0.62 | 66 | 91 | 86 |
| 60 | 2900 | 3120 | 855 | 770 | 405 | 3 | 2.5 | 73 | 75 | 86 |
| 90 | 2800 | 2700 | 1105 | 1015 | 540 | 6 | 15 | 65 | 68 | 81 |
| 120 | 2800 | 845 | 915 | 975 | 675 | 6 | 73 | 71 | 69 | 76 |
| 150 | 2800 | 1655 | 1230 | 950 | 945 | 6 | 48 | 61 | 70 | 67 |
| 180 | 2500 | 1645 | 1090 | 910 | 665 | 16 | 48 | 65 | 71 | 77 |
| 210 | 2500 | 2070 | 1050 | 890 | 810 | 16 | 35 | 67 | 72 | 72 |
| 240 | 2200 | 2145 | 980 | 925 | 635 | 26 | 32 | 69 | 71 | 78 |

Table 11. COD removal efficiency at $Fe^{3+}$:$H_2O_2$ at 1:10 and initial pH of 8.

| Time (min) | COD (mg/l) | | | | | COD removal efficiency (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{3+}$ dosage (g/l) | | | | | $Fe^{3+}$ dosage (g/l) | | | | |
| | 0.5 | 1 | 2 | 2.5 | 3 | 0.5 | 1 | 2 | 2.5 | 3 |
| 0 | 1176.9 | 1224.6 | 1205.6 | 1254.5 | 1136.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5 | 827.7 | 843.8 | 329.7 | 478.5 | 392.0 | 29.6 | 31.0 | 72.6 | 61.8 | 65.5 |
| 30 | 905.3 | 786.7 | 260.0 | 200.4 | 137.2 | 23.0 | 35.7 | 78.4 | 84.0 | 87.9 |
| 60 | 827.7 | 786.7 | 374.3 | 442.9 | 225.4 | 29.6 | 35.7 | 68.9 | 64.6 | 80.1 |
| 90 | 905.3 | 710.5 | 431.4 | 539.9 | 313.6 | 23.0 | 41.9 | 64.2 | 56.9 | 72.4 |
| 120 | 827.7 | 469.5 | 431.4 | 569.0 | 421.4 | 29.6 | 61.6 | 64.2 | 54.6 | 62.9 |
| 150 | 827.7 | 602.8 | 479.0 | 569.0 | 303.8 | 29.6 | 50.7 | 60.2 | 54.6 | 73.2 |
| 180 | 750.1 | 602.8 | 393.3 | 549.6 | 333.2 | 36.2 | 50.7 | 67.3 | 56.1 | 70.6 |
| 210 | 750.1 | 621.8 | 469.5 | 491.4 | 313.6 | 36.2 | 49.2 | 61.0 | 60.8 | 72.4 |
| 240 | 711.3 | 526.6 | 393.3 | 491.4 | 392.0 | 39.5 | 56.9 | 67.3 | 60.88 | 65.5 |

Appendix 2-5. The results of Iron concentration measurement.

Table 12. Total iron, ferrous ion and ferric ion concentration at pH of 8 and $Fe^{3+}$ dosage was 2 g/l and $Fe^{3+}$:$H_2O_2$ 1:10.

| Time (min) | Fe total (mg/l) | Ferrous (mg/l) | Ferric (mg/l) |
|---|---|---|---|
| 5 | 0.9 | 0.0 | 0.9 |
| 30 | 7.8 | 7.2 | 0.6 |
| 60 | 0.9 | 0.8 | 0.1 |
| 90 | 49.0 | 10.5 | 38.4 |
| 120 | 52.9 | 9.7 | 43.1 |
| 150 | 48.5 | 9.1 | 39.3 |
| 180 | 75.0 | 12.4 | 62.5 |
| 210 | 68.6 | 11.9 | 56.6 |
| 240 | 95.5 | 16.3 | 79.2 |

Appendix 2-6. The results of recovery iron molybdate

Table 13. Lignin removal efficiency at pH of 8 and $Fe^{3+}$ dosage was 2 g/l and $Fe^{3+}$:$H_2O_2$ 1:10.

