TREATMENT OF STABILIZED CUTTING OIL WASTEWATER BY FENTON PROCESS: EFFECT OF FENTON'S REAGENTS DOSAGE AND FEEDING MODE

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การศึกษาสภาวะที่เหมาะสมของกระบวนการเฟนตันในการบำบัดน้ำเสียปนเปื้อนน้ำมันตัด

นางสาวอาจรีย์ ประเสริฐศรี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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Thesis Title	TREATMENT OF STABILIZED CUTTING OIL WASTEWATER BY FENTON PROCESS: EFFECT OF FENTON'S REAGENTS DOSAGE AND FEEDING MODE
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อาจรีย์ ประเสริฐศรี : การศึกษาสภาวะที่เหมาะสมของกระบวนการเฟนตันในการบำบัดน้ำเสียปนเปื้อนน้ำมันตัด (TREATMENT OF STABILIZED CUTTING OIL WASTEWATER BY FENTON PROCESS: EFFECT OF FENTON'S REAGENTS DOSAGE AND FEEDING MODE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.พิสุทธิ์ เพียรมนกุล, 101 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาการบำบัดน้ำเสียปนเปื้อนน้ำมันตัดที่มีความคงตัวสูงด้วยกระบวนการเฟนตันซึ่งเป็นกระบวนการออกซิเดชันขั้นสูงโดยอาศัยความสามารถในการออกซิไดซ์ของไฮดรอกซิลเรดิคัลที่เกิดจากการทำปฏิกิริยาระหว่างสารเฟนตัน ได้แก่ เฟอร์รัสอิออนและไฮโดรเจนเปอร์ออกไซด์ จากการทดลองพบว่า การบำบัดมีประสิทธิภาพสูงสุดหลังจากเริ่มทำปฏิกิริยา 1 นาทีและเข้าสู่สภาวะคงที่ โดยเฟอร์รัสอิออน 200 มิลลิกรัมต่อลิตรและไฮโดรเจนเปอร์ออกไซด์ 500 มิลลิกรัมต่อลิตร (อัตราส่วน 1:2.5) สามารถบำบัดค่าซีโอดีของน้ำเสียความเข้มข้น 100 และ 150 มิลลิกรัมต่อลิตรได้ประสิทธิภาพสูงสุดร้อยละ 97 ส่วนน้ำเสียความเข้มข้น 50 มิลลิกรัมต่อลิตร จะต้องใช้เฟอร์รัสอิออน 200 มิลลิกรัมต่อลิตรและไฮโดรเจนเปอร์ออกไซด์ 2000 มิลลิกรัมต่อลิตร (อัตราส่วน 1:10) เพื่อให้ได้ประสิทธิภาพการบำบัดซีโอดีร้อยละ 98 อย่างไรก็ตาม การเติมสารเฟนตันในปริมาณมากเกินไปจะทำให้ประสิทธิภาพการบำบัดลดลงเนื่องจากเฟอร์รัสอิออนและไฮโดรเจนเปอร์ออกไซด์ที่เหลืออยู่จะแย่งทำปฏิกิริยากับไฮดรอกซิลแรดิคัลที่เกิดขึ้น ด้วยเหตุนี้จึงทำการศึกษารูปแบบการเติมสารเฟนตันเพื่อลดปริมาณสารที่เหลืออยู่ โดยพบว่าการเติมเฟอร์รัสอิออน 16.67 มิลลิกรัมต่อลิตร และไฮโดรเจนเปอร์ออกไซด์ 41.67 มิลลิกรัมต่อลิตร จำนวน 3 ครั้ง ให้ประสิทธิภาพการบำบัดเท่ากับการเติมเฟอร์รัสอิออน 200 มิลลิกรัมต่อลิตรและไฮโดรเจนเปอร์ออกไซด์ 500 มิลลิกรัมต่อลิตรเพียงครั้งเดียว ทั้งนี้ น้ำที่ผ่านการบำบัดด้วยกระบวนการเฟนตันไม่สามารถปล่อยออกสู่สิ่งแวดล้อมได้ทันทีเนื่องจากมีค่าพีเอชต่ำและมีเหล็กละลายอยู่มาก จึงจำเป็นต้องทำการปรับพีเอชให้เป็นกลางด้วยโซเดียมไฮดรอกไซด์และแยกเหล็กออกโดยการตกตะกอน จากการทดลองพบว่าอัตราน้ำไหลล้นผิวของถังตกตะกอนที่สามารถแยกตะกอนเหล็กออกได้มากกว่าร้อยละ 80 อยู่ในช่วง 0.2 – 0.45 เมตรต่อชั่วโมงและ 0.7 – 1.9 เมตรต่อชั่วโมง สำหรับปริมาณเฟอร์รัสอิออน 50 และ 200 มิลลิกรัมต่อลิตรตามลำดับ นอกจากนี้ตะกอนเหล็กที่เกิดจากกระบวนการเฟนตันยังถูกนำกลับมาใช้เป็นตัวเร่งในปฏิกิริยาครั้งต่อไปเพื่อลดค่าใช้จ่ายในการกำจัดตะกอนเหล็ก โดยพบว่าตะกอนเหล็กสามารถนำกลับมาใช้ใหม่ได้อย่างน้อย 5 ครั้ง โดยให้ประสิทธิภาพการบำบัดเท่าเดิมและไม่จำเป็นต้องเติมเฟอร์รัสอิออนเพิ่ม

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต ....
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5687645120 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS: CUTTING OIL WASTEWATER / FENTON / STEP FEED OF FENTON'S REAGENTS / IRON PRECIPITATION / REUSE OF IRON SLUDGE

ARCHAREE PRASERTSRI: TREATMENT OF STABILIZED CUTTING OIL WASTEWATER BY FENTON PROCESS: EFFECT OF FENTON'S REAGENTS DOSAGE AND FEEDING MODE. ADVISOR: ASSOC. PROF. PISUT PAINMANAKUL, Ph.D., 101 pp.

The objective of this research is to investigate the treatment of the stable cutting oil wastewater by Fenton process, an advanced oxidation used as a post-treatment process. Hydroxyl radical can be produced by the reactions between the Fenton's reagents including ferrous (Fe^{2+}) and hydrogen peroxide (H_2O_2). The result showed that highest COD removal efficiencies of 97% can be achieved for treating 100 and 150 mg/l oil concentration with 200 mg Fe^{2+}/l and 1:2.5 of Fe^{2+}/H_2O_2 ratio, while 98% of 50 mg/l oil concentration can be succeeded at 200 mg Fe^{2+}/l and 1:10 of Fe^{2+}/H_2O_2 ratio in 1 minute reaction time. However, excess Fenton’s reagents cause lower oxidation of cutting oil due to hydroxyl radical scavenging effect. The multiple step feedings were therefore applied. The result showed that three feedings of 16.67 mg Fe^{2+}/l and 41.67 mg H_2O_2/l at t = 0, 5, and 10 minutes reaction time provided COD removal efficiency as high as initial full feeding of 200 mg Fe^{2+}/l and 500 mg H_2O_2/l (97%). After cutting oil was oxidized by Fenton, pH of the treated water was acidic, which cannot be discharged to an environment. Therefore, the pH neutralization by NaOH was conducted. This pH adjustment causes the iron precipitation, which required the sedimentation to remove. The optimum overflow rates of sedimentation tank for 50 mg Fe^{2+}/l and 200 mg Fe^{2+}/l were in range of 0.2 – 0.45 m/h and 0.7 – 1.9 m/h, respectively. In addition, reuse of iron sludge in the Fenton reaction was carried out in order to minimize the sludge production and reduce the disposal cost. The sludge from 50 mg Fe^{2+}/l and 125 mg H_2O_2/l can be reused to treat 100 mg/l oil concentration without replacement at least 5 recycling times.

Field of Study:	Environmental Management	Student's Signature	....
		Advisor's Signature	....
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CHAPTER 1
INTRODUCTION

1.1 Introduction

In the present, the growth of economy in Thailand causes development and expending various industries, especially metal industry. This leads to high amount of wastewater production. Wastewater is the main environmental problem, because it is one of the pollutant sources that can cause adverse effect to an environment and human. Wastewater containing cutting oil which generated from the metal machining industry was focused in this study, because it has high stability and toxicity.

Cutting oil which is known as metal working fluids is employed as a lubricant and coolant during metalworking process such as drilling, mills, rolling, etc. (Cheng et al., 2005). Cutting fluids normally consist of mineral oil, emulsifiers and additives such as extreme pressure additive or biocide that provide the special properties (Debnath et al., 2014). Cutting oil properties will be changed after long usage, thus it needs to be replaced. The used cutting oil would be discharged with machining wastewater. Cutting oily wastewater require an appropriate treatment method, since it contain heavy metal and high amount of organic substance. Moreover, oil can obstruct oxygen dissolved into the water that directly affects to aquatic life. Oil can mix with water in four different forms: 1) dissolved oil, 2) oil emulsion with surfactant, 3) oil emulsion without surfactant, and 4) film of oil. However, the used cutting oil normally forms a stable emulsion in water because of the presence of surfactant. Moreover, the cutting oil wastewater is considered to be a hazardous waste, since the stable emulsion contain high amount of small droplets which are difficult to be treat by conventional treatment techniques (Aurelle, 1985).

There are many alternative treatment processes for oily wastewater, for example physical treatment, chemical treatment and biological treatment. Physical separation techniques (i.e. decantation, coalescence, floatation, adsorption and filtration) are commonly employed as a primary treatment that can remove oil from the wastewater naturally. However, high stability of this emulsion in wastewater causes treatment efficiency of physical process is lower than chemical treatment techniques. These small oil droplets take long time to separate themselves. In addition, Incineration is often applied to disposal oil-based waste in the industry (Baradie, 1996). Combustion is not appropriate to oily wastewater which contains high amount of water, since it needs high energy.

Among the chemical treatment process, advanced oxidation process is interesting for treating cutting oily wastewater because of its high performance, easy operation and non-toxic environment. Fenton is one of the advanced oxidation process which is effective to treat this kind of wastewater (Rojvilavan, 2011). Ferrous and hydrogen peroxide are needed as a Fenton's reagent. Ferrous can catalyze the production of hydroxyl radical, which is a strong oxidizing agent, from hydrogen peroxide under acidic condition ($pH\approx2-4$) (Parson, 2004). There are many factors that affect to Fenton's reaction including dosage of Fe^{2+} and H_2O_2, Fe^{2+}/ H_2O_2 ratio and pH (Rojvilavan, 2011). However, the excess amount of H_2O_2 leads to treatment efficiency reduction (Methatham, 2011), since a residue of H_2O_2 would be the scavenger of hydroxyl radical resulting in less oxidation of cutting oil. Moreover, a residue Fe^{2+} is another aspect that can also be a scavenger of hydroxyl radical (Mohajeri et al., 2010); therefore, the optimum Fe^{2+} and H_2O_2 dosage is an important parameter to evaluate in this study. In addition, step feed of Fenton's reagent is applied to improve the treatment efficiency and reduce the Fenton's reagent dosage consumption. Kinetic study of Fenton's reaction was also studied in order to provide the data for designing the completely stirred tank reactor (CSTR).

1.2 Hypotheses

1.2.1 Cutting oil can be decomposed by Fenton oxidation.

1.2.2 The removal efficiency of cutting oil by Fenton process depend on Fe^{2+}/H_2O_2 ratio, initial PH, retention time and Fenton's reagent feeding mode.

1.2.3 Step feeding mode of Fenton's reagent affects to the oxidation of cutting oil.

1.2.4 Step feeding mode of Fenton's reagent is more effective than full feeding mode for oxidizing cutting oil.

1.3 Objectives

1.3.1 To determine the optimum operating conditions of Fenton process in term of Fenton's regent dosage, Fe^{2+}/H_2O_2 ratio, feeding mode of Fenton's reagents and reaction time at several cutting oil concentration.

1.3.2 To determine the optimum overflow rate of sedimentation tank for separating the iron precipitates after Fenton oxidation was finished.

1.3.3 To investigate the reuse of iron sludge as iron catalyst for the next Fenton process.

1.4 Scope of Study

The research will be operated on a laboratory scale at Chulalongkorn University, Faculty of Engineering, Department of Environmental Engineering.

1.4.1 Synthetic wastewater was prepared from Castrol cutting oil and tap water. Cutting oil was diluted at 50 mg/l, 100 mg/l and 150 mg/l.

1.4.2 Experiment was operated in batch form that control volume at 1 liter.

1.4.3 The quantity of cutting oil was expressed in term of chemical oxygen demand (COD).

1.4.4 Fenton reaction was operated at room temperature and initial pH around 3.

1.4.5 Fenton's reagent (ferrous ion and hydrogen peroxide) was fed simultaneously in one feeding, two feeding and three feeding.

1.4.6 Iron sludge was reused as iron catalyst without regeneration and fresh iron replacement.

1.5 Result of the study

1.5.1 To gain the optimum Fenton's regent dosage, Fe^{2+}/H_2O_2 ratio, feeding mode of Fenton's reagents and reaction time that give the high cutting oil removal efficiency in each cutting oil concentration.

1.5.2 To understand influence of important factors such as Fenton's reagent dosage, step feeding mode and initial oil concentration on the oxidation of cutting oil.

1.5.4 To identify the optimum overflow rate of sedimentation tank for separating the iron precipitates after Fenton oxidation was finished.

15.5 To identify the number of reused time of iron sludge that was effective to treat cutting oil wastewater.

CHAPTER 2
LITERATURE REVIEW

2.1 Classification of oily wastewater

Hydrocarbon or oil can mix with water in 4 different form (Aurelle, 1985).

2.1.1 Dissolved oil

Oil is normally known as insoluble substance that cannot totally dissolve in water, but in fact that oil can be soluble. The solubility relies on its polarity and molecular weight. Therefore, the solubility of oil increases with decreasing molecular weight. In addition, a high volatile hydrocarbon which has low molecular weight is also highly soluble. This type of hydrocarbon is very toxic to human, for most of dissolved hydrocarbons are aromatic forms that are carcinogen.

2.1.2 Oil emulsion in the absence of surfactant

In the industrial process, water that is contaminated hydrocarbon is often found in the emulsion form. The emulsion can be generated by several tools in the manufacturing process such as elbow joint, centrifugal pump, and valve. Moreover, either agitation (disposal of oil in water) or the phenomenon of diphasic condensation can cause an emulsion of oil in water. According to interfacial tension theory, a small droplet diameter is easier to disperse the oil phase in water because of the lower interfacial tension. Thus, the interfacial tension is directly proportional to the droplet diameter of dispersed oil. This kind of emulsions is categorized to primary and secondary emulsions. A droplet diameter greater than 100 microns is classified to primary emulsions. Secondary emulsions have a diameter of drop less than 20 microns.

2.1.3 Oil emulsion in the presence of surfactants

The hydrocarbon and water with surfactants form emulsion that is very stable since surfactant molecule consists of lypophilic and polar part. Polar part of surfactant can adhere to water, and lypophilic can adhere to oil, thus the presence of surfactants in water decreases interfacial tension of hydrocarbon in water. Polar part of surfactant is mostly carbonite (COO^-Na^+), sulphate ($SO_4^-Na^+$), hydroxyl (OH^-), or sulfonate group ($SO_3^-Na^+$).

2.1.4 Sheet or film of oil

Most of oil usually have a density lower than water, thus oil can form a film layer on the water surface. Small amount of this kind of hydrocarbon can form a large of film layer on the water surface. According to oil film formation, oxygen and light cannot transfer to water that cause an environmental problem. This kind of oil is easy to detect by eye because of the presence of specific rainbow reflects on the water surface.

2.2 Cutting fluid

2.2.1 Function of cutting fluid

1) Lubrication; reduce the friction between machining tool and workpiece in metalworking process.
2) Coolant; disperse heat from machining tool and workpiece.
3) Expand tool life
4) Improve surface metal quality and provide sizing accuracy.
5) Ease of chip and swarf handling; wash away the chip or clear swarf from the cutting zone.
6) Prohibit metal corrosion of machining tool and workpiece.

2.2.2 Type of cutting fluid (Debnath et al., 2014)

Cutting fluid can be categorized into 3 main groups including 1) Oil based cutting fluid, 2) Aqueous based cutting fluid and 3) gas based coolant-lubricant.

1) Oil based cutting fluids

Oil based cutting fluids which are known as neat oil normally produce from mineral, vegetable, animal or synthetic oils. Mineral oils that come from petroleum are the main component of commercial oil based fluids since they provide lubricating property. In addition, some additives such as extreme pressure compounds and other lubricants were mixed with mineral oil for enhancing their useful properties. The oil based cutting fluids have two major categories; paraffinic mineral oil and naphthenic mineral oil which are improved their characteristics by adding fatty lubricants, extreme pressure additive, polar additive, odorants, friction modifiers, thickness modifier and viscosity index modifier. The advantages of this type of oil are to lubricate the surface between machined tool and chip, reduce the friction and prohibit metal corrosion of the machined tool and workpieces. Mineral based lubricants are good at lubricating, but poor at coolant that leads to the high flammable property.

2) Aqueous-bases cutting fluids

Aqueous-based cutting fluids (water-soluble fluids) normally consist of mineral, water, and emulsifier. The existence of water can enhance the cooling characteristic of mineral oil. The emulsifier is employed to disperse the oil droplet in water and form a stabilize oil in water emulsion. This type of fluid is recommended to use for high-speeds cutting operation since they can disperse heat from tool and metal workpiece (metal thermal deformation). The aqueous-based cutting fluid are classified into 3 type; soluble oil, synthetic and semi-synthetic fluids. The soluble oil composes of mineral oil, water and emulsifier which provide lubricating, cooling, corrosive protection characteristics. The synthetic fluids which have not mineral oil are produced from diluting organic or inorganic chemical in water. The additive chemical enhances lubrication, water softening, surface tension decreasing and corrosive protection. The synthetic fluids are recommended for low force operation because of high cooling capability and low lubrication capability. The semi-synthetic cutting fluids consist of mineral oil and additive chemicals which can reduce oil droplet size causing more lubricating capability. However, the existence of water in fluids causes micro-organism growth such as bacteria, fungi and yeasts. The presence of micro-organism leads to infestation. The growth of bacteria and fungi cause metal corrosion and low lubricant capability. Microbial problem can be resolved by adding biocides or anti-microbial which can remain property of cutting fluid.

3) Gas-based coolant lubricant

Gas-based coolant-lubricants are the substances which in form of gas. They are considered to be another kind of cutting fluid that is friendly to environment. However, the cooling characteristic of gas is lower than water. Different applications are employed to enhance the cooling characteristic of gas-based coolant lubricant such as compressing, liquefying and cooling. Carbon dioxide, air, nitrogen, helium and argon are the main gas-based coolant-lubricant.

In metal machining process, cutting fluids properties will be changed after usage. The used cutting fluids generally compose of undesirable contaminants such as fine chips, dirt, particles, scale from metal workpiece, heavy metal. These contaminants can cause undesirable reactions which lead to the breakdown of emulsion or cutting fluids oxidation. These undesirable reactions result in staining and rust of machining tool and metal workpiece, and reducing the cutting fluid life. Moreover, the presence of contaminants also affect to surface metal quality and metal sizing accuracy. Therefore, the used cutting fluids need to be replaced after machining usage. However, the used cutting fluids are considered to be a hazardous waste which needed an appropriate handling. There are two main methods for handling these fluids: recycling and disposal. For recycling method, the contaminants are separated by filtration, magnetic separation or centrifugal separation, and then cutting fluids are purified by heating or sterilizing that result in reducing of viscosity and disinfection respectively. For disposal method, Chemical processes, especially coagulation are employed to destabilize the used fluids to oil and water. However, machining industry generally dispose the used fluids by combustion which oil is one of the fuel. Disposal method will be applied when there are high amount of water in emulsion, or oil recovery is difficult.(Adler et al., 2006)

2.3 Oily wastewater treatment process

There are several treatment methods for oily wastewater: biological treatment, physic-chemical treatment, and chemical treatment. However, the forms of oil in water and the properties of oily wastewater are the important factors that have to be considered to select an appropriate treatment method (Aurelle, 1985).

2.3.1 Biological treatment

Biological process is normally employed as a post- treatment process that require pre-treatment (physical treatment process) in order to eliminate contaminated suspended solid, oil in the film and emulsion. This process is an effective treatment method to treat dissolved oil. Activated sludge, trickling filter and biological disks are the popular biological treatment that is commonly found in the industry.

2.3.2 Physical treatment

This treatment process is generally employed as a pre-treatment process in order to separate oil from water. Combination of physical and chemical treatment can enhance treatment efficiency, since chemicals are added to destabilize or destruct the stable oil emulsion, and then oil particles are separated from water by gravitation, centrifugation, filtration and floatation. There are many physico-chemical treatment methods for treating oily wastewater as follow:

1) Decantation

Decantation which is known as floating is a simple oil separation. Free oil droplet particles naturally rise up to the surface of water. Mechanism of this decantation can be explained by Stoke's law theory. Rising velocity of oil particle depends on the size of oil droplet particle, the different density of oil and water and viscosity of water. Therefore, a large oil particle can float to the surface faster than the other small particles. If high amount of small oil particles exist in water, the float of oil also take very long time. This separation technique is appropriate for primary oil emulsion and large oil particle containing in wastewater. The phenomena of decantation for removing oil is similar to the principle of oil-grease trap.

2) Skimmer

An oil skimmer is a tool which can remove oil in form of film from the water surface. Moreover, this kind of tool is basically employed for oil spill remediation, and is usually operated in the metal machining industry.

3) Coalescer

Coalescer is a process that helps to solve the limitations of decantation process for removing oil from water. Secondary oil emulsion, which have an oil droplet size less than 20 µm cannot be separated by decantation (Aurelle, 1985). Therefore, Coalescence of small oil particles (smaller than 20 µm diameter) by coalesce is applied to increase the oil droplet size. The micro oil particle will attach to the coalesce media, and then form a larger particle on the media. This larger particle can then float naturally by decantation. Coalescer media is an important constituent which is commonly hydrophobic resin, because it favors to attach with oil. Coalescer bed media can be clogged by contaminated suspended solid, thus a pre-treatment process is required for coalesce application. Moreover, the coalescer media can either be fibrous bed form or granular bed form.

4) Floatation

Floatation is an effective treatment process for treating oil and grease in water. This process are applied to increase different density of oil and water resulting in higher rising velocity of oil droplet follow by Stoke’ s law theory. In this process, air bubbles are added in the wastewater to pick up and conduct oil droplet particles float up to the surface. Oil droplet particles will agglomerate with air bubbles, and then rapidly float up itself due to the density of air is lower than water. The advantage of this process are that suspended solid can also be eliminated, and disperse oil and oil emulsion can be removed effectively. Moreover, floatation process can obtain high loading wastewater. There are various types of floatation; for example, DAF, IAF, and vaccum floatation.