| Time (min) | Lignin concentration (mg/l) | | | | Lignin removal efficiency (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | Batch | | | | Batch | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 0 | 916.66 | 926.92 | 897.43 | 908.97 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5 | 302.56 | 367.94 | 358.97 | 380.76 | 66.99 | 60.30 | 59.99 | 58.11 |
| 30 | 370.51 | 437.17 | 401.28 | 398.71 | 59.58 | 52.83 | 55.28 | 56.13 |
| 60 | 73.07 | 78.52 | 197.82 | 257.17 | 92.02 | 91.52 | 77.95 | 71.70 |
| 90 | 246.53 | 262.05 | 262.17 | 197.11 | 73.10 | 71.72 | 70.78 | 78.31 |
| 120 | 244.87 | 265.12 | 266.79 | 266.60 | 73.28 | 71.39 | 70.27 | 70.66 |
| 150 | 245.44 | 266.60 | 265.76 | 268.65 | 73.22 | 71.23 | 70.38 | 70.44 |
| 180 | 246.98 | 267.94 | 265.19 | 271.85 | 73.05 | 71.09 | 70.45 | 70.09 |
| 210 | 248.14 | 266.089 | 266.28 | 274.35 | 72.93 | 71.29 | 70.32 | 69.81 |
| 240 | 247.62 | 267.24 | 266.15 | 277.17 | 72.98 | 71.16 | 70.34 | 69.50 |

Table 14. Color removal efficiency at pH of 8 and $Fe^{3+}$ dosage was 2 g/l and $Fe^{3+}$:$H_2O_2$ 1:10.

| Time (min) | Color (color unit) | | | | Color removal efficiency (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | Batch | | | | Batch | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 0 | 2800 | 2700 | 3000 | 2800 | 0 | 0 | 0 | 0 |
| 5 | 2500 | 2700 | 3000 | 2600 | 10 | 0 | 0 | 7 |
| 30 | 2800 | 2700 | 2500 | 2400 | 0 | 0 | 16 | 14 |
| 60 | 365 | 500 | 395 | 1300 | 86 | 81 | 86 | 53 |
| 90 | 580 | 795 | 1005 | 970 | 79 | 70 | 66 | 65 |
| 120 | 680 | 985 | 1210 | 560 | 75 | 63 | 59 | 80 |
| 150 | 585 | 995 | 1060 | 730 | 79 | 63 | 64 | 73 |
| 180 | 735 | 970 | 1060 | 730 | 73 | 64 | 64 | 73 |
| 210 | 715 | 990 | 1045 | 805 | 74 | 63 | 65 | 71 |
| 240 | 740 | 1030 | 1035 | 850 | 73 | 61 | 65 | 69 |

Table 15. Color removal efficiency at pH of 8 and $Fe^{3+}$ dosage was 2 g/l and $Fe^{3+}$:$H_2O_2$ 1:10.

| Time (min) | COD (mg/l) | | | | COD removal efficiency (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | Batch | | | | Batch | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 0 | 1280.4 | 1293.3 | 1294.7 | 1270.3 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5 | 504.4 | 478.5 | 495.0 | 625.6 | 60.6 | 62.9 | 61.7 | 50.7 |
| 30 | 388.0 | 594.9 | 495.0 | 644.6 | 69.6 | 53.9 | 61.7 | 49.2 |
| 60 | 213.4 | 219.8 | 304.6 | 407.6 | 83.3 | 82.9 | 76.4 | 67.9 |
| 90 | 407.4 | 549.6 | 495.0 | 379.2 | 68.1 | 57.4 | 61.7 | 70.1 |
| 120 | 388.0 | 569.0 | 514.0 | 474.0 | 69.6 | 55.9 | 60.2 | 62.6 |
| 150 | 368.6 | 588.4 | 542.6 | 502.4 | 71.2 | 54.4 | 58.0 | 60.4 |
| 180 | 426.8 | 569.0 | 495.0 | 511.9 | 66.6 | 55.9 | 61.7 | 59.7 |
| 210 | 407.4 | 569.0 | 504.5 | 578.2 | 68.1 | 55.9 | 61.0 | 54.4 |
| 240 | 368.6 | 569.0 | 618.8 | 616.2 | 71.2 | 55.9 | 52.2 | 51.4 |

Appendix 2-7. The results of Iron concentration measurement in recovery iron molybdate.

Table 16. Total iron, ferrous ion and ferric ion concentration at pH of 8 and $Fe^{3+}$ dosage was 2 g/l and $Fe^{3+}$:$H_2O_2$ 1:10.

| | Batch 1 | | | Batch 2 | | | Batch 3 | | | Batch 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (min) | Fe total (mg/l) | $Fe^{2+}$ (mg/l) | $Fe^{3+}$ (mg/l) | Fe total (mg/l) | $Fe^{2+}$ (mg/l) | $Fe^{3+}$ (mg/l) | Fe total (mg/l) | $Fe^{2+}$ (mg/l) | $Fe^{3+}$ (mg/l) | Fe total (mg/l) | $Fe^{2+}$ (mg/l) | $Fe^{3+}$ (mg/l) |
| 5 | 0.9 | 0.0 | 0.9 | 4.9 | 1.1 | 3.7 | 1.4 | 0.0 | 1.4 | 4.4 | 3.1 | 1.2 |
| 30 | 7.8 | 7.2 | 0.6 | 5.3 | 3.6 | 1.7 | 17.6 | 8.5 | 9.1 | 6.8 | 6.7 | 0.1 |
| 60 | 0.9 | 0.8 | 0.1 | 3.4 | 0.3 | 3.1 | 4.4 | 0.8 | 3.5 | 6.8 | 3.6 | 3.2 |
| 90 | 49.0 | 10.5 | 38.4 | 48.5 | 5.1 | 43.3 | 57.3 | 7.6 | 49.7 | 4.9 | 1.6 | 3.2 |
| 120 | 52.9 | 9.7 | 43.1 | 81.8 | 18.9 | 62.9 | 63.7 | 11.3 | 52.3 | 48.5 | 7.8 | 40.7 |
| 150 | 48.5 | 9.1 | 39.3 | 85.0 | 20.2 | 64.7 | 100.9 | 17.8 | 83.0 | 61.2 | 11.0 | 50.1 |
| 180 | 75.0 | 12.4 | 62.5 | 91.6 | 17.7 | 73.8 | 107.3 | 17.5 | 89.7 | 75.4 | 16.1 | 59.3 |
| 210 | 68.6 | 11.9 | 56.6 | 96.0 | 20.1 | 75.9 | 112.2 | 19.7 | 92.5 | 82.3 | 13.9 | 68.4 |
| 240 | 95.5 | 16.3 | 79.2 | 101.9 | 19.4 | 82.5 | 109.3 | 19.7 | 89.5 | 92.1 | 14.7 | 77.4 |

# APPENDIX B-3

## Results of pulping wastewater part

Appendix 3-1. The results of removal efficiency in Fenton process.

Table 1. Lignin, color and COD removal at pH of 3, $Fe^{2+}$:$H_2O_2$ 1:2.5 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 894.87 | 6100 | 3065.2 | 0.00 | 0 | 0.0 |
| 0.083 | 92.43 | 1045 | 491.4 | 89.67 | 82 | 83.9 |
| 0.25 | 111.08 | 1340 | 485.0 | 87.58 | 78 | 84.1 |
| 0.5 | 100.44 | 1155 | 446.2 | 88.77 | 81 | 85.4 |
| 1 | 88.26 | 840 | 400.9 | 90.13 | 86 | 86.9 |
| 2 | 112.17 | 895 | 381.5 | 87.46 | 85 | 87.5 |
| 5 | 159.35 | 310 | 394.4 | 82.19 | 94 | 87.1 |
| 10 | 251.08 | 455 | 433.2 | 71.94 | 92 | 85.8 |
| 20 | 248.65 | 445 | 426.8 | 72.21 | 92 | 86.0 |
| 30 | 247.62 | 460 | 472.0 | 72.32 | 92 | 84.5 |
| 60 | 251.60 | 480 | 291.0 | 71.88 | 92 | 90.5 |

Appendix 3-2. The results of removal efficiency in heterogeneous Fenton-like process.

Table 2. Lignin, color and COD removal at pH of 8, $Fe^{3+}$:$H_2O_2$ 1:10 and $Fe^{3+}$ dosage was 2 g/l.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 956.41 | 7600 | 1599.3 | 0.00 | 0 | 0.0 |
| 5 | 211.53 | 2800 | 875.8 | 77.88 | 63 | 45.2 |
| 30 | 351.28 | 3600 | 913.9 | 63.27 | 52 | 42.8 |
| 60 | 202.75 | 970 | 780.6 | 78.80 | 87 | 51.1 |
| 90 | 203.14 | 145 | 837.7 | 78.76 | 98 | 47.6 |
| 120 | 261.15 | 640 | 837.7 | 72.69 | 91 | 47.6 |
| 150 | 264.29 | 770 | 837.7 | 72.36 | 89 | 47.6 |
| 180 | 264.93 | 775 | 856.8 | 72.29 | 89 | 46.4 |
| 210 | 263.07 | 795 | 837.7 | 72.49 | 89 | 47.6 |
| 240 | 264.23 | 800 | 799.6 | 72.37 | 89 | 50.0 |

# APPENDIX B-4

## Results of direct oxidation by $H_2O_2$

Appendix 4-1. The results of direct oxidation by $H_2O_2$.