Dissolved Air Floatation (DAF); air are dissolved in the wastewater at high pressure, and then release the air under atmospheric pressure. The released air will form micro bubbles which will attach oil particle and rise up to the surface. Oil layer on the surface can be removed by a skimmer.

5) Adsorption

Adsorption is a separation method that can treat all type of oil including dissolved oil. Oil in liquid form is adsorbed on the surface or inside the pore of adsorbent. There are many types of adsorbents which is different in term of size. Activated carbon is a popular adsorbent. However, cost of this process is high, and the carbon adsorbent has to be replaced after long usage or the presence of clogging problem.

2.3.3. Chemical treatment

It is normally used as a post-treatment due to high cost and may cause toxicity. This treatment method is operated to treat wastewater that cannot be treated by physical and biological process.

1) Coagulation

This process is a physicochemical treatment that destabilized colloidal particles (oil droplet particles) and fine suspended solid. Electrical property on colloid surface is the main mechanism that use in coagulation. The colloids are usually stable in wastewater due to electrical charge property. The charge of most colloids is negative. The colloids charges are destabilized by adding coagulant. Positive charges of coagulant lead to neutralization of electrical charges. After colloid charges are neutralized, these oil droplet particles begin to coalesce and form large floc which can rise up to the surface of water themselves. Ferric sulfate, ferric chloride, alum (Aluminum Sulfate) and ferric chloro-sulfate are the popular coagulants that are generally used in water supply and industrial wastewater treatment (Hamidreza Farajnezhad et al, 2012).

2) Chemical oxidation

This treatment method use regent which is known as oxidant to degrade, destruct or transform many toxic organic compounds to harmless compounds. Chemical oxidation is widely used in the several industries for decades to treat carbon-containing organic compounds, for instance petroleum hydrocarbons, chlorinated solvent and other organic contaminant. Chemical oxidation is a half of redox reaction which electrons are transferred from oxidizing reagent to chemical being oxidized. The by products of oxidative reaction by most chemical oxidizers are CO_2, water, nontoxic ions, salts and acid. There are four popular oxidants that are most commonly used: permanganate (MnO_4), hydrogen peroxide (H_2O_2), ozone (O_3) and persulphate. Oxidative capacity of specific oxidants and the oxidative power of the oxidants can be expressed on their standard oxidation potential (Bennedsen, 2014) as present in Table 2.1

2.4 Advanced oxidation process

Advanced oxidation process (AOP) is one of the chemical oxidation process which aim to generate hydroxyl radical. In the AOP reaction, hydroxyl radical is the main oxidant, because it has high oxidation potential and be the second powerful oxidant. Table 2.1 shows the oxidation potential of each oxidant species. AOP can be applied to treat pollutant at low or high concentration. AOP is always used to destroy recalcitrant compound that is difficult to degrade by conventional treatment process, for example biological treatment. In this process, pollutant or toxic organic compound would be mineralize which convert the construction of organic compound to simple compound or inorganic compound that is harmless and easy to treat by next conventional process (Parson, 2004).

AOP is commonly applied to many wastewater treatment processes as follow (Permchati, 2013):

1. AOP is used to treat toxic organic compound in the groundwater
2. AOP is used as a pre-treatment to treat toxic or refractory substance before sending to biological treatment process.
3. AOP can destructed heavy metal and cyanide which inhibit and destroy microorganism in the biological treatment process.
4. AOP can oxidize the residual organic as a post-treatment after finishing biological treatment process.

5. AOP can be applied with other treatment processes such as combination of coagulation and AOP i.e.

Table 2.1 Oxidation potential of common species

(Parson, 2004)

Species	**Oxidation potential (V)**
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanaganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36

There are varieties of advanced oxidation method for generating hydroxyl radical. Many methods are used at full scale such as Fenton's reagent, supercritical water oxidation, wet air oxidation and combination of ozone, UV and H_2O_2 i.e. (Parson, 2004). Table 2.2 shows advanced oxidation methods.

Table 2.2 Advanced oxidation method for wastewater treatment

(Parson, 2004).

Catalysis
Fenton's reagent
Photo Fenton's reagent
Ferrate
Ionising radiation
Electrochemical
Microwave
Wet air oxidation

Supercritical water oxidation
Ultrasound
Photocatalysis
UV
Pulsed plasma
UV/H2O2
Vacuum UV
UV/Ozone/H2O2

2.5 Fenton reaction

Fenton process is one of the advanced oxidation process that hydroxyl radical (·OH) is the main oxidant in the process. Fenton process is normally applied for treating wastewater that contain recalcitrant organic compound which can't be destructed by biological process. This process is mostly used as post treatment process. Organic compound or hazardous pollution in water or soil can be decomposed by hydroxyl radical from the Fenton reaction (Bautista et al., 2008). Hydroxyl radical is the second strongest oxidant (E_0= 2.8 V), and the first strongest oxidant is fluoride (E_0= 3.03 V) (Zhang et al., 2005).

In Fenton reaction, ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2) are needed to use as Fenton's reagent. Ferrous ion would catalyst the production of hydroxyl radical, which is a strong oxidizing agent, from hydrogen peroxide as showed in equation 2.1.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH + OH^- \qquad k_1 \approx 70\ M^{-1}s^{-1} \quad (2.1)$$

In addition, Fenton oxidation would be effective in degrading recalcitrant organic compound under acidic condition (PH≈2-4). Hydroxyl radicals (·OH) would oxidize organic substances (RH) and produce reactive organic radicals (R·) that can be oxidized further (Neyens andBaeyens, 2003). Equation 2.2-2.4 show the oxidation of organic compound by hydroxyl radical (·OH).

$$RH + \cdot OH \longrightarrow H_2O + R\cdot \qquad (2.2)$$

$$R\cdot + H_2O_2 \longrightarrow ROH + \cdot OH \qquad (2.3)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (2.4)$$

ROO· is unstable, thus they can react with ferrous ion (Fe^{2+}) and proton (H^+) to produce ROH and ROOH. Then, ROH and ROOH will be further oxidized and convert to CO_2 and H_2O (Permchati, 2013).

A residual ferrous ion would be the scavenger of hydroxyl radical as present in equation 2.5 which cause low oxidation of organic compound. The organic compound and the residual ferrous ion complete to react with the produced hydroxyl radical (·OH) from the Fenton reaction (equation 2.1), therefore the organic compound was oxidized by less amount of hydroxyl radical (Mohajeri et al., 2010).

$$Fe^{2+} + \cdot OH \longrightarrow Fe^{3+} + OH^{-} \quad k_2 \approx 3.2 \times 10^{8}\ M^{-1}s^{-1} \quad (2.5)$$

On the other hand, a residual hydrogen peroxide can be also scavenger of hydroxyl radical as can be seen in equation 2.6 (Umar et al., 2010). Hydrogen peroxide would be decomposed by hydroxyl radical to produce hydroperoxyl radical ($HO_2\cdot$) which can also oxidize organic compound, even if it has reactive power less than hydroxyl radical. When applying excess amount of H_2O_2, equation 2.1 completes with equation 2.6 in consumption of H_2O_2 resulting in low free hydroxyl radical.

$$H_2O_2 + \cdot OH \longrightarrow HO_2\cdot + H_2O \quad k_3 \approx 3.3 \times 10^{7}\ M^{-1}s^{-1} \quad (2.6)$$

$$Fe^{3+} + HO_2\cdot \longrightarrow Fe^{2+} + O_2 + H^{+} \quad k_4 \approx 1.2 \times 10^{6}\ M^{-1}s^{-1} \quad (2.7)$$

$$Fe^{2+} + HO_2\cdot + H^{+} \longrightarrow Fe^{3+} + H_2O_2 \quad k_5 \approx 1.3 \times 10^{6}\ M^{-1}s^{-1} \quad (2.8)$$

According to equation 2.9 and 2.10, ferric ion can react with hydrogen peroxide to produce hydroperoxyl radical ($HO_2\cdot$) which has oxidative power less than hydroxyl radical (·OH) (Nieto et al., 2011). These below reactions (equation 2.9 and 2.10) are known as Fenton-like reaction. The produced Ferric ion from the Fenton reaction can be changed back to ferrous ion by reacting with hydrogen peroxide. These reactions are regeneration of ferrous ion.

$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}OOH^{2+} + H^{+} \quad k_6 \approx 0.001\text{-}\ 0.01\ M^{-1}s^{-1} \quad (2.9)$$

$$Fe\text{-}OOH^{2+} \longrightarrow Fe^{2+} + HO_2\cdot \quad (2.10)$$

The effective of Fenton reaction would be depend on the Fe^{2+}/H_2O_2 ratio, initial PH and retention time (Kang andHwang, 2000).

2.6 Types of Fenton processes

Fenton process can be classified into 2 main types as follow:

2.6.1 Homogeneous process (Parson, 2004)

All of reactants are in form of dissolved phase. The solution has uniform composition. There is always only one phases in a homogeneous process. Fenton process, photo-Fenton process and Fenton-like reagent are considered to be homogeneous process.

1) Fenton process

Fe (II)/H_2O_2/dark: This process used dissolved Fe^{2+} and H_2O_2 as Fenton's reagent. Fe^{2+} will react with H_2O_2 to produce the highly reactive hydroxyl radical as shown in equation 2.1.

Fe (III)/H_2O_2/dark: Fe^{3+} form can be used initially in the Fenton reaction. The initial rate of reaction of Fe^{3+}/H_2O_2 is slower than Fe^{2+}/H_2O_2, since Fe^{3+} have to be reduced to Fe^{2+} before hydroxyl radical production.

2) Photo-Fenton process (Umar et al., 2010)

Fe (II)/H_2O_2/light: Fe^{3+} can catalyst the production of hydroxyl radicals when light of appropriate wavelength (180-400 nm) which normally is ultraviolet and visible light are irradiated in the process (Umar et al., 2010).

$$Fe^{3+} + H_2O_2 + hv \longrightarrow Fe^{2+} + H^+ + \cdot OH \qquad (2.11)$$

3) Fenton-like reagents:

Many transition metal ions and the metal complexes can react with H_2O_2 to form hydroxyl radical such as Cu(I), Ti(III), Cr(II), Co(II)

2.6.2 Heterogeneous process

The reactants have non-uniform composition. Two or more phases of matters are present in heterogeneous process. The Fenton's reagent can be produced from solid electrodes. Iron-containing minerals or iron-coated silica particles (sand) are the iron electrode which is source of ferrous. Moreover, iron adsorbed onto zeolite or ion exchange membranes can be also the source of ferrous. The advantage of heterogeneous Fenton process is that iron is easily separated from the treated water, since iron is usually in form of solid phase (electrode, granular, or membrane) (Rahim Pouran et al., 2014). But iron in homogeneous process is soluble in the treated water. The dissolved iron can be removed by raising the pH of the treated water that cause high amount of iron-containing sludge.

1) Iron oxide catalysts

Iron oxide can be employed for both water treatment and soil remediation. There are several forms of iron oxide such as a bed containing the iron oxide and iron content sand.

(1) Fe(III)oxide/H2O2/dark

Iron catalyst is a particulate mineral oxide, which has size in rage of 10μm to 5 nm. Goethite is a popular mineral oxide catalyst, since it can react with H_2O_2 fast. Moreover, it can be used in a long time without replacement or regeneration (Cao et al., 2009).

(2) Fe(III)oxide/H2O2/light

2) Electrochemical Fenton process

Electro-Fenton process is classified into two major types as follow:

(1) Cathodic Fenton process

In this process, Fe^{2+} would be provided by direct addition, or it may be generated by the reduction of Fe^{3+} at cathode (equation 2.12). According to equation 2.13, H_2O_2 may be generated by the reduction of dioxygen at cathode (Pozzo et al., 2005) with providing oxygen. The anode normally produces from inert material, for example platinum and platinised titanium. The cathode is produced from carbon containing materials, for example carbon felt or carbon polytrafluoroethylene.

$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+} \qquad (2.12)$$

$$O_2 + 2H^{+} + 2e^{-} \longrightarrow H_2O_2 \qquad (2.13)$$

(2) Anodic Fenton Process

The source of Fe^{2+} is iron electrode. Fe^{2+} is supplied by iron anode. The cathode normally made from graphite. In this process, H_2O_2 is added directly. Moreover, the reaction occurs at acidic condition (pH 2-3) that leads to high oxidative efficiency. The cathodic Fenton process is usually performed under neutral condition.

Effect of system composition and process condition

1. pH

Fenton reaction is normally effective in acidic condition (pH≈2-4). Highest oxidation can be provided at pH around 3. Oxidative efficiency decreases with increasing pH, since the presence of less Fe^{2+} at high pH causes less hydroxyl radical production. Moreover, H_2O_2 can decompose into water and oxygen at pH above 10 (Kang et al., 2000).

2. Fe:H_2O_2 ratio

Increasing of H_2O_2 concentration tends to increase the reaction rate. However, ferrous and H_2O_2 can be the scavengers of hydroxyl radicals that result in low oxidation in case of excess amount of Fe^{2+} and H_2O_2 as show in equation 2.5 and 2.6. The production of hydroxyl radical depend on the ratio of Fe^{2+} to H_2O_2, therefore it is important to use the optimum Fe^{2+}:H_2O_2 ratio.

3. Temperature

Fenton oxidation is usually operated under 20-40°C. The reaction rate inclines to increase when temperature increase. However, the reaction rate would be decreased when temperature rise up to above 40-50 °C, because H_2O_2 would decompose to water and oxygen at 40-50 °C that tend to low production of hydroxyl radical.

2.7 Reaction kinetic

Chemical kinetics is an important aspect of chemical reaction, because kinetics can describe about the rate or how fast of the reaction takes place. It relates to species or chemical concentration respect to time. In this section, an irreversible reaction that occur in one phase and the reactants are dispersed uniformly through the liquid phase is mainly discussed (Reynolds andRichards, 1996).

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2.7.1 Chemical reaction rates are the rates of change in an amounts of either reactants or products or species concentrations. The reaction rate can be expressed in many forms as follow:

$$\text{A (reactant)} \longrightarrow \text{B (product)}$$

$$-r_A = \frac{1}{V}\frac{dN_A}{dt} = \frac{amount\ of\ A\ disappearing}{(volume)(time)}\ ,\left[{}^{mol}/_{m^3.s}\right]$$

The reaction rate is in form of mass basis as:

$$-r_A = \frac{1}{V}\frac{dM_A}{dt} = \frac{mass\ of\ A\ disappearing}{(volume)(time)}\ ,\left[{}^{kg}/_{m^3.s}\right]$$

Another form of rate is on concentration basis as:

$$-r_A = \frac{dC_A}{dt} = \frac{concnetration\ of\ A\ disappearing}{time}\ ,\left[{}^{kg}/_{m^3.s}\right]$$

Moreover, reaction rate can be expressed by elementary reaction that associate to the stoichiometric as follow:

$$\text{aA + bB} \longrightarrow \text{cP}$$

$$-\,r_A = \frac{dC_A}{dt} = k[A]^a[B]^b$$

K is the reaction rate constant, $time^{-1}$

a, b are the order of reaction

2.8 Literature review

2.8.1 Fenton process

Lucas and Peres (2009) applied Fenton's reagent to reduce COD in olive mill wastewater. COD and BOD of this wastewater was around 60.5 g/l and 102 g/l**,** respectively. This research aims to investigate the effect of ferrous ion concentration, hydrogen peroxide concentration, initial pH and temperature on COD removal. In the experiment, the raw olive mill wastewater was diluted to reduce the COD loading to 2 g/l. All experiments were performed with 500 ml of diluted wastewater. Fe^{2+} in form of solid $FeSO_4.7H_2O$ and 30% H_2O_2 were added into 1000 ml batch reactor after the wastewater was adjusted pH to 2-4. Na_2SO_3 was added in the taken sample for stopping Fenton reaction. Na_2SO_3 can consume the residual hydrogen peroxide in the sample. The result in this study demonstrated that 70% COD removal was achieved at initial pH 3.5, molar ratio Fe^{2+}/H_2O_2= 1:15, H_2O_2/COD= 1.75, and temperature 30°C.

Lee and Shoda (2008) studied treatment of livestock wastewater by Fenton process. Livestock wastewater consists of COD, color, phosphorous, BOD_5, and suspended solid. COD of this wastewater was in range of 5000-5700 mg/l, the maximum color absorbance was 2.1 at 287 nm, and the initial pH was around 8.4-8.7. Strong odor, pathogenic distribution, and toxicity of some constituent are the pollutant which can contaminate in surface water and ground water. Advanced oxidation treatment technic was applied to treat this kind of wastewater which is difficult treat by conventional process. This study aims to determine the optimum condition of Fenton reaction in order to remove COD and color in livestock wastewater. Effect of initial pH, ferrous dosage, H_2O_2 dosage, reaction time, ratio of H_2O_2 to Ferrous, and dosage type were also studied in this research. For the experiment, 100 ml livestock wastewater sample were oxidized in 200 ml flask. H_2O_2 and $FeSO_4.7H_2O$ powder were added into flask after the sample were adjusted pH to acidic condition (pH=2-4). 1N NaOH was added to neutralized the sample (pH=7-8). NaOH addition leads to iron precipitation which precipitates were allowed to settle for 1 h. For the dosage type, There are division of ferrous and H_2O_2 dosages into 1 to 5 aliquotes and 1 to 3 aliquotes. The result showed that 88% COD and 95.4% color removal can be achieved at 2 of H_2O_2 to ferrous ratio, 1.05 of H_2O_2 to initial COD ratio and 3.5-4 of pH in 30 min. Moreover, the dosage type of ferrous and H_2O_2 did not effect to the removal of COD and color. The maximum COD and color removal was presented by adding ferrous and H_2O_2 in 1 aliquotes.

Chu et al. (2012) applied Fenton oxidation method to treat coking wastewater which contain high amount of refractory organic substances. Heterocyclic compounds, phenolics, polynuclear aromatic carbons and cyanide ammonia are the organic component in the coking wastewater that cause persist environmental problem. Moreover, these components also are carcinogenic, toxic and mutagenic. Fenton reaction were selected to oxidize the recalcitrant substance to less toxic and lower chain compound which can continuously be treated by biological treatment process. In this study, Fenton was considered to be a pretreatment method for treating coking wastewater, although ferrous salt provide iron sludge that needed an appropriated separation method. This study used zero-valent iron (size 30-70 µm) and 30% H_2O_2 as Fenton's reagent because of low cost, low amount of iron in effluent and fast ferric recycling. Influence of initial pH, H_2O_2 dosage and reaction time for wastewater treatment were investigated. COD of the coking wastewater was around 7500-8400 mg/l, total phenol was in rage of 1700 to 1900 mg/l, initial ammonium was 400-480 mg/l, initial cyanide was 7.5-8.5 mg/l, and initial pH was around 9.1-9.3. This experiment was performed in a batch that has 300 ml coking wastewater. The result indicated that 44-50% COD and 95% total phenol was eliminated by adding 0.3 M H_2O_2 at initial pH less than 6.5 for 1 hr. reaction time. Moreover, the oxygen uptake rate of oxidized sample (OUR) increased 65% when compared with the raw wastewater. This implied that biodegradation of this wastewater was enhanced by Fenton oxidation.

Rojvilavan (2011) studied the treatment of stabilized oil by Electro-coagulation and Fenton process. Cutting oily wastewater usually was in a form of stabilized emulsion that was difficult to be treated conventional physical treatment method. For electro-coagulation method, effect of current density, electrode between electrode and characteristic of treated wastewater in term of pH, total dissolve solid and conductivity were investigated. In the experiment, 1 g/l of cutting oil was operated in batch reactor that has two iron electrodes connecting a DC power supply. The size of these electrodes was 6×10×0.2 cm^3 which have 0.042 m^2 submerged area. COD of 1g/l cutting oil was around 3,750 mg/l. The result demonstrated that 90% COD removal can be achieved at 1-3 cm electrode distance, 36-60 A/m^2 current density and 30-45 min reaction time. However, COD of the effluent wastewater exceeded the standard regulation value. Fenton process was applied to oxidize the residual COD of the effluent as a post- treatment. Both of Fenton and Electro Fenton was operated to compare the treatment efficiency. The optimum conditions of Fenton were also determined in term of Fe^{2+}/H_2O_2 ratio (F/H), current density and reaction time. The optimum conditions of Electro Fenton were 23.8 A/m^2, 1:5-1:10 F/H and 15-60 min reaction time. Combination of Electro-coagulation and Electro Fenton can obtain 99% overall COD removal efficiency, therefore the treated water can be discharged to an environment.

Seo et al. (2007) investigated Ultrasonic- Fenton oxidation process can treat non-biodegradable cutting oil wastewater. This contaminated cutting oil consist of ethylenediamine tetraacetic acid (EDTA) and Triethanolamine (TEA). From the previous research, Cutting oily wastewater was examine by three different processes such as activated sludge process, ultrasonic Fenton process and coagulation process. They found that the ultrasonic Fenton process give the pollutant removal efficiency higher than other processes. The optimum condition of ultrasonic Fenton is the main purpose of this research. The optimum condition of ultrasonic Fenton process were that Ferrous sulfate and hydrogen peroxide 0.3 g/l and 10% respectively. The removal efficiency of the optimum condition were 98% COD, 93% SS, 75% T-N and 95% T-P respectively.

2.8.2 Step feeding mode in Fenton process

Zhang et al. (2006) studied the treatment of landfill leachate by Fenton’s reaction. For the characteristic of this leachate sample, COD was in rage of 8298 to 8894 mg/l, pH was around 6.65-6.69, and alkalinity as $CaCO_3$ was 3500-4600 mg/l. In this study, the effect of the important factors in the Fenton’s reaction was evaluated. These important factors include Fenton’s reagent dosage, pH, H_2O_2/ Fe^{2+}

ratio, reaction time, temperature, initial COD concentration, feeding mode, and flocculant type. The Fenton experiment was performed in a batch reactor which have 4 baffles for minimizing rotational and vortexing. The result showed that Fenton process can effectively oxidize refractory organics in the leachate. The pH value of the sample affect to the oxidative efficiency and the optimum pH in this reaction was 2.5. Treatment efficiency of Fenton was increased by increasing Fenton's reagent dosage. The optimum H_2O_2/ Fe^{2+} ratio was 1.5. Multiple step feeding mode of Fe^{2+} and H_2O_2 can improve the organic removal efficiency than a single step feeding, because it reduced the scavenger of hydroxyl radical by residual Fe^{2+} and H_2O_2. Higher temperature enhanced the organic removal. Moreover, Fenton's reaction was completed in 30 min reaction time.

Mohajeri et al. (2010) investigated the influence of Fenton's reagent oxidation that can mineralize and decolorize the municipal landfill leachate. Characteristics of this leachate were COD 2320-2480 mg/l, pH 8.3-8.8, color 3900-4250. In this study, the effect of H_2O_2/ Fe^{2+} molar ratio, pH, agitation rate, reaction time, concentration of Fenton's reagent and feeding type which related to the efficiency of Fenton process were studied. The Fenton oxidation was operated in 500 mL beakers as a batch reactor. Sulfuric acid and sodium hydroxide were added to adjust pH value. Fenton's reaction (560 mg/l Fe^{2+} and 1020 mg/l H_2O_2) were fed simultaneously in one time (at 0 min), two time (at 0 and 60 min), three time (at 0, 40, 80 min), and four time (0, 30, 60, and 90 min). This result indicate the best condition that provide the maximum removal efficiency of COD and color (58.1% and 78.3%) were H_2O_2 = 1020 mg/l, Fe^{2+} = 560 mg/l, agitation rate = 400 rpm, pH =3, H_2O_2/ Fe^{2+} molar ratio = 3 and reaction time = 120 min. Moreover, the result of feeding type showed that step feed of Fenton's reagent in four times can obtain highest treatment efficiency. It is implied that stepwise addition of Fe^{2+} and H_2O_2 has higher effective oxidation than adding all in a single feeding. The residual H_2O_2 and Fe^{2+} can be a scavenger of hydroxyl radical and reduce the oxidation of recalcitrant organic in the leachate.

2.8.3 Reuse of iron sludge as iron catalyst in Fenton process

Cao et al. (2009) study regeneration and reuse of iron sludge for Fenton-like process since large amount of iron sludge was generated from Fenton process. After the water sample was oxidized by Fenton reaction, the pH of treated water was highly acidic that cannot be discharge to an environment. Neutralization by adding NaOH is always operated after Fenton process was finished. Soluble iron will precipitate with hydroxide in form of $Fe(OH)_2$ and $Fe(OH)_3$ while NaOH was added to neutralize. This research aims to use this produced iron sludge as iron catalyst in the next Fenton. A simple regeneration method that can eliminate the adsorbed organics in the sludge was presented. Iron sludge regeneration consists of dewatering, drying, baking and dissolving residual iron in acidic solution. In the experiment, wastewater containing 1100-1300 mg/l was treated by using fresh ferric sulfate in the first time. Then, treated water was adjusted pH to 7-8. Iron hydroxide flocs were allowed to settle for 24 hr. After that a glass-fiber filter was used to dewater the sludge. The concentrated sludge was dried at 105°C, and then the dried sludge was baked in a furnace at 300-500°C. This regenerated sludge was dissolved in acidic solution before they were added in the next Fenton process as iron catalyst. There is addition of fresh ferric sulfate in order to replace the iron lost during the regeneration. This research investigated the effect of reused time, baking time and baking temperature on COD removal. The result indicated that baking at 330-450°C for 20-30 min provided highest treatment efficiency. COD removal efficiency of 6 times recycling was nearly the COD removal of 1 time recycling. Moreover, there is the COD removal comparative between using fresh ferric sulfate and regenerated iron sludge. The result showed that the regenerated iron sludge was more effective than the fresh ferric sulfate. This was due to some Fe^{3+} in sludge could be changed to Fe^{2+} due to incomplete combustion.

CHAPTER 3

METHODOLOGY

3.1 Experimental overview

The research experiment is divided into 4 parts as follow:

3.1.1 Analysis of synthetic cutting oily wastewater

3.1.2 Treatment of stable oil emulsion wastewater by Fenton oxidation process

1) Effect of Fenton's reagents dosage

2) Effect of Fenton's reagent feeding mode

3) Control Experiments (controlling pH to 3, ferrous iron coagulation/precipitation and H_2O_2 oxidation)

3.1.3 Evaluation of operating parameters for designing the complete Fenton process

1) The optimum reaction time, reaction rate constant and reaction order

2) Residual Fe^{2+} and Fe^{3+} in the Fenton reaction

3) Iron precipitation after Fenton process

3.1.4 Reuse of iron sludge as iron catalyst for the next Fenton process

3.2 Experimental set up

3.2.1 Chemical agent used in this research

1) Cutting oil; Castrol Cooledge BI

2) Ferrous Sulfate ($FeSO_4.7H_2O$); Ajax Finchem Plt Ltd.

3) Hydrogen peroxide (H_2O_2); Carlo Erba Co.,Ltd.

4) Sodium hydroxyl (NaOH); Ajax Finchem Plt Ltd.

5) Sulfuric Acid (H_2SO_4); Carlo Erba Co.,Ltd.

6) Ferrous Ammonium Sulphate ($NH_4Fe(SO_4)_2 \bullet 12\ H_2O$); Carlo Erba Co.,Ltd.

7) Potassium Dichromate, $K_2Cr_2O_7$

8) Silver sulfate, Ag_2SO_4

9) Mercury Sulphate ($HgSO_4$); Qrec Co.,Ltd.
10) 1,10-phenanthroline (C12H8N2.H2O); Ajax Finchem Plt Ltd.
11) Acetic Acid (CH3COOH); Qrec Co.,Ltd.

3.3.2 Equipment

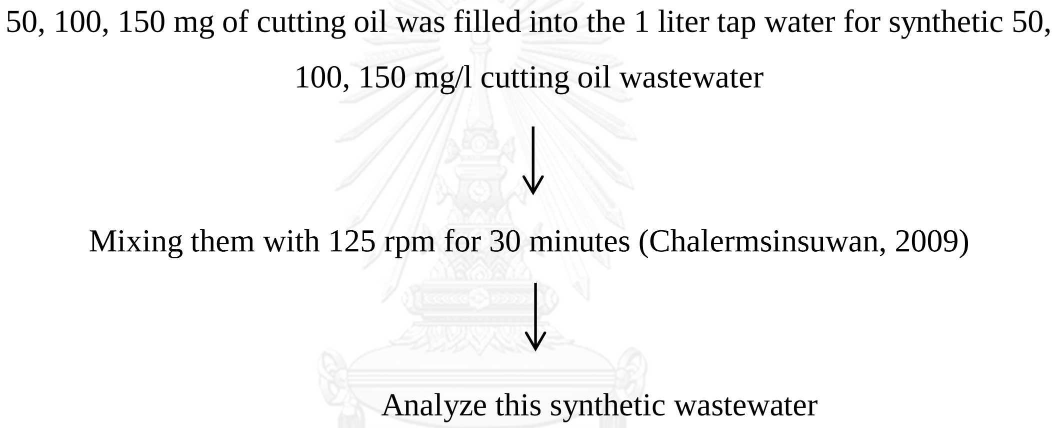
1) Jar test device
2) pH meter
3) Hot air oven (150°C)
4) Turbidity meter
5) Test tube (160x150 mm) with Tetrafluoroethylene cap
6) Cylinder size 500, 1000 ml
7) Pipet size 1,5 and 10 ml
8) Volumetric Flask size 100 and 1000 ml.
9) Beaker size 1, 2 liter
10) Pump
11) Spectrophotometer
12) 1.2 µm filter paper

3.3 Experimental procedures

3.3.1 Synthesis of cutting oil wastewater (Sample preparation)

The stable oily wastewater that used in this study was synthesized by diluting commercial cutting oil (Castrol cooledge BI) with tap water. Fenton process was employed as a post-treatment process after physical separation process, therefore the initial concentration of cutting oil wastewater were 50, 100, 150 mg/l (Rojvilavan, 2011). The preparation process of cutting oil wastewater and measured parameters for analyzing are shown in Figure 3.1, Table 3.1

Method



50, 100, 150 mg of cutting oil was filled into the 1 liter tap water for synthetic 50, 100, 150 mg/l cutting oil wastewater

↓

Mixing them with 125 rpm for 30 minutes (Chalermsinsuwan, 2009)

↓

Analyze this synthetic wastewater

Figure 3.1 synthesis of cutting oil wastewater

3.3.2 Analysis of the synthetic cutting oil wastewater

Table 3.1 measured parameter for analyzing the synthetic cutting oil wastewater

Fixed Variables	Parameter
Type of oil	Cutting oil
Type of water	Tap water
Mixing rate	125 rpm for 30 min
Independent Variable	Parameter
Concentration of cutting oil	50, 100, 150 mg/l
Dependent Variable	Parameter
Concentration of synthetic wastewater	COD, Turbidity, pH

3.3.3 Treatment of synthetic oily wastewater by Fenton oxidation process

1) Effect of Fenton's reagent dosage

This part aims to investigate the effect of Fenton's reagents dosage on COD removal efficiency and determine the optimum dosage of Fe^{2+} and H_2O_2 at different initial oil concentration. Effect of Fenton's reagent at different initial oil concentration was also investigated. The initial pH of wastewater was adjusted to 3 in order to obtain effective Fenton oxidation (Rojvilavan, 2011). The reaction time of Fenton's reaction was fixed at 30 min, since the COD removal efficiency was steady after 30 minutes suggesting that the oxidation was complete (Permchati, 2013).

Table 3.2 Variable of study the optimum Fenton's reagent dosage

Fixed Variables	Parameter
Volume of synthetic wastewater	1 liter
Initial pH of wastewater	3 ± 0.2
Mixing rate	200 rpm (provided by J-test-blading)
Sampling time (reaction time)	30 min
Independent Variable	Parameter
Concentration of cutting oil	50, 100 and 150 mg/l
Ferrous dose (Fe^{2+})	50, 200 and 500 mg/l
Fe^{2+}/H_2O_2 ratio by mass	1:2.5, 1:6, 1:10
Dependent Variable	Parameter
Residual oil concentration	COD

Method

1. Fill 1 liter of the synthetic wastewater into a 2 liter batch reactor
2. Adjust pH of wastewater to 3 by adding 2 M H_2SO_4
3. Add Fe^{2+} in form of solid $FeSO_4.7H_2O$ and 30% H_2O_2
4. Take sample at 30 minutes
5. Adjust pH of the taken sample to 9 by adding 2M NaOH for stopping Fenton's reaction
6. Analyze the sample for COD

2) Effect of Fenton's reagents feeding mode

This part aims to prove that step feeding mode of Fenton's reagent affects to the oxidation of cutting oil since multiple step feeding of Fenton's reagent can reduce the scavenger of hydroxyl radical from excess Fe^{2+} and H_2O_2 (Mohajeri et al., 2010). Moreover the optimum feeding mode that provided maximum COD removal was also determined. In this study, Fe^{2+} and H_2O_2 are added simultaneously at several reaction times.

Table 3.3 Variable of study the optimum step feeding mode of Fenton's reagent

Fixed Variables	Parameter
Volume of synthetic wastewater	1 liter
Initial pH of wastewater	3 ± 0.2
Mixing rate	200 rpm (provided by J-test-blading)
Sampling time (reaction time)	30 min
Concentration of cutting oil	100 and 150 mg/l
Total ferrous dose (Fe^{2+})	50 mg/l
Fe^{2+}/H_2O_2 ratio by mass	The optimum ratio of 50 mg Fe^{2+} from part 3.3.3.1
Independent Variable	Parameter
Step feeding mode	One feeding (at t= 0) two feeding (t= 0,5 min) three feeding (t= 0, 5, 10 min)
Dependent Variable	Parameter
Residual oil concentration	COD

Method

1. Fill 1 liter of the synthetic wastewater into a 2 liter batch reactor
2. Adjust pH of wastewater to 3 by adding 2 M H_2SO_4
3. Add Fe^{2+} and H_2O_2 simultaneously in one feeding (at 0 min), two feeding (at 0, 5 min), three feeding (at 0, 5, 10 min)
4. Take sample at 30 min
5. Adjust pH of the taken sample to 9 by adding 2M NaOH for stopping Fenton's reaction
6. Analyze the sample for COD

3) Control experiments

This part aims to investigate the effect of controlling pH of wastewater to 3, ferrous coagulation/precipitation and H_2O_2 oxidation on cutting oil removal. Treatment efficiency of controlling pH of wastewater, ferrous coagulation/precipitation and H_2O_2 oxidation were also investigated in order to compare with Fenton oxidation

Table 3.4 Variable of study controlling pH of wastewater to 3, ferrous coagulation/precipitation and H_2O_2 oxidation

Fixed Variables	Parameter
Volume of synthetic wastewater	1 liter
Initial pH of wastewater	3 ± 0.2
Mixing rate	200 rpm (provided by J-test-blading)
Sampling time (reaction time)	30 min
Concentration of cutting oil	100
ferrous dose (Fe^{2+})	50 and 200 mg/l
Fe^{2+}/H_2O_2 ratio by mass	The optimum ratio of 50 mg Fe^{2+} and 200 mg Fe^{2+} from part 3.3.3.1
Independent Variable	**Parameter**
Controlling pH to 3	Synthetic wastewater was adjusted pH to 3 by adding H_2SO_4.
Ferrous Coagulation/precipitation	Fe^{2+} was added after adjusting pH of synthetic wastewater to 3. Then, NaOH was added to neutralize.
H_2O_2 oxidation	H_2O_2 were added into synthetic wastewater.
Dependent Variable	**Parameter**
Residual oil concentration	COD

Method

1. Fill 1 liter of the synthetic wastewater into a 2 liter batch reactor
2. Adjust pH of wastewater to 3 by adding 2 M H_2SO_4
3. Add Fe^{2+} for ferrous coagulation/precipitation or add H_2O_2 for H_2O_2 oxidation
4. Take sample at 30 min

5. Adjust pH of the taken sample to 7 for ferrous coagulation/precipitation
6. Analyze the sample for COD

3.3.4 Evaluation of operating parameters for designing the complete Fenton process

1) The optimum reaction time, reaction rate constant and reaction order

This part aims to find the optimum reaction time or saturation time of oily wastewater treatment by Fenton oxidation that imply to cutting oil was oxidized completely. Moreover, the reaction rate constant (K) and the reaction order (n) which can be calculated from the result in this part were used to design the completely stirred tank reactor (CSTR)

Table 3.5 Variable of study the optimum reaction time

Fixed Variables	Parameter
Volume of synthetic wastewater	1 liter
Initial pH of wastewater	3 ± 0.2
Mixing rate	200 rpm (provided by J-test-blading)
Concentration of cutting oil	50, 100 and 150 mg/l
Ferrous dose (Fe^{2+})	the optimum dosage of each cutting oil concentration which is the result from 3.3.3.1
Fe^{2+}/H_2O_2 ratio by mass	The optimum ratio of each cutting oil concentration which is the result from 3.3.3.1
Independent Variable	**Parameter**
Sampling time	0, 0.2, 0.5, 1, 5, 10, 20, 30, 60 min
Dependent Variable	**Parameter**
Residual oil concentration	COD

Method

1. Fill 1 liter of the synthetic wastewater into a 2 liter batch reactor
2. Adjust pH of wastewater to 3 by adding 2 M H_2SO_4
3. Add Fe^{2+} and H_2O_2

4. Take sample at 0, 0.2, 0.5, 1, 5, 10, 20, 30, 60 min after star reaction
5. Adjust pH of the taken sample to 11 by adding 2M NaOH for stopping Fenton's reaction
6. Analyze the sample for COD

2) Residual Fe^{2+} and Fe^{3+} in the Fenton reaction

Table 3.6 Variable of study the residual Fe^{2+} and Fe^{3+} in the Fenton reaction

Fixed Variables	Parameter
Volume of synthetic wastewater	1 liter
Initial pH of wastewater	3 ± 0.2
Mixing rate	200 rpm (provided by J-test-blading)
Concentration of cutting oil	100 mg/l
Ferrous dose (Fe^{2+})	the optimum dosage of 100 mg/l oil concentration from 3.3.3.1
Fe^{2+}/H_2O_2 ratio by mass	the optimum dosage of 100 mg/l oil concentration from 3.3.3.1
Independent Variable	Parameter
Sampling time	0, 0.2, 0.5, 1, 5, 10, 20, 30, 60 min
Dependent Variable	Parameter
Residual iron concentration	Amount of Fe^{2+} and total Fe

3) Iron precipitation after Fenton process

After stabilized oil was oxidized by Fenton process, the pH of treated water still was around 3 that cannot be discharged to an environment. Thus, the treated water has to be adjusted pH to 7 under standard discharge regulation by adding NaOH know as neutralization. Fe^{2+} and Fe^{3+} precipitated with hydroxide in form of $Fe(OH)_2$ and $Fe(OH)_3$ in sedimentation tank as shown in figure 3.2. In this part, Iron sedimentation mechanism were also studied, especially overflow rate of sedimentation tank that can control suspended solid discharge.

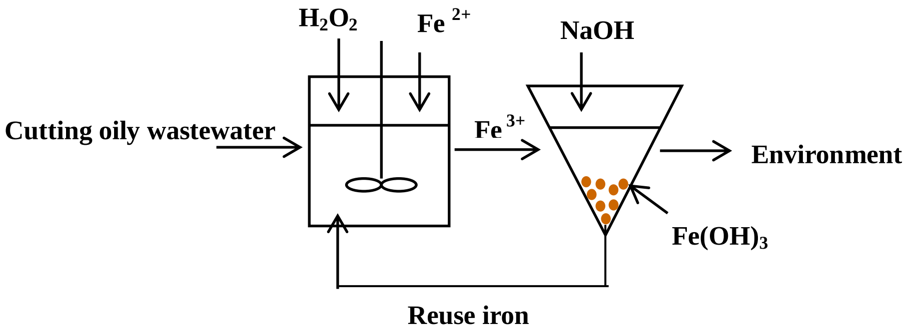


Figure 3.2 Fenton and iron precipitation process

From the observation, sedimentation of $Fe(OH)_2$ and $Fe(OH)_3$ was considered to be discrete settling. The standard discharged regulation of suspended solid (SS in the discharge should not exceed 50 mg/l) was employed to determine the optimum overflow rate of sedimentation tank.

Table 3.7 Variable of study the iron precipitates

Fixed Variables	Parameter
Volume of synthetic wastewater	1 liter
pH of wastewater	7
Concentration of cutting oil	50, 100 and 150 mg/l
Ferrous dose (Fe^{2+})	50 and 200 mg/l
Fe^{2+}/H_2O_2 ratio by mass	The optimum ratio of each cutting oil concentration which is the result from 3.3.3.1
Independent Variable	Parameter
Sampling time (Settling time)	0, 3, 5, 7, 11, 15, 20, 30, 60 min
Dependent Variable	Parameter
Amount of insoluble particle	Total suspended solid (TSS)

Method

1. Add NaOH into a batch reactor to adjust pH around 7 after Fenton oxidation was finished.
2. Pour the treated water containing suspended solid into settling column as shown in Figure 3.3
3. Take sample at 0, 3,5,7,11, 15, 20, 30, 60 min

4. Analyze the sample for total suspended solid
5. Calculate the setting velocity of insoluble particle and overflow rate of settling tank by discrete setting method

Figure 3.3 Settling column

3.3.5 Reuse of iron sludge as iron catalyst for Fenton-like reactions

This part aims to reuse iron sludge that was produced during neutralization after Fenton process as shown in figure 3.2, since iron sludge ($Fe(OH)_2$ and $Fe(OH)_3$) known as a hazardous waste requires high disposal cost. Iron sludge can be reused as iron catalyst for Fenton-like reactions (Cao et al., 2009) in the next Fenton process.

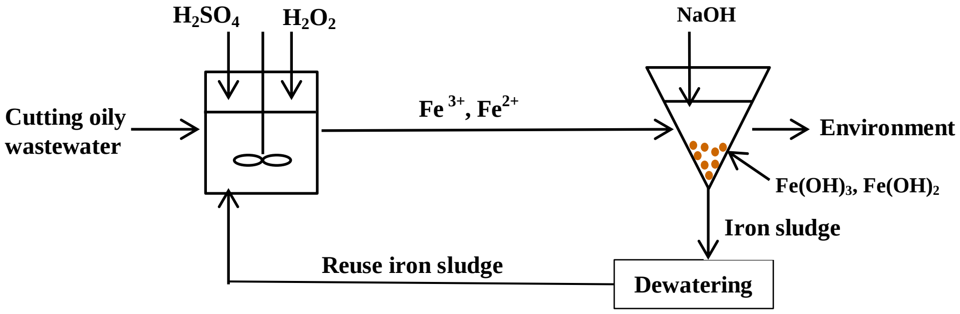


Figure 3.4 Reuse of iron sludge for the next Fenton process

Method

1. Neutralization: add NaOH into a batch reactor to adjust pH around 7-8, after Fenton process was finished. Soluble iron will precipitated with hydroxide to form iron containing sludge
2. Precipitation: leave iron sludge to settle for 24 hr.
3. Dewatering: separate iron precipitates from the solution by centrifugation at 10000 rpm for 10 min
4. Dissolved the concentrated sludge in a sulfuric acid solution
5. Add all dissolved iron sludge into a batch reactor containing synthesize wastewater for the next process without fresh iron replacement
6. Adjust pH of wastewater to 2.5 to ensure the residual iron was dissolved
7. Add H_2O_2 into a batch reactor for starting Fenton reaction
8. Take sample at 30 min after star reaction
9. Adjust pH of the taken sample to 9 by adding 2M NaOH for stopping Fenton's reaction
10. Analyze the sample for COD
11. Reuse: perform follow by 1 again (Reuse iron solid until Fenton oxidation is not effective to treat oil emulsion)

3.4 Analytical parameter

Parameter	**Analytical method**
pH	pH-meter
Turbidity	Turbidity meter
COD	Dichromate Close Reflux Method (AWWA 508A.)
Amount of Fe^{2+} and Fe^{3+}	Phenanthroine method (AWWA.)

CHAPTER 4
RESULT AND DISCUSSION

This research investigates the treatment of cutting oil wastewater by Fenton process as post- treatment after physical separation process. This study focuses on effect of Fenton's reagent dosage and step feeding mode of Fenton's reagent. Moreover, iron precipitation after Fenton process, and reuse of iron sludge as iron catalyst were also studied. The result and discussion in this chapter are divided into 5 parts. The first part presents characteristics of the synthetic oily wastewater. Part 2 describes the treatment of synthetic oily wastewater by Fenton process focusing on effects of Fenton's reagent dosage on COD removal efficiency. To enhance removal efficiency, multiple feeding of Fenton's reagent was applied. Effect of step feeding mode is also explained in this part. In addition, the optimum reaction time, reaction rate constant and reaction order, which can be applied to design a continuous process, is demonstrated in part 3. For understanding the mechanism of Fenton reaction, the change of iron species in form of Fe^{2+} to Fe^{3+} was also studied as in part 3. After Fenton oxidation was finished, the soluble iron would precipitate by the pH neutralization. The optimal overflow rates of the sedimentation tank were calculated for an effective removal of the iron precipitates in part 3. The obtained reaction rate constant, reaction order and the optimum overflow rate of sedimentation tank were employed to design the continuous Fenton process in part 4. Finally, the reuse of the iron sludge in order to reduce its disposal cost was study as displayed in part 5.