Table 1. Lignin removal efficiency.

| Time | $H_2O_2$ concentration (mg/l) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 240 (1:0.6) | 400 (1:1) | 1000 (1:2.5) | 2000 (1:5) | 4,000 (1:10) | 6,000 (1:15) | 8,000 (1:20) |
| 0 | 912.46 | 955.38 | 974.10 | 920.51 | 912.82 | 947.69 | 926.67 |
| 0.083 | 910.05 | 935.64 | 965.13 | 917.95 | 891.28 | 941.03 | 860.00 |
| 0.5 | 907.18 | 948.46 | 962.82 | 920.51 | 908.97 | 937.69 | 857.18 |
| 1 | 908.46 | 952.82 | 958.97 | 900.26 | 910.26 | 928.72 | 847.44 |
| 2 | 908.46 | 945.38 | 961.28 | 906.41 | 896.15 | 912.56 | 876.15 |
| 5 | 903.33 | 955.13 | 958.72 | 906.41 | 903.59 | 945.13 | 906.41 |
| 10 | 907.18 | 946.41 | 970.87 | 903.69 | 882.31 | 923.08 | 882.05 |
| 20 | 904.62 | 933.85 | 958.72 | 905.38 | 898.46 | 939.74 | 868.97 |
| 30 | 903.33 | 928.97 | 962.31 | 907.69 | 889.74 | 938.72 | 876.92 |
| 60 | 905.90 | 945.13 | 958.46 | 892.82 | 908.97 | 933.85 | 878.21 |

Table 2. Color removal efficiency.

| Time | $H_2O_2$ concentration (mg/l) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 240 (1:0.6) | 400 (1:1) | 1000 (1:2.5) | 2000 (1:5) | 4,000 (1:10) | 6,000 (1:15) | 8,000 (1:20) |
| 0 | 2500 | 2600 | 2400 | 2400 | 2300 | 2300 | 2500 |
| 0.08 | 2500 | 2500 | 2300 | 2300 | 2200 | 2200 | 2500 |
| 0.5 | 2400 | 2400 | 2400 | 2300 | 2300 | 2100 | 2300 |
| 1 | 2500 | 2400 | 2400 | 2400 | 2300 | 2200 | 2400 |
| 2 | 2400 | 2400 | 2300 | 2400 | 2200 | 2100 | 2400 |
| 5 | 2500 | 2500 | 2300 | 2300 | 2200 | 2200 | 2300 |
| 10 | 2500 | 2500 | 2400 | 2400 | 2300 | 2200 | 2400 |
| 20 | 2400 | 2600 | 2300 | 2300 | 2200 | 2200 | 2300 |
| 30 | 2400 | 2600 | 2200 | 2200 | 2300 | 2100 | 2200 |
| 60 | 2500 | 2600 | 2300 | 2200 | 2200 | 2200 | 2200 |

Table 3. COD removal efficiency.

| Time | $H_2O_2$ concentration (mg/l) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 240 (1:0.6) | 400 (1:1) | 1000 (1:2.5) | 2000 (1:5) | 4,000 (1:10) | 6,000 (1:15) | 8,000 (1:20) |
| 0 | 1131 | 1254 | 1132 | 1154 | 1155 | 1255 | 1194 |
| 0.083 | 1131 | 1135 | 1055 | 1058 | 1155 | 1178 | 1078 |
| 0.5 | 1077 | 1154 | 1055 | 1098 | 1085 | 1178 | 1078 |
| 1 | 1115 | 1248 | 1103 | 1072 | 1117 | 1055 | 1017 |
| 2 | 1054 | 1215 | 1117 | 1062 | 1155 | 1178 | 1040 |
| 5 | 1092 | 1244 | 1055 | 1043 | 1097 | 1140 | 1055 |
| 10 | 1092 | 1214 | 1055 | 1102 | 1055 | 1078 | 1078 |
| 20 | 1077 | 1244 | 1055 | 1123 | 1017 | 1098 | 1040 |
| 30 | 1111 | 1215 | 1132 | 1138 | 1055 | 1101 | 1040 |
| 60 | 1131 | 1215 | 1120 | 1062 | 1098 | 1140 | 1001 |

## Results of iron coagulation

Appendix 4-2. The results of iron coagulation.