4.1 Characteristic of synthetic cutting oil wastewater

Cutting oil wastewater was synthesized by diluting 50, 100, and 150 mg of the commercial Castrol Cooledge BI cutting oil with 1 liter tap water and then mixed by Jar-test-blading at 125 rpm for 30 minutes (Chalermsinsuwan, 2009). All concentration of these synthetic wastewater were very low since this research aims to study a post treatment process for the residual oil after physical separation process. In order to study the treatment of cutting oil wastewater, this synthetic wastewater was analyzed for several parameters as shown in Table 4.1. COD and turbidity of wastewater were varied with amount of cutting oil in the water; therefore, COD was used as main parameter to calculate the removal efficiency in this research.

Table 4.1 Properties of synthetic cutting oil wastewater

Parameter	**Concentration of synthetic cutting oil wastewater (mg/L)**			**Standard discharge regulation ***
	50	100	150	
COD (mg/L)	120±20	210±20	290±20	120
Turbidity	128±10	145±10	165±10	-
pH	7.8-8.0			5.5-9.0

* Source: Notification the Ministry of Science, Technology and Environment, No. 3, B.E.2539 (1996) issued under the Enhancement and Conservation of the National Environmental Quality Act B.E.2535 (1992)

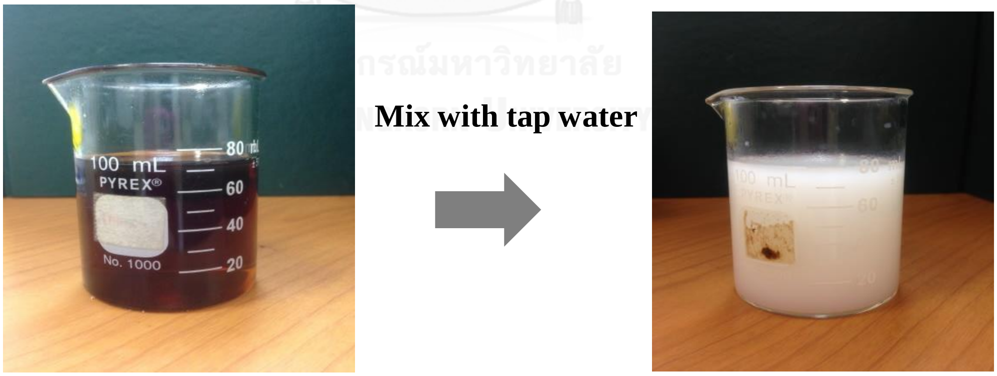


Figure 4.1 Concentrated commercial Cutting oil and synthetic oil wastewater

In Figure 4.1, the appearance of synthetic cutting oil wastewater was milky emulsion that is very stable and unlikely to separate from water naturally because of the presence of surfactant. The surfactant causes the decrease of interfacial tension between oil and water and acts as barrier that prevents the collision and the coalescence between oil droplets; thus, oil droplets remain small and contain very small rising velocity (Nesterenko et al., 2014). The study of Chalermsinsuwan (2009) confirms that cutting oil emulsion is highly stable since the suspended oil cannot be separated or remove from water by decantation for 5 days. COD was not reduced significantly. Therefore, it was implied that stable oil emulsion is difficult to be treated by a conventional physical separation process. However, coagulation known as a chemical destabilization provided 90% COD removal of 1 g/l oil concentration (Rojvilavan, 2011) that the effluent COD still exceed the standard discharge regulation (COD of the discharged water should not exceed 120 mg/l). Therefore, Fenton process known as the advanced oxidation process was selected to treat the residual oil in this research since this treatment process has many advantages as follow:

1. Fenton can completely destruct the contaminants to harmless compound such as carbon dioxide and water (a complete mineralization).

2. Fenton doesn't require energy input to produce hydroxyl radical which is a strong oxidative power.

3. The destruction or oxidation of contaminants is very fast; hydroxyl radical react rapidly with the contaminants within minutes-hour depending on H_2O_2 concentration (Umar et al., 2010).

4. Fenton is easy to operate and no need for special equipment.

5. Fenton's reagents are available at moderate cost.

4.2 Treatment of synthesis oily wastewater by Fenton process

In Fenton process, ferrous ions (Fe^{2+}) catalyze the production of hydroxyl radical (·OH) from hydrogen peroxide as shown in equation 2.1 (Kang et al., 2000). Hydroxyl radical has high oxidative power that can react unselectively with organic substance (RH) as presented in equation 2.2 (Zhang et al., 2005). Cutting oil was oxidized rapidly by this radical. The important factors that affect to Fenton oxidation are Fenton's reagent dosage (Fe^{2+} and H_2O_2), initial pH of the solution, and reaction time (Kang et al., 2000). To achieve high efficiency in Fenton process, initial pH should be controlled around 2-4 (Kallel et al., 2009). As found in the study of (Rojvilavan, 2011), the optimal initial pH of Fenton process for maximum cutting oil removal is 3, which was applied in this study. According to the experiment of (Permchati, 2013), COD was rapidly reduced at the initial reaction time and became steady after 30 minutes suggesting that the oxidation was completed. Therefore, the reaction time of Fenton's reaction in all experiment was fixed at 30 min.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH + OH^- \qquad (2.1)$$

$$RH + \cdot OH \longrightarrow H_2O + R\cdot \qquad (2.2)$$

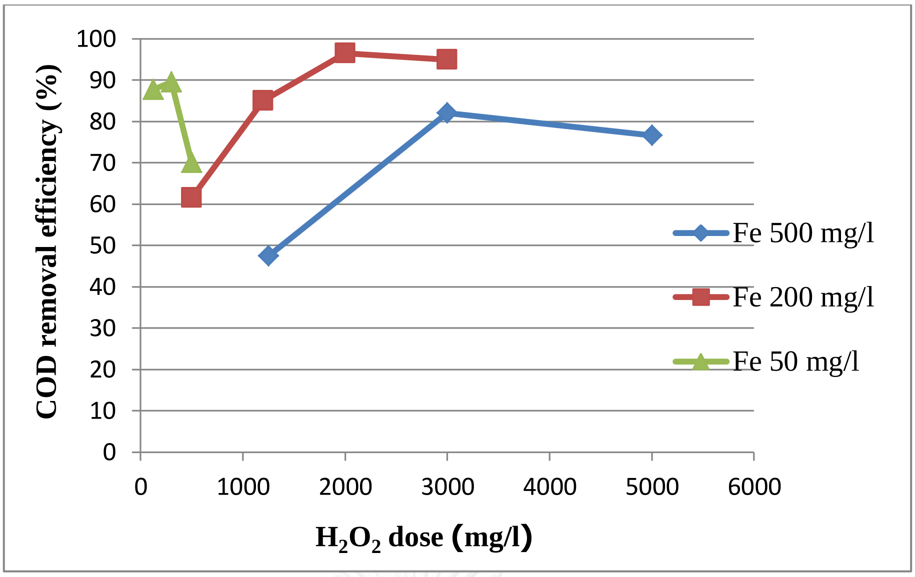
In the Fenton Experiment, pH of the synthetic oily wastewater in a batch reactor was firstly adjusted to 3. Ferrous ion (Fe$^{2+)}$ in form of $FeSO_4.7H_2O$ was added in a desired amount. Stable oil emulsion was mixed with Fe^{2+} by Jar-test-blading before adding H_2O_2. It was observed that color of aqueous solution which contains oil and Fe^{2+} would change from white to yellow when H_2O_2 was added as shown in Figure 4.2. After that, the color of Fenton solution wasn't changed along with 90 minutes reaction time. However, the study of Kavitha and Palanivelu (2004) found that H_2O_2 caused the color change in solution that contains phenol and Fe^{2+}. Within 30 seconds after adding H_2O_2, the color of the solution changed from colorless to brown. Along with Fenton reaction, the brown color of the solution was changed to light yellow in 45 minutes reaction time. They indicated that Fenton reaction completed in 45 minutes. Thus, the color changes of solution after adding H_2O_2 could confirm that Fenton reaction occur in this experiment.

(a) (b) (c)

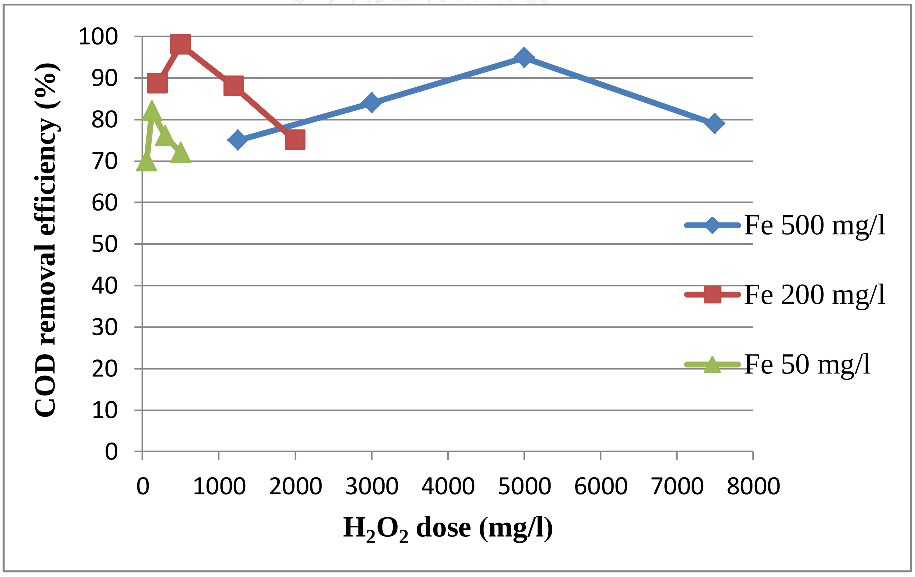
Figure 4.2 Color change of Fenton reaction (a) 100 mg/l stable oil emulsion, (b) stable oil mix with 50 mg Fe^{2+}/l, (c) Fenton solution after adding H_2O_2

4.2.1 Effect of Fenton's reagents dosage on cutting oil removal in Fenton process

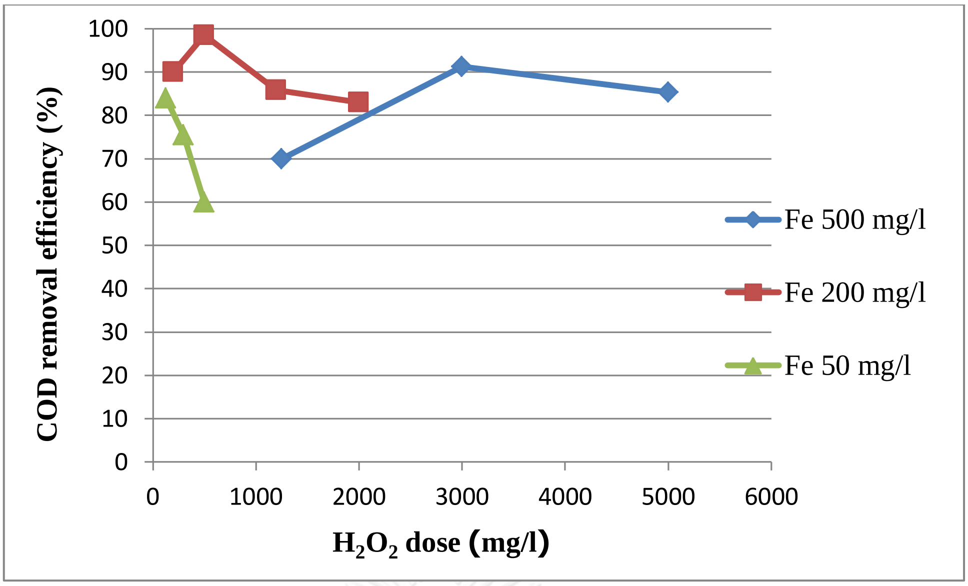
The dosage of Fe^{2+} and H_2O_2 are important parameters to be investigated since they directly affect the oxidation potential of cutting oil as well as an operating cost. The amount of produced hydroxyl radicals depend on the dosage of Fe^{2+} and H_2O_2. In addition, Fenton's regent dosages are the main operating cost of Fenton process, especially H_2O_2 (Asghar et al., 2015). Therefore, the optimum dosage of Fe^{2+} and H_2O_2 are highly necessary to be determined. To investigate effects of Fenton's reagent dosage and determine the optimum dosage of Fe^{2+} and H_2O_2, the experiments were carried out by varying Fe^{2+} dosage to 50, 200, and 500 mg/l; and Fe^{2+}/H_2O_2 ratio by mass to 1:2.5, 1:6, and 1:10 (Permchati, 2013; Rojvilavan, 2011). Three different synthetic cutting oil concentrations (50 mg/l, 100 mg/l, and 150 mg/l) were treated with these varied Fe^{2+} dosages and Fe^{2+}/H_2O_2 ratios. Figure 4.3 shows the COD removal efficiency at different Fe^{2+} and H_2O_2 concentrations. The result demonstrated that Fenton process can effectively treat cutting oil emulsion with high efficiency under these conditions.


COD removal efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
H_2O_2 dose (mg/l)
Fe 500 mg/l
Fe 200 mg/l
Fe 50 mg/l

(a)


COD removal efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
7000
8000
H_2O_2 dose (mg/l)
Fe 500 mg/l
Fe 200 mg/l
Fe 50 mg/l

(b)



(c)

Figure 4.3 Effect of H_2O_2 concentration on COD removal efficiency at different Fe^{2+} concentration for different initial oil concentration of (a) 50 mg/l, (b) 100 mg/l and (c) 150 mg/l

According to Figure 4.3, the COD removal efficiencies were increased along with the H_2O_2 concentration until reaching the maximum COD removal efficiency. Further increase of H_2O_2 dosage resulted in the lower COD removal due to the hydroxyl radical scavenging effect from the excess amount H_2O_2 (Mohajeri et al., 2010). Residual H_2O_2 would be the scavenger of hydroxyl radical producing hydroperoxyl radical ($HO_2\cdot$), which has less oxidative power than the hydroxyl radical as presented in equations 2.6 – 4.2. When a large amount of H_2O_2 is available, cutting oil as an organic compound and the residual H_2O_2 competed to react with produced hydroxyl radical resulting in the lower oxidation of cutting oil. It can be clearly seen from Figure 4.3 (a) that increasing of H_2O_2 concentration from 3000 to 5000 mg/l at Fe^{2+} concentration of 500 mg/l reduced COD removal efficiencies from 82% to 76%. At 50 mg/l initial oil concentration and 200 mg Fe^{2+}/l, 61%, 80%, 96% and 94% of COD removal can be attained with the applied H_2O_2 concentrations of 500, 1200, 2000 and 3000 mg/l (i.e. $Fe^{2+/}H_2O_2$ ratio = 1:2.5, 1:6, 1:10, and 1:15), respectively. The highest COD removal efficiency for treating 50 mg/l initial oil concentration was achieved at 200 mg Fe^{2+}/l and 2000 mg H_2O_2/l (Fe^{2+}/H_2O_2 ratio= 1:10). However, the highest

COD removal efficiency of 100 and 150 mg/l initial oil concentration was achieved at 200 mg Fe^{2+}/l and 500 mg H_2O_2/l (Fe^{2+}/H_2O_2 ratio= 1:2.5).

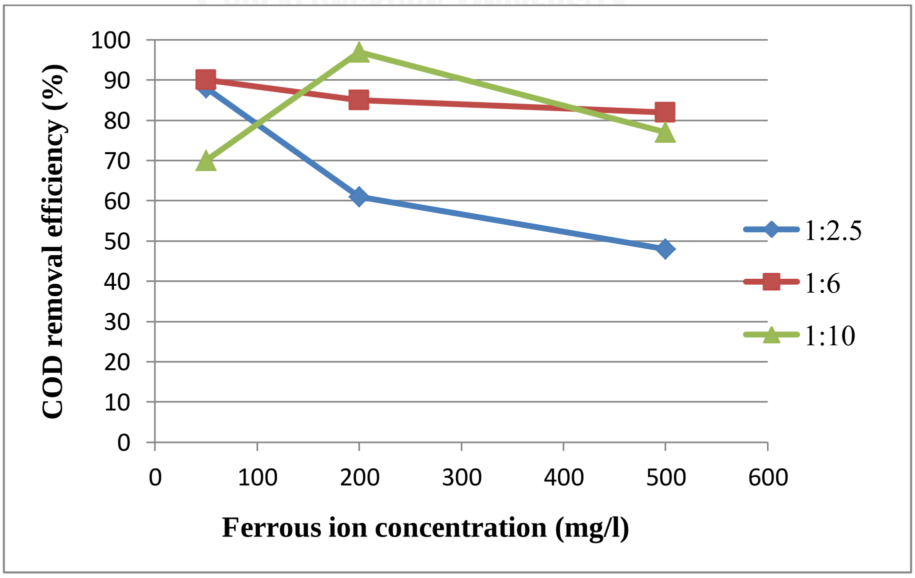
$$\cdot OH + H_2O_2 \longrightarrow HO_2\cdot + H_2O \tag{2.6}$$

$$HO_2\cdot + \cdot OH \longrightarrow O_2 + H_2O \tag{4.1}$$

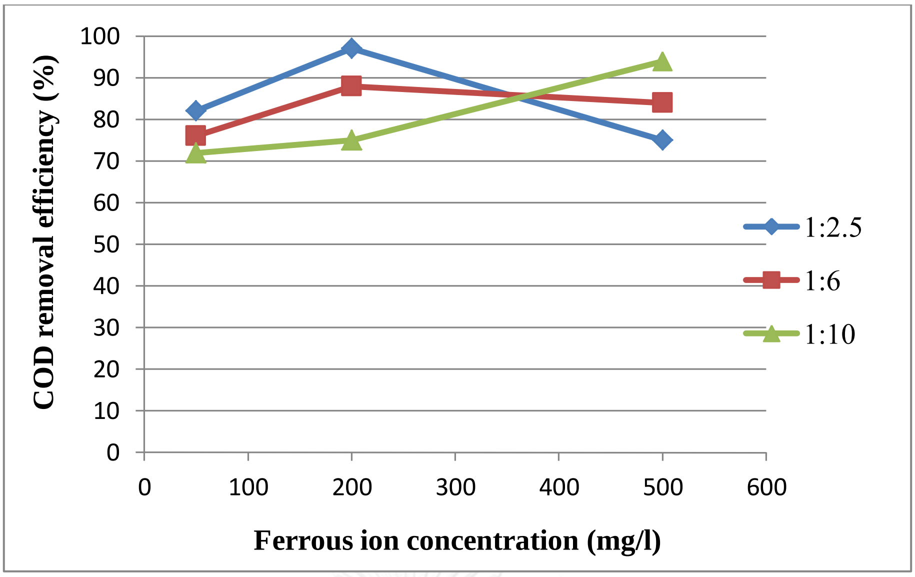
$$\cdot OH + \cdot OH \longrightarrow O_2 + H_2O \tag{4.2}$$

Moreover, effect of Fe^{2+} concentration on COD removal was also investigated, since Fe^{2+} act as a catalyst in Fenton process. Catalyst concentration increases the oxidation rate as Fe^{2+} activates H_2O_2 to produce hydroxyl radicals (Lucas et al., 2009). The results in figure 4.4 (a) - 4.4 (c) were the COD removal efficiencies at different Fe^{2+} concentrations. The oxidation efficiency in term of COD removal was increased with increasing Fe^{2+} concentrations. However, using higher dosage of Fe^{2+} provided lower COD removal. This is due to the excess amount of Fe^{2+} would be a scavenger of hydroxyl radical as in Equation 2.5 (Zhang et al., 2007). This radical scavenging effect can be clearly seen at 500 mg Fe^{2+}/l (high Fe^{2+} concentration) and 1:2.5 Fe^{2+}/H_2O_2 ratio (low H_2O_2 concentration) where low COD removal efficiency was obtained.

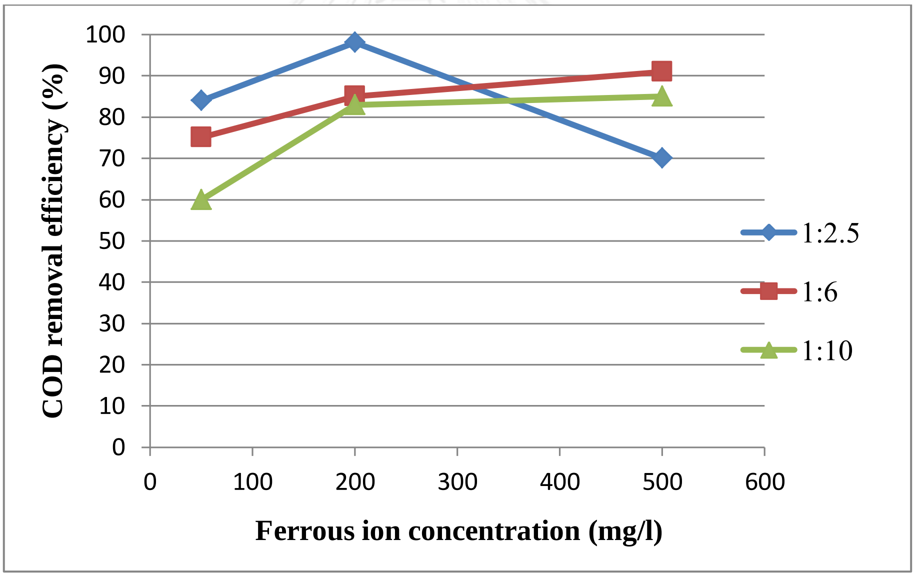
$$Fe^{2+} + \cdot OH \longrightarrow Fe^{3+} + OH^- \tag{2.5}$$



(a)



(b)



(c)

Figure 4.4 Effect of Fe^{2+} concentration on COD removal efficiency at different Fe^{2+}/H_2O_2 ratio for different initial oil concentration of (a) 50 mg/l, (b) 100 mg/l, and (c) 150 mg/l

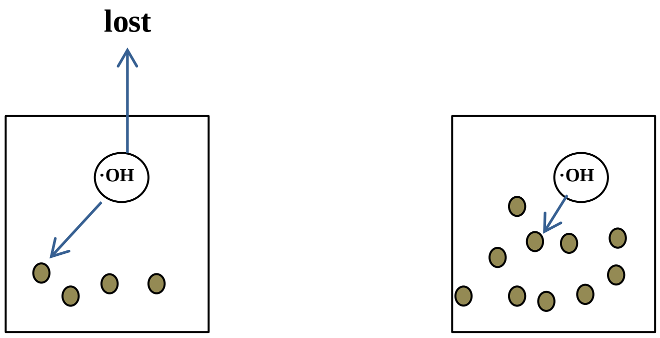
According to Figure 4.4 (b), when Fe^{2+} concentration was lowest (50 mg/l), highest COD removal was achieved at low amount of H_2O_2 (1:2.5). On the contrary, when

Fe^{2+} concentration was highest (500 mg/l), highest COD removal was achieved at high amount of H_2O_2 (1:10). Therefore, it can be concluded that high oxidation efficiency was provided at the optimum Fe^{2+}/H_2O_2 ratio. Table 4.2 summarized the Fe^{2+} and H_2O_2 concentrations that gave the maximum COD removal efficiency at different initial oil concentrations.