Table 4. Lignin, color and COD removal at pH of 3 and $Fe^{2+}$ dosage was 300 mg/l.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 906.41 | 3000 | 970.0 | 0.00 | 0 | 0.0 |
| 15 | 394.87 | 2900 | 465.6 | 56.43 | 3.33 | 52.0 |
| 30 | 789.74 | 5000 | 465.6 | 12.87 | 22 | 52.0 |
| 45 | 706.41 | 5500 | 310.4 | 22.06 | 22 | 68.0 |
| 60 | 169.23 | 600 | 155.2 | 81.32 | 80 | 84.0 |

Table 5. Lignin, color and COD removal at pH of 3 and $Fe^{2+}$ dosage was 400 mg/l.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 916.02 | 3300 | 2652.7 | 0.00 | 0 | 0.0 |
| 1 | 102.56 | 800 | 183.1 | 88.80 | 75 | 93.0 |
| 15 | 100.00 | 650 | 287.7 | 89.08 | 80 | 89.1 |
| 30 | 112.82 | 800 | 366.1 | 87.68 | 75 | 86.1 |
| 45 | 114.10 | 850 | 313.8 | 87.54 | 74 | 88.1 |
| 60 | 122.43 | 1450 | 392.2 | 86.63 | 56 | 85.2 |

Table 6. Lignin, color and COD removal at pH of 3 and $Fe^{2+}$ dosage was 500 mg/l.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 914.74 | 2900 | 1047.6 | 0.00 | 0 | 0.0 |
| 1 | 387.82 | 1230 | 242.5 | 57.60335954 | 57 | 76.8 |
| 15 | 407.90 | 1290 | 271.6 | 55.40761067 | 55 | 74.0 |
| 30 | 396.15 | 1250 | 281.3 | 56.69235735 | 56 | 73.1 |
| 45 | 385.04 | 1220 | 271.6 | 57.90702694 | 57 | 74.0 |
| 60 | 380.76 | 1200 | 266.7 | 58.37420755 | 58 | 74.5 |

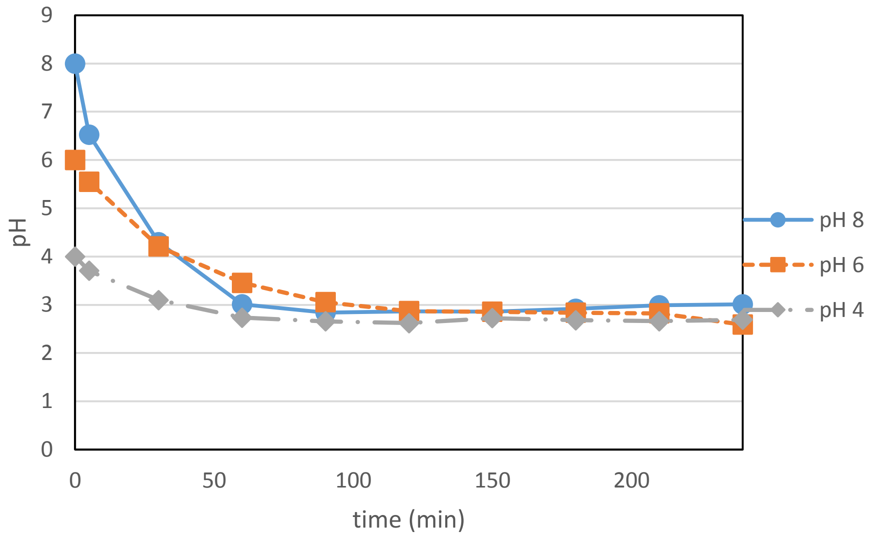
Appendix 4-3. Calculation for removal efficiency of Fenton oxidation at optimum $Fe^{2+}$:$H_2O_2$ ratio of 1:2.5

From table below, the approximately minimum of Fenton oxidation can be calculated by subtract of iron coagulation from overall removal efficiency. But it has to notice that, this is a roughly value to observe how much of removal efficiency that got from Fenton oxidation.

| Parameter | % Overall removal efficiency | % Iron coagulation | % Minimum of Fenton oxidation |
|---|---|---|---|
| Lignin | 92 | 87 | 5 |
| Color | 90 | 72 | 18 |
| COD | 92 | 88 | 4 |

# APPENDIX B-5

Appendix 5-1. The pH profile of heterogeneous Fenton-like process



Appendix 5-2. Result of trial experiment

Table 1. Lignin, color and COD removal efficiency at $Fe^{3+}$:$H_2O_2$ ratio of 1:2.5, $Fe^{3+}$ dosage of 0.4 g/l at initial pH of 3.

| Time (min) | Lignin concentration (mg/l) | Color (color unit) | COD (mg/l) | Lignin removal efficiency (%) | Color removal efficiency (%) | COD removal efficiency (%) |
|---|---|---|---|---|---|---|
| 0 | 944.23 | 3000 | 1333.3 | 0.00 | 0 | 0 |
| 1 | 885.25 | 3000 | 1333.3 | 6.24 | 0 | 0 |
| 5 | 903.84 | 3000 | 1300 | 4.27 | 0 | 2.4 |
| 15 | 892.94 | 3000 | 1333.3 | 5.43 | 0 | 0 |
| 30 | 895.51 | 3000 | 1306.6 | 5.15 | 0 | 1.9 |
| 45 | 892.94 | 3000 | 1253.3 | 5.43 | 0 | 5.9 |
| 60 | 897.43 | 3000 | 1333.3 | 4.95 | 0 | 0.0 |
| 90 | 876.28 | 3000 | 1306.6 | 7.19 | 0 | 1.9 |
| 120 | 878.20 | 3000 | 1306.6 | 6.99 | 0 | 1.9 |
| 150 | 871.79 | 3000 | 1173.3 | 7.67 | 0 | 11.9 |
| 180 | 860.89 | 3000 | 1293.3 | 8.82 | 0 | 2.9 |

Table 2. Lignin, color and COD removal efficiency at $Fe^{3+}$:$H_2O_2$ ratio of 1:2.5, $Fe^{3+}$ dosage of 1 g/l at initial pH of 4, 6 and 8

| Time (min) | pH 4 | | | pH 6 | | | pH 8 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) |
| 0 | 916.02 | 2950 | 1265.8 | 1001.28 | 3200 | 1253.6 | 916.02 | 2950 | 1190.6 |
| 5 | 740.38 | 2950 | 1077.8 | 900.00 | 3200 | 1133.6 | 755.76 | 2950 | 940.0 |
| 30 | 802.56 | 2950 | 927.4 | 975.64 | 3200 | 1213.6 | 742.94 | 2950 | 958.8 |
| 60 | 786.53 | 2950 | 1027.7 | 953.84 | 3200 | 1253.6 | 745.51 | 2950 | 864.8 |
| 90 | 782.69 | 2950 | 1027.7 | 956.41 | 3200 | 1053.6 | 753.84 | 2950 | 902.4 |
| 120 | 781.41 | 2950 | 1027.7 | 978.20 | 3200 | 933.6 | 742.30 | 2950 | 902.4 |
| 150 | 854.48 | 2950 | 990.1 | 974.35 | 3200 | 893.6 | 737.82 | 2950 | 883.6 |
| 180 | 736.53 | 2950 | 914.9 | 935.899 | 3200 | 973.6 | 735.89 | 2950 | 883.6 |
| 210 | 716.66 | 2950 | 1002.6 | 956.41 | 3200 | 973.6 | 728.84 | 2950 | 883.6 |
| 240 | 729.48 | 2950 | 852.2 | 1038.46 | 3200 | 973.6 | 726.92 | 2950 | 902.4 |

Table 3. Lignin, color and COD removal efficiency at $Fe^{3+}$:$H_2O_2$ ratio of 1:2.5, $Fe^{3+}$ dosage of 2 g/l at initial pH of 4, 6 and 8