Table 4.2 the Fenton's reagent dosage that provide maximum COD removal at different initial oil concentration.

Cutting oil concentration (mg/l)	**Fe^{2+} (mg/l)**	**H_2O_2 (mg/l)**	**Fe^{2+}/H_2O_2 ratio (mass: mass)**	**COD removal efficiency (%)**
50	200	2000	1:10	97
100	200	500	1:2.5	97
150	200	500	1:2.5	98

From the obtained Fenton's reagents dose that provide maximum COD removal in Table 4.2, it was observed that low cutting oil concentration (50 mg/l) can achieved high oxidation by using high amount of H_2O_2: this can be possibly explained as small number of oil droplets would rarely collide with hydroxyl radicals. As the hydroxyl radical can disappear in a short period (Tahara andOkubo, 2012), a high amount of H_2O_2 was therefore required for the effective oxidation of the emulsion with lower concentration. The suggested mechanism can be concluded as in Figure 4.5.



50 mg/l of cutting oil concentration **100 mg/l of cutting oil**

Figure 4.5 Density of oil particle in different oil concentration

4.2.2 Effect of Fenton's reagent feeding mode

From the finding in the previous part, oxidation of cutting oil was low when applying excess dose of H_2O_2. Reaction 2.1 completes with reaction 2.6 in consumption of H_2O_2 resulting in low free hydroxyl radical. On the contrary, when an excess amount of Fe^{2+} was used, a residual Fe^{2+} and organic compounds competed to react with hydroxyl radical. Then, free hydroxyl radical would decrease and the oxidation of cutting oil would also reduce. These reactions are known as hydroxyl radical scavenging reaction which causes lower oxidation. Therefore, multiple feeding modes of Fenton's reagents were applied to reduce the excess amount of Fe^{2+} and H_2O_2 in this part. The experiments were operated to treat 100 and 150 mg/l initial oil concentration by using low Fenton's reagent dose (Fe^{2+} = 50 mg/l and Fe^{2+}/H_2O_2 ratio= 1:2.5) in order to reduce chemical usage. 50 mg/l initial oil concentration wasn't operated in this part, since initial full feeding of 50 mg Fe^{2+}/l and 125 mg H_2O_2/l provided high COD removal (90%). In this part, Fenton's reagents were added in several modes as follow:

Case1: Both Fe^{2+} (50 mg/l) and H_2O_2 (125 mg/l) were added simultaneously in one feeding (t = 0 min), two feeding (at t = 0 and 5 min) and three feeding (at t = 0, 5, and 10 min). The reaction time was 30 minutes.

Case 2: Fe^{2+} (50 mg/l) was added in an initial full feeding (at t = 0 min). On the other hands, H_2O_2 (125 mg/l) was added in one feeding (t = 0 min) and two feeding (at t = 0 and 5 min). The reaction time was 30 minutes.

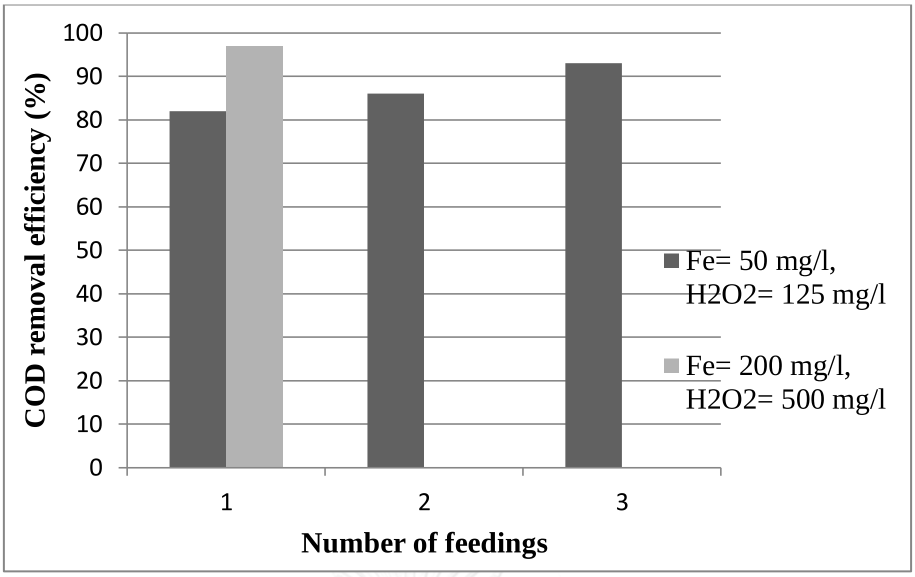


Figure 4.6 Effect of Fenton's reagents feeding modes on COD removal efficiency (initial oil concentration= 100 mg/l, case 1)

According to Figure 4.6 (Case 1), the results show that better COD removal was obtained when Fe^{2+} and H_2O_2 were added in two feeding and three feeding compared to the initial full feeding (one feeding). This result was similar with the study of Zhang et al. (2006) and Mohajeri et al. (2010) as the multiple step feeding of Fenton's reagents can increase the oxidation rate of organic compound in term of COD removal. The COD removal efficiency was increased from 82% to 86% by two feedings of 25 mg Fe^{2+}/l and 62.5 mg H_2O_2/l (total Fe^{2+} and H_2O_2 = 50 mg/l and 125 mg/l, respectively) as shown in Figure 4.6. Moreover, three feeding of 16.67 mg Fe^{2+}/l and 41.67 mg H_2O_2/l (total Fe^{2+} and H_2O_2= 50 mg/l and 125 mg/l) increased COD removal from 82% to 93% that was close to the highest efficiency at the optimum Fenton's reagent dosage (Fe^{2+}= 200 mg/l and H_2O_2= 500 mg/l) of 97%. It can be concluded that multiple feeding of Fenton's reagents can minimize hydroxyl radical scavenging effect from residual Fe^{2+} and H_2O_2 since the stepwise addition can retain the Fenton's reagents dose at low levels. More hydroxyl radicals could be employed to oxidize cutting oil. The benefits of multiple feedings are the increase of oxidation rate and reduction of chemical usage that lead to lower operating cost.

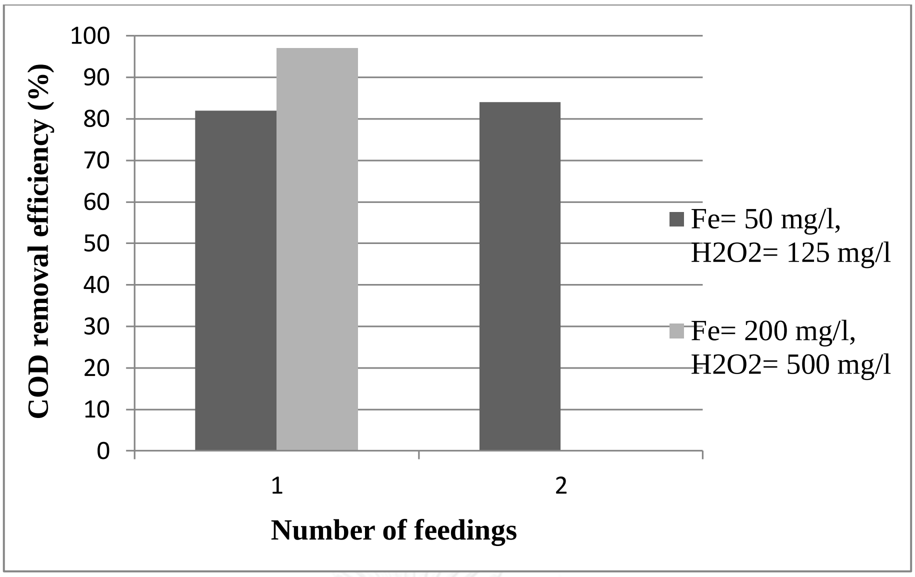


Figure 4.7 Effect of Fenton's reagents feeding modes on COD removal efficiency (initial oil concentration= 100 mg/l, case 2)

According to figure 4.7 (Case2), two feeding of 62.5 mg H_2O_2/l (at t = 0, 5 min) and initial full feeding of 50 mg Fe^{2+}/l (at t = 0 min) increased the COD removal slightly from 82% to 84%. This could be due to amount of Fe^{2+} was exceed comparing with amount of H_2O_2 in the first addition (at t = 0 min). A residual Fe^{2+} and cutting oil would compete to react with hydroxyl radical; thus, less hydroxyl radical could oxidize cutting oil resulting in low COD removal. Cutting oil oxidation by applying multiple feeding in Case 1 was higher than Case 2 because both Fe^{2+} and H_2O_2 were added simultaneously in Case 1, which kept the Fe^{2+}/H_2O_2 ratio at the optimum value of 1:2.5 at every addition. Therefore, the hydroxyl radical scavenging effects by Equation 2.5 and Equation 2.6 were minimized and COD removal was also improved. This suggested that the dosage of Fe^{2+} and H_2O_2 should be added in the optimum Fe^{2+}/H_2O_2 ratio at every addition.

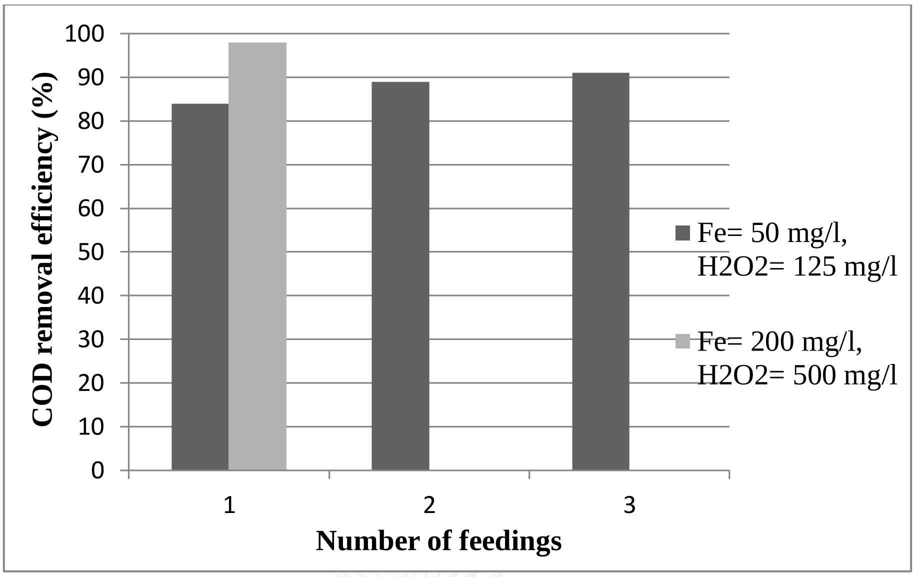


Figure 4.8 Effect of Fenton's reagents feeding modes on COD removal efficiency (initial oil concentration = 150 mg/l, Case 1)

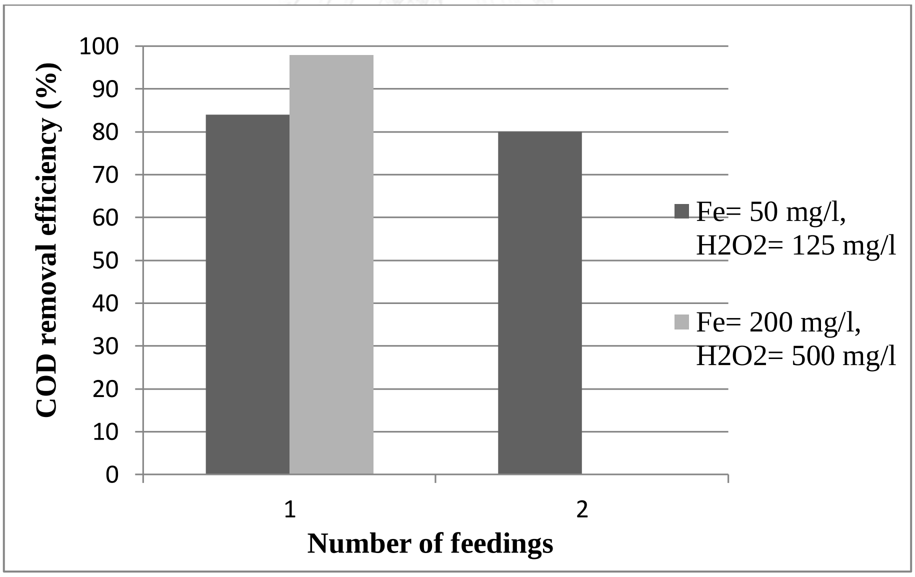


Figure 4.9 Effect of Fenton's reagents feeding modes on COD removal efficiency (initial oil concentration = 150 mg/l, Case 2)

For 150 mg/l initial oil concentration in Figure 4.8 and 4.9, multiple step feedings also improved COD removal as same as 100 mg/l oil concentration that was described previously.

Table 4.3 Optimum operating condition of Fenton process at different initial oil concentration

Cutting oil concentration (mg/l)	**Optimum operating condition of Fenton process**				
	Fe^{2+} (mg/l)	**H_2O_2 (mg/l)**	**Fe^{2+}/H_2O_2 ratio**	**Feeding mode of Fe^{2+} and H_2O_2**	**COD removal efficiency (%)**
50	50	300	1:6	one feeding (at t= 0)	90
100	50	125	1:2.5	three feeding (at t= 0, 5, 10 min)	93
150	50	125	1:2.5	three feeding (at t= 0, 5, 10 min)	91

The optimum operating conditions of Fenton process that use low chemical reagents and provide high treatment efficiency are presented in Table 4.3. From the previous part, using 50 mg Fe^{2+} by applying multiple feeding of Fe^{2+} and H_2O_2 (low reagents usage) provided the COD removal efficiency as high as the initial full feeding of 200 mg Fe^{2+} (high reagents usage) which provide maximum COD removal. For 50 mg/l initial oil concentration, initial full feeding of Fenton's reagent is enough to achieve high oxidation. Therefore, the multiple step feeding was unnecessary. However, the initial full feeding of Fenton's reagents for treating 100 mg/l and 150 mg/l initial oil concentration provided 82% and 84% COD removal, respectively. Three-steps feeding of Fenton's reagents were required to succeed the high oxidation of cutting oil.

4.2.3 Treatment of synthetic cutting oil wastewater by other treatment methods (Control experiment)

In this part, the control experiments were conducted to study effects of coagulation/precipitation by $Fe(OH)_2$ and oxidation by H_2O_2 on the cutting oil removal. Treatment efficiencies of the coagulation/precipitation of $Fe(OH)_2$ and H_2O_2 oxidation were also investigated in order to compare with Fenton oxidation. The control experiments were divided into 3 sub experiments as follow: 1) controlling pH to 3, 2) coagulation/precipitation of $Fe(OH)_2$ by adding Fe^{2+} and NaOH, and 3) H_2O_2 oxidation. Three sub experiments were performed with 100 mg/l initial oil concentration by using the optimum Fenton’s reagents dosage from Table 4.2. The initial pH was adjusted to 3 by H_2SO_4. The procedure of these experiments can be described as follow:

1. For pH controlling; Synthetic wastewater was adjusted pH to 3 by adding H_2SO_4. Then take the sample at 30 minutes reaction time.

2. For coagulation/precipitation by $Fe(OH)_2$; 50 and 200 mg Fe^{2+}/l were added after adjusting pH of synthetic wastewater to 3. Then, NaOH was added to neutralize at 30 minutes reaction time.

3. For H_2O_2 oxidation; the optimum dosage of H_2O_2 (125 and 500 mg H_2O_2/l) were added into the synthetic wastewater. The reaction time was fixed at 30 minutes. The sample was taken at 30 minutes.

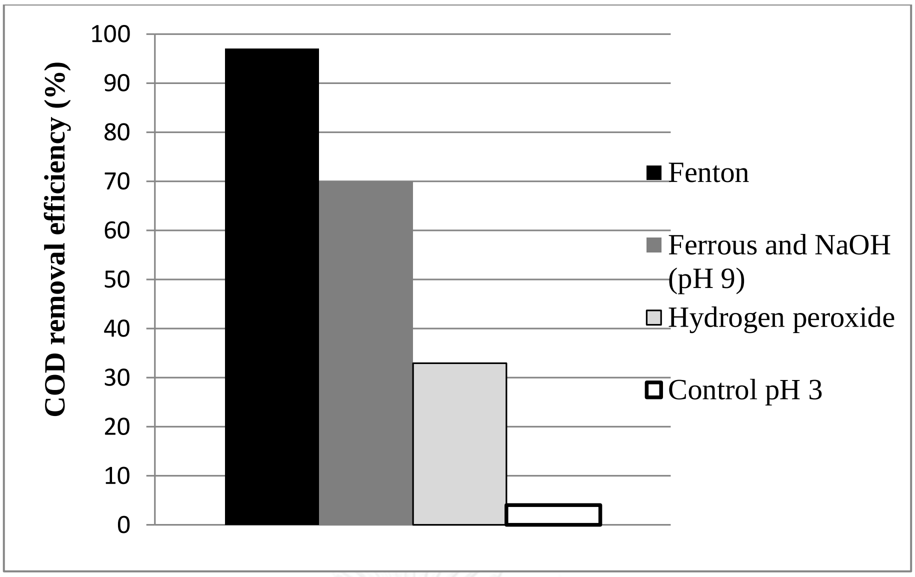


Figure 4.10 (a) COD removal at different treatment method (initial oil concentration= 100 mg/l, the Fenton's regents dosage that provide maximum COD removal; Fe^{2+}= 200 mg/l and H_2O_2= 500 mg/l)

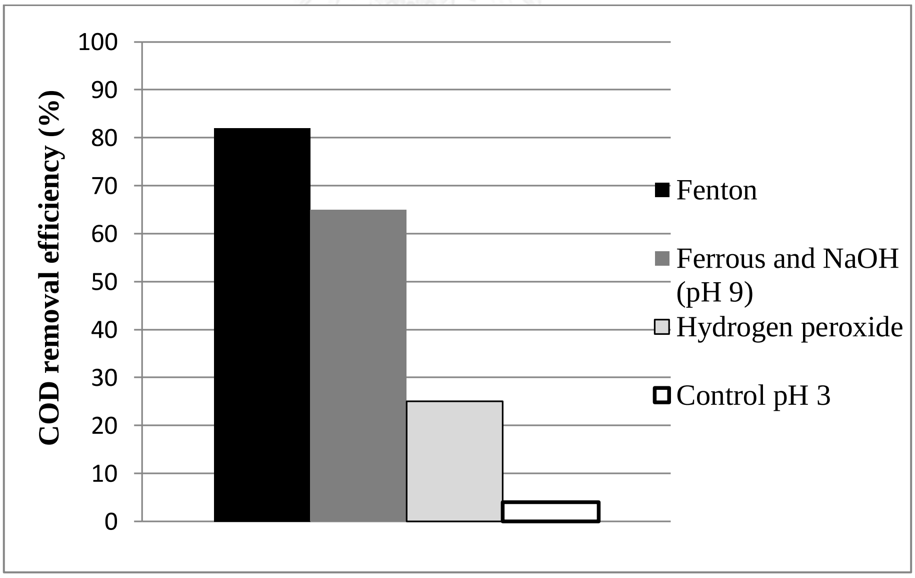


Figure 4.10 (b) COD removal at different treatment method (initial oil concentration= 100 mg/l, Fe^{2+}= 50 mg/l and H_2O_2= 125 mg/l)

In Figure 4.10 (a) and (b), it was observed that control pH of stable oil emulsion around 3 wasn't provide COD removal significantly. This means that positive charge as H^+ cannot destabilize stable oil emulsion in this research. However, the addition of ferrous ion (Fe^{2+}) and NaOH known as coagulation/precipitation method could treat 70% and 64% of initial cutting oil in case of using 200 mg $Fe^{2+/}$l and 50 mg $Fe^{2+/}$l, respectively. This could be explained by the fact that stable oil emulsion was destabilized by adding ferrous ion, and destabilized oil droplets could be removed with iron precipitation. At alkaline condition, Fe^{2+} would precipitate with hydroxide in form of insoluble $Fe(OH)_2$. From the study of ferrous iron coagulation by Arslan (2001), it was found that pH can affect the COD removal in ferrous iron coagulation. Therefore, effect of pH on coagulation efficiency in term of COD removal was investigated by varying pH to 7, 9, and 11. As presented in Figure 4.11, the COD removal by coagulation/precipitation was highest at pH 11. The COD removal increased with pH. Moreover, amount of Fe^{2+} also affected the coagulation/precipitation. The usage of 200 mg Fe^{2+}/l provided higher COD removal comparing to the 50 mg Fe^{2+}/l at every pH. It can be concluded that iron coagulation/precipitation efficiency depended on amount of Fe^{2+} and pH value. For H_2O_2 oxidation, the result in Figure 4.10 (a) and 4.10 (b) showed that hydrogen peroxide could oxidize 33% and 25% of initial cutting oil by using 500 mg H_2O_2/l and 125 mg H_2O_2/l, respectively. Although iron coagulation/precipitation and H_2O_2 oxidation could treat stable oil emulsion, the most effective treatment of stable oil emulsion that gave maximum COD removal was Fenton process.

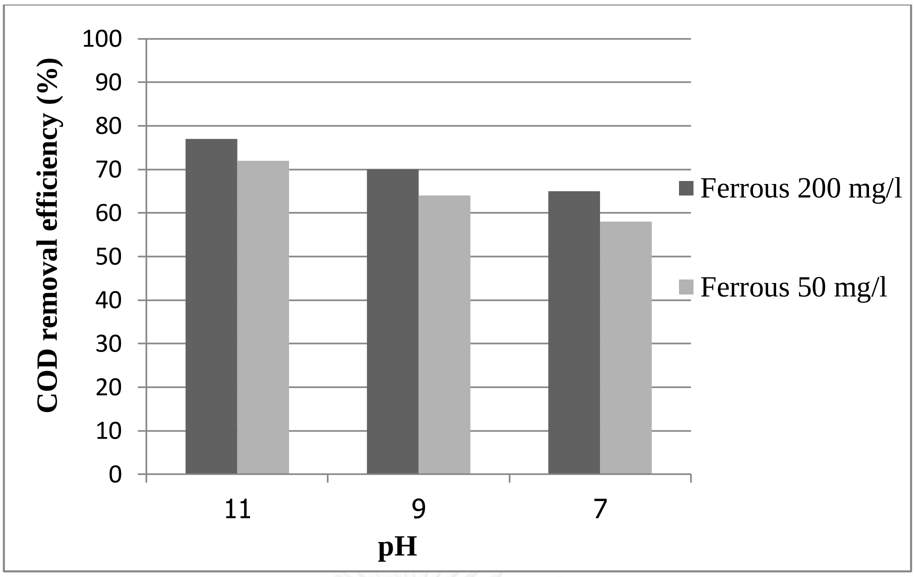


Figure 4.11 Effect of pH on COD removal in ferrous iron coagulation (initial oil concentration= 100 mg/l)

4.3 Evaluation of operating parameter for designing complete Fenton process

After stabilized oil was oxidized by Fenton process, the pH of treated water was still around 3, which cannot be discharged to an environment. Note that pH of the discharged water should be in the range of 5.5 – 9 under the standard discharge regulation in Thailand. Therefore, the treated water has to be neutralized to pH 7 by adding NaOH. Moreover, the treated water from Fenton oxidation process still has soluble iron which would be precipitated with hydroxide during the pH neutralization in forms of $Fe(OH)_2$ and $Fe(OH)_3$. To remove these insoluble compounds, the sedimentation tank was needed. Figure 4.12 presents the schematic diagram of the complete Fenton process with the pH neutralization and sedimentation.

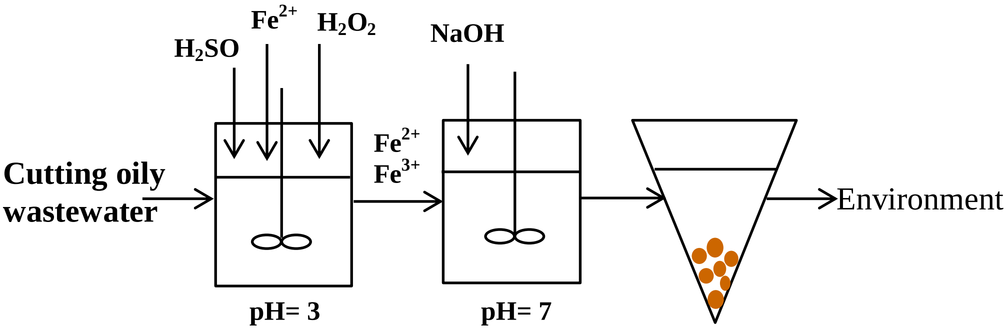


Figure 4.12 Fenton process and iron precipitation process

To design the complete continuous Fenton process in the next part, the reaction rate constant, reaction order and the optimum overflow rate of sedimentation tank as operating parameters were investigated in this part. Therefore, the studies in this part consist of kinetic of Fenton reaction, residual Fe^{2+} and Fe^{3+} in the Fenton reaction, and iron precipitation.

4.3.1 The optimum reaction time, reaction rate constant and reaction order

This part aim to determine the optimum reaction time, reaction rate constant and reaction order, which can be employed to design a continuously stirrer tank reactor and recommend the effective operation of Fenton process. The reaction rate constant (k) and reaction order (n) were calculated by the differentiation method in this research. The COD value representing the amount of cutting oil was used in this study. The experiments in this part were performed with 50, 100, and 150 mg/l oil concentration with their Fe^{2+} and H_2O_2 concentrations that provide the maximum COD removal from part 4.2.1. Figure 4.13 shows the COD variation of the synthetic wastewater with time under the Fenton reaction. The result demonstrates that COD was reduced to 11 mg/l in the first 12 seconds when using 200 mg Fe^{2+}/l and 500 mg H_2O_2/l for treating 100 mg/l initial oil concentration. This fast decrease was due to the fact that Fe^{2+} can quickly react with H_2O_2 to produce hydroxyl radical, which can oxidize oil droplet rapidly. After 1 minute, COD values became steady suggesting that the reaction was completed. Thus, the optimum reaction time for the cutting oil oxidation could be 1 minutes. However, the optimum reaction time to complete the oxidation depends on the dosage of Fe^{2+} and H_2O_2 (Neyens et al., 2003). For 50 mg/l and 150 mg/l initial oil concentrations with their Fenton's reagent dose that provide maximum COD removal, the trend of COD reduction was similar with 100 mg/l oil concentration, but the initial reduction rates were different as present in Figure 4.14.

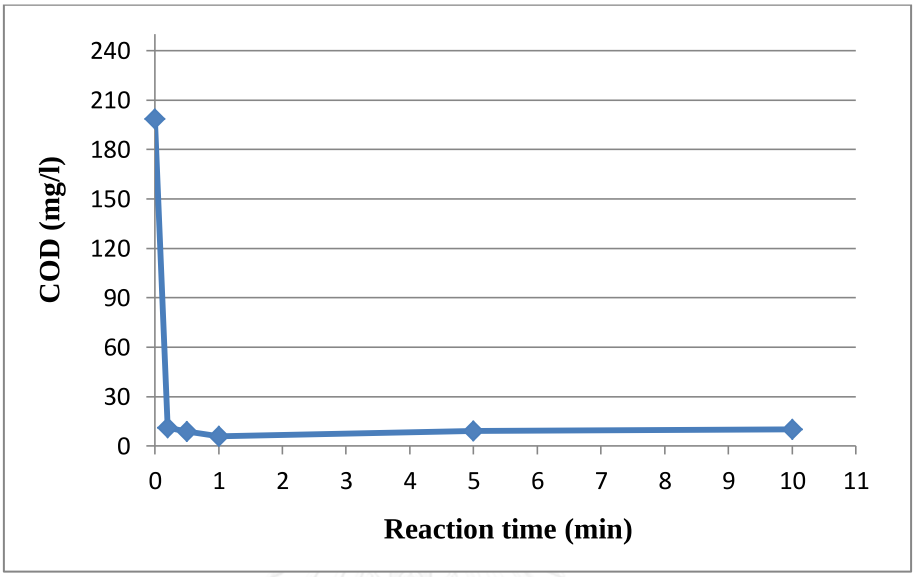


Figure 4.13 Effect of reaction time on COD of synthetic wastewater. (initial oil concentration= 100 mg/l, Fe^{2+}= 200 mg/l and H_2O_2= 500 mg/l)

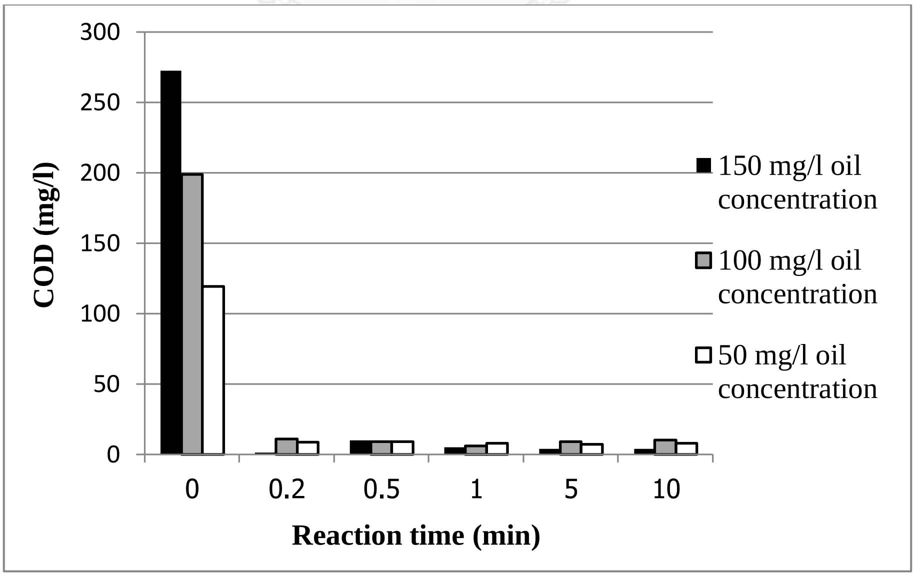


Figure 4.14 Effect of reaction time on COD of synthetic wastewater. (Operated by using their Fe^{2+} and H_2O_2 dosages that provide maximum COD removal)

From the reduction of COD at the initial reaction time in Figure 4.13, the oxidative reaction was a one-stage reaction. Therefore, the reaction rate constant and reaction order were determined by the initial reaction time from 0 to 0.2 minutes. The reaction rate constant (k) and reaction order (n) were calculated from the following basic kinetic equations, where r is reaction rate (mg/l.min), c is oil concentration (mg/l), k is reaction rate constant (min^{-1}), and n is reaction order.

$$r = \frac{dc}{dt} \tag{4.3}$$

$$r = -kc^n \tag{4.4}$$

$$\ln(-r) = \ln(k) + n\ln(c) \tag{4.5}$$

The slope of the relation between the concentration and time in Equation 4.3 expresses the reaction rate in a certain period. Then, the linear correlation between reaction rate (r) and concentration (c) can be written in the logarithm form as in Equation 4.5 with the reaction order (n) as the slope of this equation. The rate constant (k) can be obtained from the y-axis interception in the term of ln(k) (Metcalf & Eddy, 2004).

Table 4.4 The optimum reaction time, reaction rate constant, and reaction order at different initial oil concentration using the Fe^{2+} and H_2O_2 dosages that provide maximum COD removal.

Cutting oil concentration (mg/l)	**Fenton' reagents dose (mg/l)**		**k**	**n**	**Reaction time (t) at stabilized COD**
	Fe^{2+}	**Fe^{2+}/H_2O_2**	**(min^{-1})**		
50	200	1:10	147.82	0.34	1 min
100	200	1:2.5	164.84	0.41	
150	200	1:2.5	188.48	0.44	

As can be seen in Table 4.4, the k value of 150 mg/l oil concentration was higher than those of 100 mg/l and 50 mg/l. This can be implied as the oxidation rate of 150 mg/l was the highest among these concentrations. The 150 mg/l emulsion was oxidized faster than 100 mg/l and 50 mg/l emulsion due to the difference of the collision probability between oil droplet and hydroxyl radicals as previously presented in

Figure 4.5. It can be concluded that the initial oil concentration affected the oxidation rate. The obtained values of k and n from the calculation can be used to design the completely stirrer tank reactor (CSTR) for continuous treatment process.

4.3.2 Residual Fe^{2+} and Fe^{3+} in the Fenton reaction

From the Fenton reaction in Equation 2.1, ferrous ion (Fe^{2+}), which was used as Fenton's reagent, can be changed to ferric ion (Fe^{3+}) when it reacts with H_2O_2. Therefore, Real amount of Fe^{2+} that was react with H_2O_2 at different reaction time was studied in order to see changes of iron form during Fenton reaction. The amount of used Fe^{2+} can be determined by measuring the residual Fe^{2+} and Fe^{3+} in the treated water. The measurement of the residual Fe^{2+} and Fe^{3+} during Fenton reaction was performed with 100 mg/l initial oil concentration by using the optimum Fenton's reagents dosages (Fe^{2+}= 50 mg/l and 200 mg/l, and Fe^{2+}/H_2O_2= 1:2.5). The phenanthroline method was employed to detect amount of residual Fe^{2+} and Fe^{3+} (Gao et al., 2004). Figure 4.15 displays the amount of the residual Fe^{2+} and Fe^{3+} at different reaction time. Result indicated that Fe^{2+} was rapidly changed to Fe^{3+} at the initial reaction time, which can be seen by the reduction of residual Fe^{2+} (200 mg/l to 4.3 mg/l) and the increase of Fe^{3+} (0 to 195 mg/l) at the reaction time between 0 and 12 seconds. It can be implied that Fe^{2+} reacted rapidly with H_2O_2. This result corresponded with the COD removal efficiency that was high at the initial reaction time and afterward steady with the reaction time.

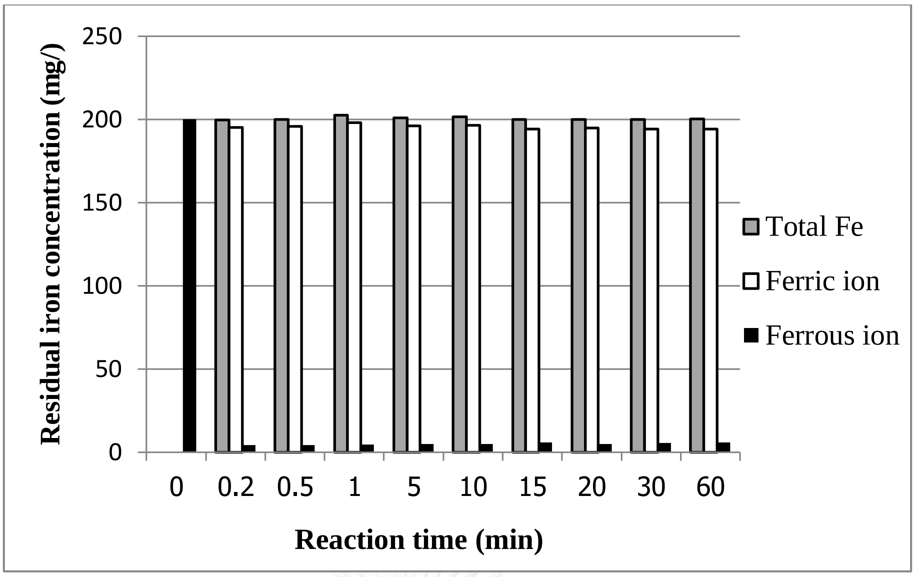


Figure 4.15 (a) Residual iron concentration at different reaction time (initial oil concentration= 100 mg/l and the Fenton's reagent dosage that provide maximum COD removal: Fe^{2+}= 200 mg/l and H_2O_2 = 500 mg/l)

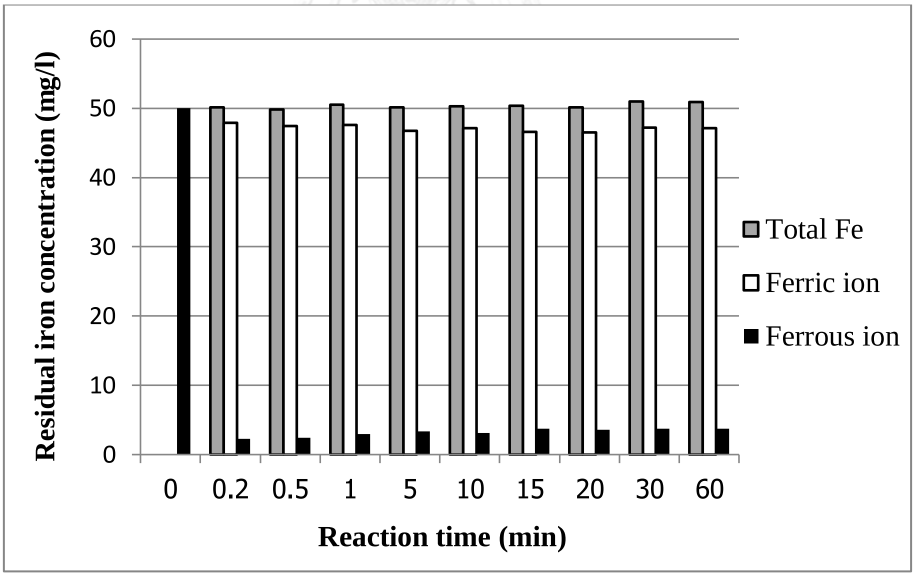


Figure 4.15 (b) Residual iron concentration at different reaction time (initial oil concentration= 100 mg/l, Fe^{2+}= 50 mg/l and H_2O_2 = 125 mg/l)

4.3.3 Iron precipitation after Fenton process

In this part, overflow rate of sedimentation tank which can control suspended solid discharge was investigated as a main topic. The optimum overflow rate of sedimentation at different initial oil concentrations and ferrous concentrations were also determined in this part.

To investigate the effect of overflow rate of sedimentation tank on settling efficiency and determine the optimum overflow rate, the experiments were conducted with 50 mg/l, 100 mg/l, and 150 mg/l initial oil concentrations by using the Fenton’s reagents doses that provide maximum COD removal as in Table 4.2 (Fe^{2+}= 200 mg/l for all initial oil concentration and Fe^{2+}/H_2O_2 ratio= 1:10, 1:2.5 and 1:2.5 for 50 mg/l, 100 mg/l, and 150 mg/l initial oil concentration, respectively). Moreover, the 50 mg Fe /l, which provided effective oxidation in multiple step feeding, was also employed to study the overflow rate of sedimentation tank in order to make the appropriate treatment options. These Fenton’s reagents dosages were added to a batch reactor for oxidizing the stable cutting oil emulsion as shown in Figure 4.16 (a). After 30 minutes reaction time, pH of the treated water was neutralized to pH 7 by adding NaOH into a batch reactor as shown in Figure 4.16 (b). Then, the soluble iron would be precipitated in the forms of insoluble $Fe(OH)_2$ and $Fe(OH)_3$. After that, the treated water containing suspended solid was allowed to settle down in a settling column as shown in Figure 4.16 (c). From the observation of suspended solid sedimentation in the settling column, the sedimentation of these iron precipitates can be classified as the discrete settling type since the precipitates were unlikely to aggregate while settling down in the column (Reynolds et al., 1996). No significant interaction with neighboring particles can be observed. Therefore, effects of the overflow rate on the settling efficiency were investigated by the discrete settling method as shown below.

(a) (b) (c)

Figure 4.16 (a) Fenton reaction in a batch reactor, (b) a treated water containing suspended solids after neutralizing by adding NaOH and (c) settling column

In the discrete settling experiment, the color of the water containing iron precipitates changed with the increase of reaction time as shown in Figure 4.17 due to the fact that iron precipitates settled down along the time. The treated water became clear at 60 minutes settling time.

(a) (b) (c) (d)

Figure 4.17 Sedimentation of iron precipitates at different time (a) t = 0 min, (b) t = 20 min, (c) t = 30 min, (d) t = 60 min

Discrete setting efficiency

Settling efficiency at different settling velocity can be calculated from Equation 4.7, which was derived from Figure 4.18 (Reynolds et al., 1996). The samples taken from the sampling point of the settling column at each time interval were analyzed for the amount of suspended solid (SS). Then, the SS value at different sampling time was plotted with the settling velocity calculating from the depth of the sampling point (H) and the sampling time (t) as shown in Figure 4.18. The area above this curve is the fraction of particles with the settling velocity less than V_0 that could be removed.

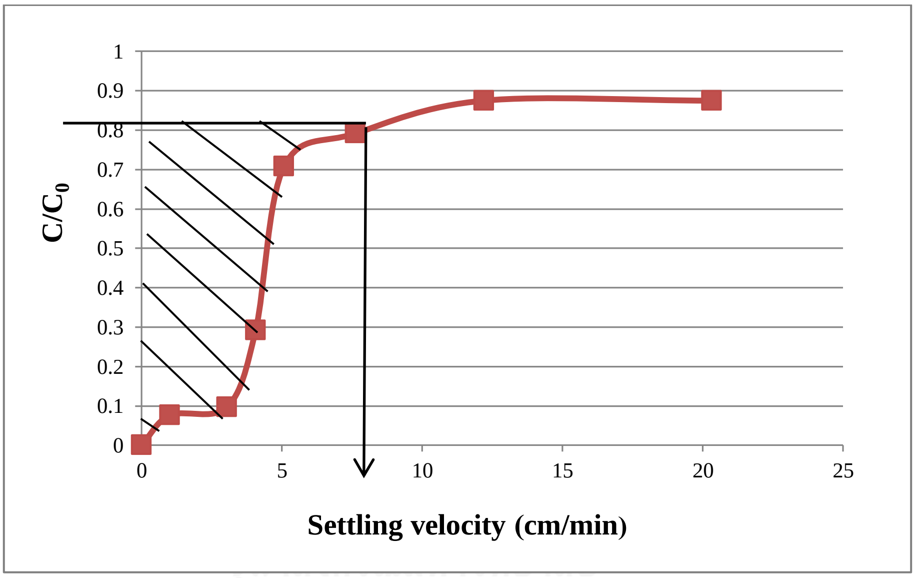


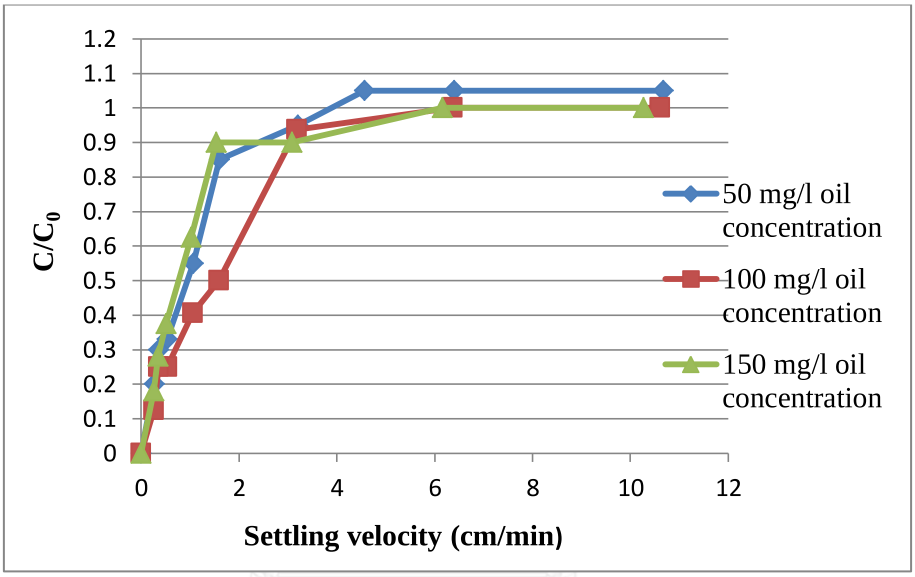
Figure 4.18 C/C_0 or SS_t/SS_0 at different settling velocity

$$Settling\ velocity = \frac{H}{t} \tag{4.6}$$

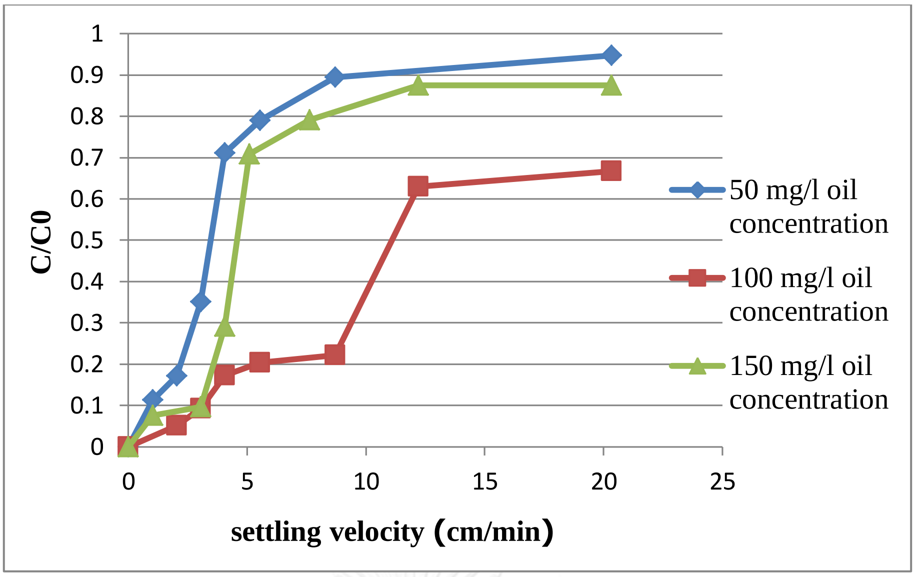
$$Settling\ efficiency(P) = \underbrace{(1 - P_0)}_{\substack{\text{Fraction particles}\\ \text{with velocity}\\ \text{greater than } V_0}} + \underbrace{\int_0^{P_0} (V_i/V_0)\, dP_i}_{\substack{\text{Fraction particles}\\ \text{with removed}\\ \text{with velocity less}\\ \text{than } V_0}} \tag{4.7}$$

$$P_0 = \frac{C}{C_0} = \frac{SS_t}{SS_0} \tag{4.8}$$

Furthermore, the standard discharge regulation of suspended solid (SS in the discharge should not exceed 50 mg/l) was employed to determine the optimum overflow rate of sedimentation tank. The results shown in Figure 4.19, which were obtained by the discrete settling test were used to identify the optimum overflow rate of sedimentation tank at different iron concentration and initial oil concentration.