| Time (min) | pH 4 | | | pH 6 | | | pH 8 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) |
| 0 | 935.89 | 3000 | 1421.9 | 930.76 | 3000 | 1463.4 | 1007.69 | 3000 | 1205.6 |
| 5 | 805.12 | 3000 | 1193.4 | 858.97 | 3000 | 1051.8 | 828.20 | 3000 | 1053.2 |
| 30 | 622.43 | 3000 | 1060.1 | 870.51 | 3000 | 1071.4 | 943.59 | 2990 | 1167.5 |
| 60 | 853.84 | 3000 | 1022.0 | 879.48 | 3000 | 836.2 | 878.20 | 3000 | 939.0 |
| 90 | 653.84 | 2700 | 1060.1 | 580.12 | 1500 | 522.6 | 875.64 | 2600 | 939.0 |
| 120 | 711.53 | 3000 | 964.9 | 912.17 | 2450 | 757.8 | 723.46 | 2000 | 596.3 |
| 150 | 699.35 | 1920 | 926.8 | 944.23 | 2550 | 797.0 | 809.51 | 2600 | 900.9 |
| 180 | 520.51 | 355 | 698.3 | 930.76 | 2750 | 679.4 | 895.51 | 2800 | 1008.8 |
| 210 | 683.97 | 345 | 546.0 | 930.76 | 2550 | 757.8 | 865.25 | 2700 | 900.9 |
| 240 | 669.87 | 870 | 736.4 | 930.76 | 2650 | 757.8 | 925.90 | 2850 | 977.1 |

Table 4. Lignin, color and COD removal efficiency at $Fe^{3+}$:$H_2O_2$ ratio of 1:10, $Fe^{3+}$ dosage of 1 g/l at initial pH of 4, 6 and 8

| Time (min) | pH 4 | | | pH 6 | | | pH 8 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) |
| 0 | 955.12 | 2600 | 978.8 | 916.66 | 3000 | 1071.6 | 929.48 | 3200 | 1224.6 |
| 5 | 792.30 | 2600 | 758.0 | 732.05 | 3000 | 940.0 | 644.87 | 3156 | 843.8 |
| 30 | 821.798 | 2600 | 647.6 | 761.53 | 3000 | 864.8 | 629.48 | 3180 | 786.7 |
| 60 | 921.79 | 2600 | 684.4 | 705.12 | 2700 | 639.2 | 701.28 | 3120 | 786.7 |
| 90 | 253.07 | 465 | 305.4 | 258.20 | 1085 | 535.8 | 608.97 | 2700 | 710.5 |
| 120 | 258.84 | 900 | 342.2 | 254.23 | 765 | 460.6 | 255.70 | 845 | 469.5 |
| 150 | 259.10 | 990 | 342.2 | 263.46 | 1325 | 601.6 | 263.14 | 1655 | 602.8 |
| 180 | 257.88 | 1075 | 379.0 | 266.41 | 1870 | 658.0 | 264.80 | 1645 | 602.8 |
| 210 | 259.55 | 1080 | 397.4 | 269.10 | 1945 | 564.0 | 268.58 | 2070 | 621.8 |
| 240 | 261.02 | 1140 | 434.2 | 264.67 | 1565 | 526.4 | 270.89 | 2145 | 526.6 |

Table 5. Lignin, color and COD removal efficiency at $Fe^{3+}$:$H_2O_2$ ratio of 1:10, $Fe^{3+}$ dosage of 2 g/l at initial pH of 4, 6 and 8

| Time (min) | pH 4 | | | pH 6 | | | pH 8 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) | Lignin (mg/l) | Color (Pt-co unit) | COD (mg/l) |
| 0 | 975.64 | 3100 | 1304 | 925.64 | 3000 | 1294.8 | 896.15 | 3200 | 1205.6 |
| 5 | 661.53 | 3100 | 864 | 657.69 | 3000 | 809.2 | 342.30 | 6700 | 329.7 |
| 30 | 666.66 | 2500 | 784 | 619.23 | 2500 | 659.7 | 170.64 | 1065 | 260.0 |
| 60 | 251.66 | 330 | 472 | 253.71 | 635 | 367.2 | 261.47 | 855 | 374.3 |
| 90 | 257.75 | 705 | 492 | 258.20 | 805 | 423.2 | 263.14 | 1105 | 431.4 |
| 120 | 257.30 | 680 | 512 | 257.75 | 910 | 423.2 | 255.89 | 915 | 431.4 |
| 150 | 258.71 | 710 | 492 | 259.03 | 990 | 404.6 | 259.35 | 1230 | 479.0 |
| 180 | 257.56 | 715 | 512 | 258.39 | 835 | 404.6 | 263.91 | 1090 | 393.3 |
| 210 | 259.42 | 730 | 472 | 258.33 | 875 | 740.8 | 259.55 | 1050 | 469.5 |
| 240 | 258.71 | 695 | 532 | 258.33 | 845 | 441.9 | 260.44 | 980 | 393.3 |

# VITA

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