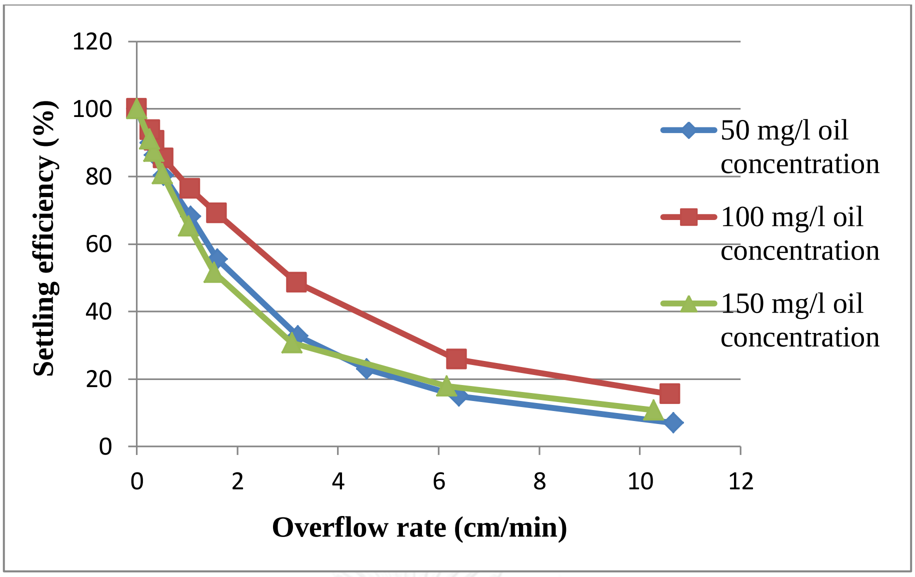
(a)



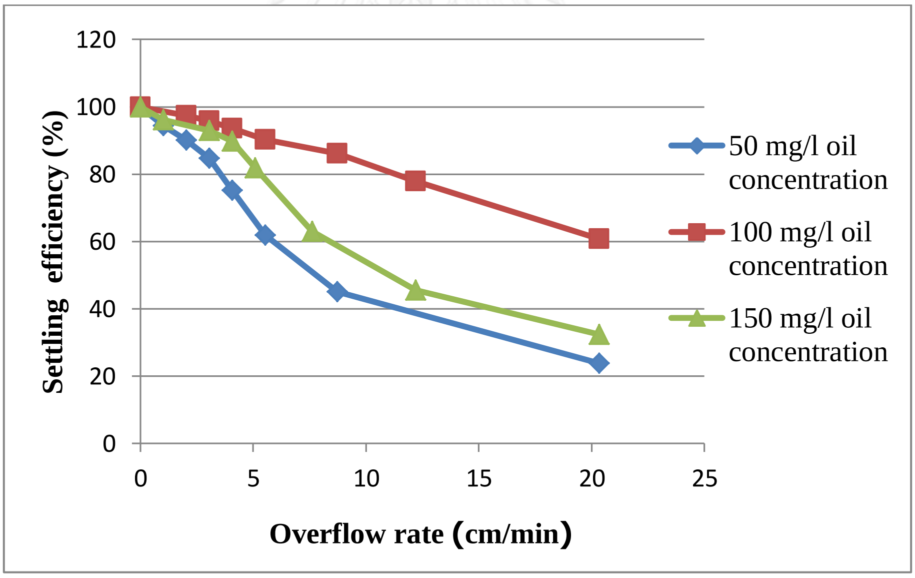
(b)

Figure 4.19 Settling velocity analysis of suspension of discrete particles (a) Fe^{2+}= 50 mg/l and Fe^{2+}/H_2O_2= 1:2.5, (b) Fe^{2+}= 200 mg/l and H_2O_2= 1:10, 1:2.5, 1:2.5 for 50 mg/l, 100 mg/l and 150 mg/l initial oil concentration)

According to the increasing overflow rate in Figures 4.20 (a) and 4.20 (b), the settling efficiency will be decreased due to the fact that particles require higher setting velocity for being eliminated. Insoluble particles of the 100 mg/l oil concentration precipitated easier than those of the 50 and 150 mg/l oil concentrations. Moreover, increasing of oil concentration increase the probability of collision among oil, $Fe(OH)_2$, and $Fe(OH)_3$; therefore, the formed insoluble particles would be larger. According to Stoke's law, larger particles with similar density in the same liquid phase have higher settling velocity than smaller particles. Tables 4.5 and 4.6 shows the optimum overflow rate of sedimentation tank and settling efficiency at different oil concentrations for removing 50 mg Fe/l and 200 mg Fe/l, respectively.



(a)



(b)

Figure 4.20 Settling efficiency at different overflow rate (a) Fe^{2+}= 50 mg/l and H_2O_2= 1:2.5, (b) Fe^{2+}= 200 mg/l and H_2O_2= 1:10, 1:2.5, 1:2.5 for 50 mg/l, 100 mg/l and 150 mg/l initial oil concentration

At low overflow rate, settling efficiency of insoluble iron particle was high, since insoluble iron particles got a long time to settle in settling column. Therefore, using low overflow rate made small insoluble particles, which has low settling velocity, settle more. On the contrary, the settling efficiency was low at higher overflow rate as only small amount of particles can settle in this settling period.

The precipitation of 50 mg Fe/l can be seen in Table 4.5. The increase of the initial oil concentration resulted in increasing suspended solid (SS). The SS value of 150 mg/l oil concentration was higher than those of 100 mg/l and 50 mg/l because higher oil concentration with higher density of oil droplets increases the probability of collision among oil particles, insoluble $Fe(OH)_2$ and $Fe(OH)_3$ as previously explained in Figure 4.5. From the Fenton oxidation, it was found that residual oil of 150 mg/l after Fenton oxidation was higher than 100 mg/l and 50 mg/l. Therefore, it can be concluded that number of residual oil particle can affect the weight of suspended solid.

Table 4.5 Optimum overflow rate of sedimentation tank for removing 50 mg Fe/l and settling efficiency at different initial oil concentration

Cutting oil concentration (mg/l)	**Suspended solid (mg/l)**	**Fe/H_2O_2 ratio**	**Over flow rate (m/h)**	**Settling efficiency (%)**	**Design criteria for over flow rate ***
50	133	1:2.5	0.39	77.8	0.5-2 m/h 1.5-2 hr
100	160		0.45	81.8	
150	200		0.2	88.6	

* Source: Wastewater Engineering, 2004, Treatment and Reuse; McGraw-Hill

However, precipitation of 200 mg Fe/l provided the different trend of suspended solid values comparing to the precipitation of 50 mg Fe/l. This was due to the different amount of iron concentration and Fe^{2+}/H_2O_2 ratio used in Fenton oxidation. For precipitation of 200 mg Fe/l as in Table 4.6, SS value of 50 mg/l oil is the lowest one, which did not relate with high formation of $Fe_2(O)_3$, FeO, $Fe(OH)_3$ and $Fe(OH)_2$. Note that this oily emulsion could be oxidized by high amount of hydrogen peroxide (1:10 F/H ratio) which can be decomposed to oxygen and water. Free oxygen from hydrogen peroxide would react with Fe^{2+} and Fe^{3+} ion to form $Fe_2(O)_3$ and FeO that led to high insoluble formation. In this case, the phenomena can be possibly explained that the particle size of $Fe_2(O)_3$ and FeO (in the range of 0.05-0.4 µm) (Mohapatra andAnand, 2010) are smaller than 1.2 µm filter membrane used in the SS analysis. Moreover, the number of oil particles affected the quantity of insoluble formation due to the difference of the collision probability between oil particle, $Fe(OH)_2$, $Fe(OH)_3$, $Fe_2(O)_3$, and FeO. Therefore, the values of SS from 100 and 150 mg/l oil concentration were higher than the 50 mg/l one.

Table 4.6 Optimum overflow rate of sedimentation tank for removing 200 mg Fe/l, and settling efficiency at different initial oil concentration

Cutting oil concentration (mg/l)	**Suspended solid (mg/l)**	**Fe^{2+}/H_2O_2 ratio**	**Over flow rate (m/h)**	**Settling efficiency (%)**	**Design criteria for over flow rate ***
50	380	1:10	0.78	92.7	0.5-2 m/h 1.5-2 hr
100	540	1:2.5	1.83	95	
150	480	1:2.5	1.85	92.8	

* Source: Wastewater Engineering, 2004, Treatment and Reuse; McGraw-Hill

Moreover, it can be observed that the setting efficiency of 150 mg/l oil is lower than the 100 mg/l oil as shown in Table 4.6. The difference in the amount of additives, which is the positive charged ions in cutting oil, could act as a scavenger of hydroxide. Less insoluble species can precipitate as a result. In this case, the number of oil droplet particles was not the main factor for the different settling efficiency (about 98% of overall treatment efficiency). Note that the optimum overflow rate for removing 200 mg Fe/l in Table 4.6 was in the range of the suggested design criteria for wastewater treatment (0.5-2 m/h) (Metcalf & Eddy, 2004).

4.4 Reactor Design

This part aims to design continuous Fenton process for treating stable oil emulsion. This process mainly consists of 1) a mixing tank for adjusting pH to 3, 2) Fenton reactor tank, 3) a mixing tank for neutralization and 4) a sedimentation tank. Figure presents the schematic diagram of the complete Fenton process.

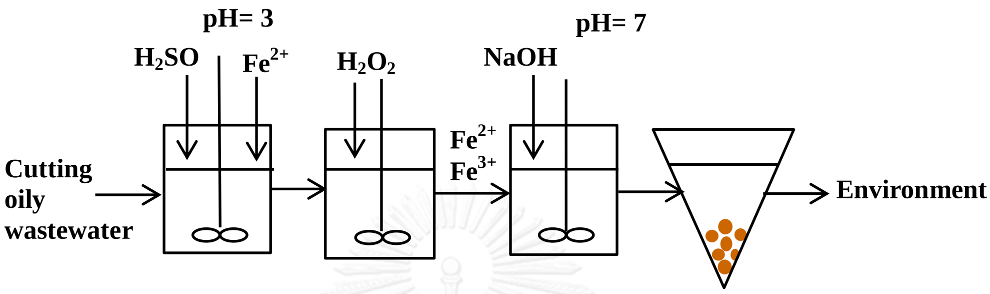


Figure 4.21 the overall continuous process for treating stable oil emulsion (Fenton process and iron precipitation process)

A given situation: 15 cubic meter of cutting oil wastewater is generated per day. Concentration of this oily wastewater was 100 mg/l containing COD 220 mg/l that still exceeds the standard discharge regulation (COD of the discharge should not exceed 120 mg/l). Thus, the continuous Fenton and iron precipitation process was required to treat this oily wastewater in order to reduce COD value to standard discharge regulation.

1) Mixing tank for adjusting pH to 3

This tank will be used for adjusting pH of wastewater to 3. H_2SO_4 will be added into a rapid mixing tank which velocity gradient (G) is 900 s^{-1}, and mixing time (T) is one minute (Kawamura, 2000). Mixing volume (V) could be calculated from a given flow rate and mixing time as follow:

$$V = QT$$

$$V = \left(\frac{1500\,L}{day}\right)\left(\frac{1}{24}\frac{day}{hr}\right)\left(\frac{1}{60}\frac{hr}{min}\right)(1\,min)$$

$$V = 10.417\,L = 0.01042\,m^3$$

Moreover, Input power of mixing (P) could be determined by the velocity gradient (G) and the obtained mixing volume (V) as shown in a below equation.

$$G = \sqrt{P/_{\mu V}}$$

$$P = G^2\mu V = (900^2\ 1/s^{-2})(0.00089\ kg/m.s)(0.01042\ m^3)$$

$$P = 7.55\ W$$

Energy consumption of mixing for a liter of wastewater is

$$Energy\ consumption\ (E) = {}^{P}/_{Q}$$

$$E = {}^{(7.55\,J/s)(60\,s/\text{min})}\Big/_{10.417\ L/min}$$

$$E = 43.49\ J/liter$$

2) Fenton reactor tank

This second tank is used to operate Fenton oxidation. Oxidation of cutting oil will be performed within a continuously stirred tank reactor (CSTR) which provided completely mixing to the solution. From completely mixing of CSTR, the concentration of output stream is same as the uniform content in the reactor. The below equation is a mass-balance equation for the CSTR.

[Accumulate] = [Input] – [Decrease due to reaction] – [Output]

$$dC_{out}V\ = C_{in}Qdt - VkC_{out}{}^{n}dt - C_{out}Qdt$$

$$\frac{dC_{out}}{dt} = C_{in}\frac{Q}{V} - kC_{out}{}^{n} - C_{out}\frac{Q}{V}$$

At steady-state, $\frac{dC}{dt} = 0$;

$$0 = C_{in}\frac{Q}{V} - kC_{out}{}^{n} - C_{out}\frac{Q}{V}$$

$$kC_{out}{}^{n} = \frac{Q}{V}(C_{in} - C_{out}) \qquad (4.10)$$

Q is flow rate of oily wastewater (m^3/day), V is volume of the reactor, C is oil concentration (mg/l), k is reaction rate constant or reaction rate (min^{-1}), and n is reaction order.

For CSTR designing, Equation 4.10 was employed to calculate volume of the reactor. The obtained k and n value from above kinetic study were used to determine volume of the reactor. Moreover, Equation 4.10 can be used to predict the effluent COD value in case that flow rate and reactor volume are known.

From a given situation: Flow rate of wastewater (Q) = 15 m^3/day or 10.417 l/min,

Input COD (C_{in}) = 220 mg/l, and

Expected output COD (C_{out}) = 6.6 mg/l

97% of COD removal can be achieved in this system.

From kinetic study at 100 mg/l oil concentration: k = 164.84 min^{-1}

n = 0.41

From the optimum Fenton' reagent dose for treating 100 mg/l oil concentration: Amount of Fe^{2+} and H_2O_2 = 200 mg/l and 500 mg/l, respectively

Volume of the reactor could be calculated as follow:

$$kC_{out}{}^{n} = \frac{Q}{V}(C_{in} - C_{out})$$

$$(164.844\, min^{-1})(6.6\, mg/l)^{0.41} = \frac{10.417\, l/min}{V}(220\, mg/l - 6.6\, mg/l)$$

$$V = 6.22\, L$$

Thus, the volume of reactor is 6.2 liter.

As reactor volume is 6.2 L, the retention time of reactor (T) could be calculated as follow:

$$T = \frac{V}{Q}$$

$$T = \frac{6.2\, l}{10.417\, l/min}$$

$$T = 0.6\, minutes$$

From above calculation, the volume of the reactor is small and a detention of reactor is low, since Fenton reaction was rapidly completed at the initial reaction time. Fe^{2+} reacted quickly with H_2O_2 to produce hydroxyl radical which also oxidized cutting oil rapidly. High reaction rate of Fenton reaction could be shown by a one stage COD reduction at the initial reaction time in Figure 4.13.

In case that volume of CSTR was selected to be 1 liter, the effluent COD can be predicted as follow:

$$kC_{out}{}^{n} = \frac{Q}{V}(C_{in} - C_{out})$$

$$(164.844\, min^{-1})(C_{out})^{0.41} = \frac{0.69\, l/min}{1L}(220\, mg/l - C_{out})$$

$$C_{out} = 0.81\, mg/l$$

Thus, the effluent COD is 0.81 mg/l, COD removal efficiency is 99.63%.

3) Mixing tank for neutralization

This tank is used for adjusting pH of the treated water to 7 under standard discharge regulation. NaOH will be added into a rapid mixing tank as shown in Figure 4.21. This mixing tank has velocity gradient equals to 900 S^{-1} and mixing time equals 1 minute. Mixing volume (V) could be calculated from a given flow rate and mixing time as follow:

$$V = QT$$

$$V = \left(\frac{1500\,L}{day}\right)\left(\frac{1}{24}\frac{day}{hr}\right)\left(\frac{1}{60}\frac{hr}{min}\right)(1\,min)$$

$$V = 10.417\,L = 0.01042\,m^3$$

Moreover, Input power of mixing (P) could be determined by the velocity gradient (G) and the obtained mixing volume (V) as shown in a below equation.

$$G = \sqrt{P/_{\mu V}}$$

$$P = G^2\mu V = (900^2\,1/s^{-2})(0.00089\,kg/m.s)(0.01042\,m^3)$$

$$P = 7.55\,W$$

Energy consumption of mixing for a liter of wastewater is

$$Energy\ consumption\ (E) = {}^{P}/_{Q}$$

$$E = {}^{(7.55\,J/s)(60\,s/\text{min})}/_{10.417\,L/min}$$

$$E = 43.49\,J/liter$$

4) Sedimentation tank

Rectangular tank will be performed to remove iron precipitates. The optimum overflow rate of sedimentation tank was provided by discrete settling method in the previous part. For 200 mg Fe^{2+}/l and 100 mg/l initial oil concentration, the optimum over flow rate was 1.83 m/h. Tank dimension could be calculated from a given flow rate (Q) and an optimum overflow rate (v):

$$Q = vA$$

$$A = {}^{Q}/_{v}$$

$$A = {}^{(10.417\,l/\text{min})(1\,m^3/1000\,l)}/_{(1.83\,m/h)(1\,h/60\text{ min})}$$

$$A = 0.3415\ m^2$$

Length: Wide= 3:1; $w(3w) = 0.3415\ m^2$

$$w = 0.3374\ m = 33.74\ cm$$

$$L = 3w = 3(0.3374) = 1.012\ m = 101.22\ cm$$

Length: Depth= 4:1; $H = {}^{L}/_{4} = {}^{1.012}/_{4} = 0.253\ m = 25.31\ cm$

Thus, sedimentation tank dimension would be 34 cm width, 101.2 cm length, and 25 cm depth. The volume of sedimentation tank is 86 liter.

As volume of sedimentation tank is 86 L, the retention time of this tank (T) could be calculated as follow:

$$T = \frac{V}{Q}$$

$$T = \frac{86\ l}{10.417\ l/min}$$

$$T = 8.3\ minutes$$

For chemical usage in this continuous process, Fe^{2+} and H_2O_2 are needed as catalyst and oxidant in Fenton process. Fe^{2+} and H_2O_2 will be supplied by $FeSO_4.7H_2O_2$ and 30% H_2O_2. Moreover, H_2SO_4 and NaOH are required for adjusting initial pH to acidic condition, since Fenton oxidation was effective at pH around 2-4 (Neyens et al., 2003). To estimate chemical usage in this continuous process, the Fenton's reagents dosage of 100 mg/l oil concentration from the Table 4.2 will be used. To treat 100 mg/l oil concentration effectively, 200 mg Fe^{2+} (1 g of $FeSO4.7H_2O_2$) and 500 mg H_2O_2 (1.49 ml of 30% H_2O_2 solution) should be added into a liter of wastewater. From a given situation, 15000 liter of cutting oil wastewater is generated per day, therefore daily usage of solid $FeSO_4.7H_2O$ and 30 % H_2O_2 solution should be 15 kg and 22.35 liter, respectively. Moreover, Fe^{2+} and H_2O_2 will be fed into a reactor by pumps. Fe^{2+}/ H_2O_2 ratio will be fixed at 1:2.5 every feeding. For example, flow rate of oily wastewater is 10.417 L/min, Mass rate of Fe^{2+} and H_2O_2 will be 2.08 g/min

(10.417 g of $FeSO_4.7H_2O$/min) and 5.2 g/min (15.52 ml of 30% H_2O_2/min). Table 4.7 showed designed parameters and operating condition of this continuous Fenton process.

Table 4.7 Designed parameters and operating condition of the continuous Fenton process that provide maximum COD removal.

Parameter	**Description**
Input:	
Flow rate of wastewater	15 m^3/day (10.417 L/min)
Cutting oil concentration	100 mg/l
Influence COD	220 mg/l
pH of wastewater	7.5-8
Rapid mixing tank (adjust pH to 3)	
Velocity gradient	900 s^{-1}
Mixing time	1 min
Gt	900
Volume of tank	10.417 L
Input power of mixing	7.55 W
CSTR (Fenton oxidation)	
Volume of reactor	6.22 L
Detention time	0.6 minutes
Rapid mixing tank (adjust pH to 7)	
Velocity gradient	900 s^{-1}
Mixing time	1 minute
Gt	900
Volume of tank	10.417 L
Input power of mixing	7.55 W

Sedimentation tank (iron precipitation)	
Overflow rate	1.83 m/h
Size of tank	34 cm width 101.2 cm length 33 cm depth
Detention time	8.3 minutes
Chemical usage:	
1. $FeSO_4.7H_2O$	
Required dosage	1 g/ liter of oily wastewater (Fe^{2+}= 200 mg/ liter of wastewater)
Daily usage	15 kg of solid $FeSO_4.7H_2O$
2. H_2O_2 (30%)	
Required dosage	1.49 ml/liter of wastewater (H_2O_2= 500 mg/liter of wastewater)
Daily usage	22.35 liters
Out put	
Expected effluent COD	6.6 mg/l
Expect COD removal efficiency	97%

4.5 Reuse of iron sludge as iron catalyst

From the previous part, the pH neutralization before discharging the treated water to an environment cause iron precipitates in form of $Fe(OH)_2$ and $Fe(OH)_3$ which are a solid waste sludge. Large amount of iron precipitation after Fenton oxidation by neutralization is a disadvantage and limitation of Fenton process. Iron sludge is a hazardous waste that requires appropriate treatments and disposal since iron is a heavy metal. This sludge also contains residual organic from adsorption during the treatment process. To minimize the sludge production that leads to lower disposal cost, iron sludge can be reused as iron catalyst for next Fenton oxidation without iron regeneration and replacement (Bolobajev et al., 2014). The study of (Cao et al., 2009) found that Fe^{2+} and Fe^{3+} in the produced iron sludge can catalyst the production of hydroxyl radical ($\cdot OH$) and hydroperoxyl radical ($HO_2\cdot$) from hydrogen peroxide those are Fenton process and Fenton-like process as shown in equations 2.9-2.10.

Fenton- like reaction: $Fe^{3+} + H_2O_2 \longrightarrow Fe\text{-}OOH^{2+} + H^+$ (2.9)

$$Fe\text{-}OOH^{2+} \longrightarrow Fe^{2+} + HO_2\cdot \quad (2.10)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH + OH^- \quad (2.1)$$

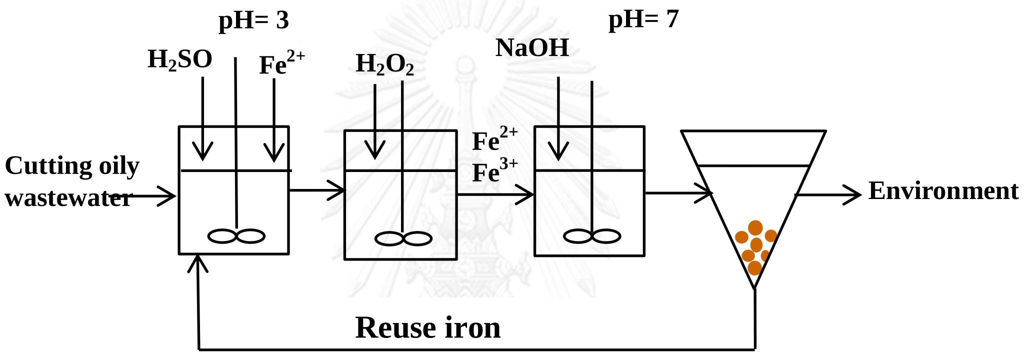


Figure 4.22 Reuse of iron sludge in the Fenton process

Therefore, this part aim to reuse the iron sludge as iron catalyst instead of using fresh Fe^{2+} from $FeSO_4.7H_2O$ in the next Fenton process. Figure 4.22 presents the schematic diagram of the complete Fenton process with the reuse of iron sludge. Treatment efficiency of oily wastewater by using iron sludge was investigated in term of COD removal. Moreover, the effect of the amount of the reuse time on COD removal was also studied in order to indicate the optimum number of reuse in which the iron sludge is still effective to treat the stable oil emulsion. The experiments in this part were operated to treat 100 mg/l initial oil concentration by using iron sludge and the optimum H_2O_2 concentration. Iron sludge was came from Fenton process that operated at low Ferrous concentration (Fe^{2+}= 50 mg/l) and the optimum Fe^{2+}/H_2O_2 ratio (1:2.5) in order to prove that iron sludge containing low iron concentration can be reused. If the reuse of iron sludge containing low iron concentration is effective to treat this kind of oil, the reuse of the iron with higher iron concentration will also be effective. Iron sludge was separated from the Fenton solution by centrifugation after it was allowed to settle in a batch reactor for 24 hr. Then, the concentrated sludge as shown in Figure 4.23 was added into a batch reactor as iron catalyst for the next oxidation without fresh iron replacement. In addition, reuse of iron sludge in coagulation/precipitation process was also performed to study the effect of iron coagulation on COD removal. Since, iron coagulation/precipitation would occur while Fenton reaction was stopped by adjusting pH to 9 (Mohajeri et al., 2010).

(a) (b)

Figure 4.23 Concentrated iron sludge from centrifugation (Fenton process operated at 100 mg/l initial oil concentration, Fe^{2+}= 50 mg/l and Fe^{2+}/H_2O_2 ratio= 1:2.5) (a) reuse time = 0, (b) reuse time = 4

The concentrated iron sludge was analyzed by the Energy Dispersive Spectroscopy in order to identify the concentration of major and minor elements in form of a weight percentage. Effects of iron percentage in iron sludge at different number of reuse on COD removal efficiency were mainly investigated since iron is the catalyst in Fenton reaction. Iron can catalyst the production of hydroxyl radical (·OH) from the appearance of H_2O_2 (Kang et al., 2000).

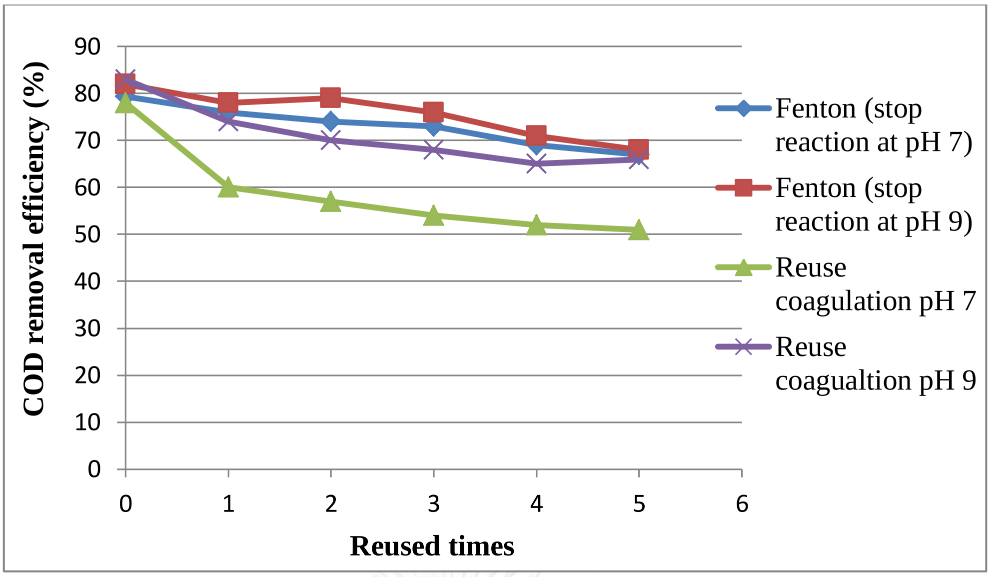


Figure 4.24 Effect of reuse time of iron sludge on COD removal efficiency (initial oil concentration= 100 mg/l, Fe^{2+}= 50 mg/l and Fe^{2+}/H_2O_2 ratio= 1:2.5)

Figure 4.24 presents the COD removal efficiency using the reused iron sludge as catalyst at different number of reuse time. The obtained results indicated that COD removal of Fenton oxidation by using iron sludge was higher than that of iron coagulation/precipitation in all experiments. This can be implied that there was oxidation of cutting oil from reusing iron sludge, and Fe^{2+} and Fe^{3+} in the sludge could catalyst the production of hydroxyl radical and hydroperoxyl radical from hydrogen peroxide, respectively. However, amount of ferrous ions (Fe^{2+}) in sludge was very low since ferrous ions would rapidly react with H_2O_2 and were changed to ferric ion (Fe^{3+}) in Fenton reaction that had discussed previously in part 4.3.2 (a residual Fe^{2+} and Fe^{3+} part). Therefore, the iron species in iron sludge was mainly ferric species, which led to Fenton-like reaction. The result in Figure 4.24 shown that the sludge from the 50 mg Fe^{2+}/l and 125 mg H_2O_2/l used in Fenton process can be reused to treat 100 mg/l oil concentration without regeneration and replacement at least 5 recycling times with the high efficiencies. Furthermore, it was observed that the COD removal efficiency was decreased with increasing reused times. There are several possible reasons for this decrease as follow: (1) amount of iron sludge decreased every reuse time due to sludge losing during dewatering by centrifugation. (2) Fe^{3+} and H_2O_2 produced hydroperoxyl radical ($HO_2\cdot$), which has oxidative power less than hydroxyl radical (OH·) from Fe^{2+}. (3) Organic which were adsorbed in sludge would be dissolved in the Fenton solution that was increasing the organic loading of the oxidation system resulted in lower COD removal. This reason can be confirmed by the increase of carbon element representing the amount of organic in the reused sludge as in Table 4.8.

Table 4.8 Percent of elements by weight in iron sludge from analyzing by Energy Dispersive Spectroscopy technique (EDS)

Reused time	**% Fe**	**% C**	**% other**
0	18.93	34.32	46.75
1	16.24	40.37	43.39
4	11.95	50.24	37.81

Note that the reduction of iron element proportion in this table may occur from the increasing of carbon element proportion.

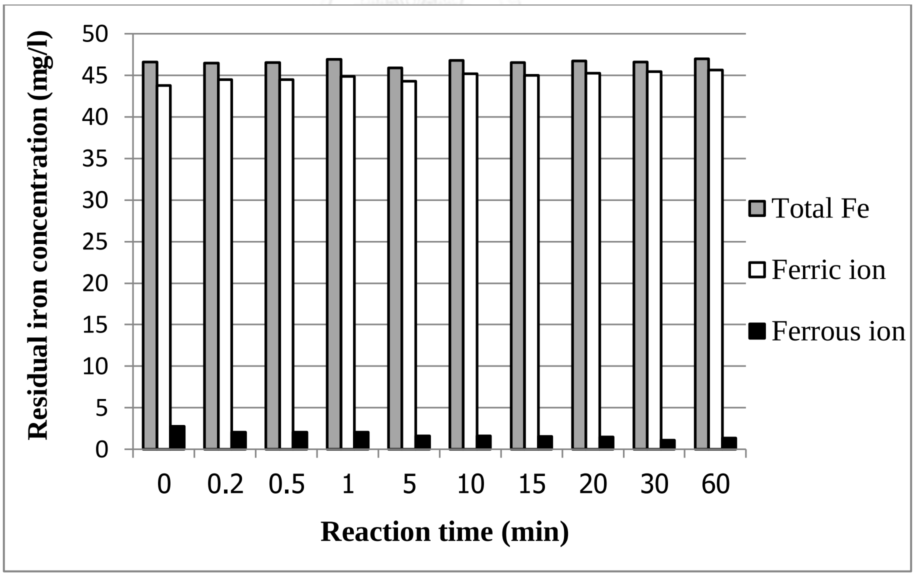


Figure 4.25 Residual iron concentration at different reaction time of reuse 1st (initial oil concentration= 100 mg/l, iron sludge from Fe^{2+}= 50 mg/l and H_2O_2= 125 mg/l)

Figure 4.25 showed the amount of residual iron at different Fenton reaction time when iron sludge was used as iron catalyst in the first time. Before iron sludge was used in Fenton process, total iron concentration in a batch reactor after 60 min reaction time was 50 mg/l consisting of 3 mg Fe^{2+} and 47 mg Fe^{3+}. However, the result of iron concentration at the first reuse showed that initial iron concentration was 46.5 mg/l before Fenton oxidation started (at t = 0 min). This indicated the decrease of the amount of total iron from 50 mg/l (0st reuse) to 46.5 mg/l (1st reuse). This was due to iron loss during dewatering by centrifugation. The 46.5 mg total iron/l of the 1st reuse consisted of 2.7 mg Fe^{3+} and 43.8 Fe^{3+}. Both Fe^{2+} and Fe^{3+} presented in the iron sludge; thus, Fenton and Fenton-like reaction would occur in the 1st reuse after H_2O_2 was added. However, no change of Fe^{2+} and Fe^{3+} after H_2O_2 was added can be seen. This can be explained that H_2O_2 would react rapidly with Fe^{2+} and Fe^{3+} at the initial reaction (within 0.2 min). Fe^{2+} were rapidly changed to Fe^{3+} and produce hydroxyl radical (·OH) by H_2O_2 as presented in Equations 2.1, and then Fe^{3+} would react with H_2O_2 to produce Fe^{2+} and hydroperoxyl radical ($HO_2\cdot$) in Equations 2.9 and 2.10, although the reaction rate of Fe^{3+} and H_2O_2 was slow. After that, the produced Fe^{2+} reacted rapidly with residual H_2O_2 to produce hydroxyl radical (·OH) and Fe^{3+} again. This cycle resulted in the constant amount of Fe^{2+} and Fe^{3+} throughout the reaction.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

This research aims to investigate the treatment of cutting oil wastewater by Fenton process as a post treatment process. The results can be concluded as follow.

- **Emulsion characteristics**

  Synthetic cutting oil wastewater appears in form of milky emulsion which is very stable and doesn’t tend to separate from water naturally because of the presence of surfactant. Conventional physical separation process such as decantation cannot separate this suspended oil from the water (Chalermsinsuwan, 2009). However, coagulation known as a chemical destabilization provided 90% COD removal of 1 g/l oil concentration (Rojvilavan, 2011) that the effluent COD still exceed the standard discharge regulation (120 mg/l). Therefore, Fenton process was applied as a post- treatment process to treat the residual oil in this research.

- **Effects of operating conditions of Fenton process**

  In Fenton reaction, ferrous ions (Fe^{2+}) can catalyst the production of hydroxyl radical, which is a strong oxidizing agent, from hydrogen peroxide (H_2O_2) under the acidic condition. Residual cutting oil process would be oxidized by the produced hydroxyl radical. Three different synthetic cutting oil concentrations (50 mg/l, 100 mg/l and 150 mg/l) were treated by varying Fe^{2+} dosage to 50, 200 and 500 mg/l, and $Fe^{2+/}H_2O_2$ ratio by mass to 1:2.5, 1:6 and 1:10 in order to determine the optimum Fenton’s reagents dosages. The result showed that COD removal efficiency increased with the increase of Fe^{2+} and H_2O_2 concentrations. The highest COD removal efficiencies of 97% can be achieved for the oil concentrations of 100 and 150 mg/l with 200 mg Fe^{2+}/l and 1:2.5 of Fe^{2+}/H_2O_2 ratio, while the 98% in the case of 50 mg/l oil concentration can be succeed at 200 mg Fe^{2+}/l and 1:10 of Fe^{2+}/H_2O_2 ratio in 1 minute reaction time. However, excess Fenton’s reagents can result in lower oxidation of cutting oil due to hydroxyl radical scavenging effect. To reduce this radical scavenging effect and reduce the Fenton 's reagent usage, the multiple step feeding concepts were applied by using 50 mg total Fe^{2+}/l and 125 mg H_2O_2/l (Fe^{2+}/H_2O_2 ratio= 1:2.5) for treating 100 mg/l oil concentration and 150 mg/l oil concentration. The result demonstrated that three feedings of 16.67 mg Fe^{2+}/l and 41.67 mg H_2O_2/l (total Fe^{2+} = 50 mg/l and total H_2O_2= 125 mg/l) at t = 0, 5, and 10 minutes reaction time with 100 and 150 mg/l oil concentration provided COD removal efficiency almost as high as initial full feeding of 200 mg Fe^{2+}/l and 500 mg H_2O_2/l (97%). This can be concluded that multiple step feeding can reduce Fenton's reagent usage and increase oxidation efficiency.

- **The optimal condition for Fenton process in this study can be concluded in Table 5.1.**

  For 50 mg/l oil concentration, initial full feeding of Fenton's reagent is enough to achieve high oxidation (COD removal efficiency= 90%), thus multiple step feeding was not necessary. However, 100 mg/l and 150 mg/l oil concentration should be treated by three feeding of 16.67 mg Fe^{2+}/l and 41.67 mg H_2O_2/l (total Fe^{2+}= 50 mg/l and total H_2O_2= 125 mg/l) at t= 0, 5, 10 reaction time to achieve high COD removal efficiency.

Table 5.1 Summary of the optimal condition of Fenton process for treating the cutting oil wastewater in this study

Cutting oil concentration (mg/l)	**Optimum operating condition of Fenton process**					
	Fe^{2+} (mg/l)	**H_2O_2 (mg/l)**	**Fe^{2+}/H_2O_2 ratio**	**Feeding mode of Fe^{2+} and H_2O_2**	**Reaction time (min)**	**COD removal efficiency (%)**
50	50	300	1:6	one feeding at t= 0	3 min	90
100	50	125	1:2.5	three feeding at t= 0, 5, 10 min	30 min	93
150	50	125	1:2.5	three feeding at t= 0, 5, 10 min	30 min	91

- **pH neutralization and iron sludge precipitation**

  After cutting oil was oxidized by Fenton process, the pH of the treated water was extremely acid, which cannot be discharged to an environment directly. Therefore, the pH neutralization by NaOH was conducted. This pH adjustment also cause the precipitation of the solid $Fe(OH)_2$ and $Fe(OH)_3$, which required the sedimentation to remove from water. The optimum overflow rate of sedimentation tank was determined by the standard discharge regulation of suspended solid (SS in the discharge should not exceed 50 mg/l) to make sure that the water can be discharge to an environment. The optimum overflow rates of sedimentation tank obtained from the discrete settling test for the 50 mg Fe^{2+}/l and 200 mg Fe^{2+}/l providing the 80% settling efficiency were in range of 0.2 – 0.45 m/h and 0.7-1.9 m/h, respectively.

- **Iron sludge reuse**

  Iron precipitates which were formed by neutralizing require the appropriate treatment and disposal. To minimize the iron sludge production that leads to lower disposal cost, iron sludge was reused as iron catalyst for next Fenton oxidation process. The sludge from the 50 mg Fe^{2+}/l and 125 mg H_2O_2/l used in Fenton process can be reused to treat 100 mg/l oil concentration without iron regeneration and replacement at least 5 recycling times with the high efficiencies. This was due to Fe^{2+} and Fe^{3+} in iron sludge can catalyst the production of hydroxyl radical and hyproperoxyl radical from H_2O_2 in Fenton reaction and Fenton-like reaction, respectively.

From the results, the continuous process that should be applied for further study on oily wastewater treatment can be proposed as in Figure 5.1. The process consists of 1) a mixing tank for adjusting pH to 3, 2) Fenton reactor tank, 3) a mixing tank for neutralization and 4) a sedimentation tank.

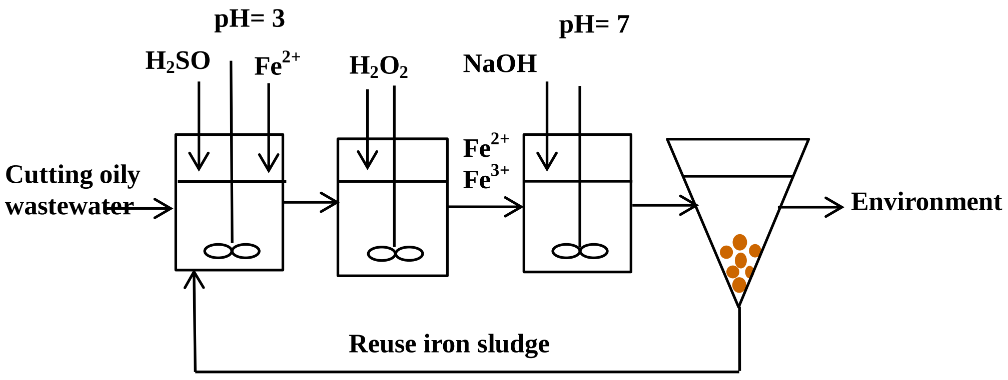


Figure 5.1 Schematic diagram of the Fenton process proposed for further study

5.2 Recommendation

1. Continuous system of Fenton process should be operated to represent more practical treatment process as in an industry.
2. This process should be applied with the real wastewater from metalworking industry.
3. The study on the iron sludge reuse should be further conducted, particularly the regeneration of iron sludge by heating. This could improve the efficiency in the reuse as the adsorbed organic would be removed under high temperature.

5.3 Suggestion for the industry

Application of Fenton oxidation process for industrial operation, amount of chemical usage and reaction time are the important aspects that have to be considered in order to reduce the treatment cost. From the obtained result, Fenton oxidation and iron coagulation/precipitation by using Fe^{2+} 50 mg/l are enough to treat 100 mg/l cutting oil wastewater because 82% COD removal and 58% COD removal of 100 mg/l oil concentration were achieved by Fenton oxidation and iron coagulation/precipitation, respectively. The effluent COD values of Fenton and iron coagulation process (41.4 mg/l and 96.6 mg/l, respectively) were lower than the standard discharge regulation (120 mg/l), thus the treated water can be discharged to an environment. However, iron coagulation requires higher reaction time comparing with Fenton oxidation since Fenton oxidation can destruct or oxidize cutting oil very fast; hydroxyl radical, which is a strong oxidative power, react rapidly with cutting oil. The oxidation of cutting oil was completed within minute.

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APPENDIX

Appendix A Fenton process

Table A-1 Effect of Fenton’s reagent dosages on COD removal at different initial oil concentration

Cutting oil concentration (mg/l)	**Fe^{2+} (mg/l)**	**H_2O_2 (mg/l)**	**F/H Ratio**	**initial COD (mg/l)**	**COD at 30 min reaction time (mg/l)**	**COD removal efficiency (%)**
50	50	125	1:2.5	290.065	34.8078	88
		300	1:6	304.832	30.4832	90
		500	1:10	300.41	90.123	70
	200	500	1:2.5	295.23	115.1397	61
		1200	1:6	299.214	44.8821	85
		2000	1:10	309.216	9.27648	97
	500	1250	1:2.5	295.2	153.504	48
		3000	1:6	302609	54469.62	82
		5000	1:10	305.697	70.31031	77
100	50	125	1:2.5	217.45	39.141	82
		300	1:6	198.693	47.68632	76
		500	1:10	210.345	58.8966	72
	200	500	1:2.5	205.186	6.15558	97
		1200	1:6	213.854	25.66248	88
		2000	1:10	198.562	49.6405	75
	500	1250	1:2.5	199.129	49.78225	75
		3000	1:6	210.068	33.61088	84
		5000	1:10	219.52	13.1712	94
150	50	125	1:2.5	198.693	31.79088	84

		300	1:6	213.027	53.25675	75
		500	1:10	208.314	83.3256	60
	200	500	1:2.5	199.972	3.99944	98
		1200	1:6	197.932	29.6898	85
		2000	1:10	212.542	36.13214	83
	500	1250	1:2.5	209.431	62.8293	70
		3000	1:6	200.528	18.04752	91
		5000	1:10	215.852	32.3778	85

Table A-2 Effect of controlling pH 3, ferrous coagulation and H_2O_2 oxidation (Control experiment)

Control experiment	**Fe^{2+} (mg/l)**	**H_2O_2 (mg/l)**	**initial COD (mg/l)**	**COD at 30 min reaction time (mg/l)**	**COD removal efficiency (%)**
Control pH 3	-	-	217.157	208.47072	4
iron coagulation (pH7)	50	-	210.642	88.46964	58
iron coagulation (pH9)		-	215.86	77.7096	64
iron coagulation (pH11)		-	211.931	59.34068	72
iron coagulation (pH7)	200	-	199.998	69.9993	65
iron coagulation (pH9)		-	207.52	62.256	70
iron coagulation (pH11)		-	211.031	48.53713	77
H_2O_2 oxidation	-	125	215.456	161.592	25
H_2O_2 oxidation	-	500	217.219	145.53673	33

Table A-3 Effect of feeding mode of Fenton's reagents

cutting oil concentration (mg/l)	**Total Fe^{2+} (mg/l)**	**Total H_2O_2 (mg/l)**	**Feeding mode**	**initial COD (mg/l)**	**COD at 30 min (mg/l)**	**COD removal efficiency (%)**
100	50	125	One feeding of Fe^{2+} and H_2O_2 (at t=0, 10 min)	210	38	82
			Two feeding of Fe^{2+} and H_2O_2 (at t=0, 10 min)	227	32	86
			Three feeding of Fe^{2+} and H_2O_2 (at t= 0,5, 10)	219	15	93
			Initial full feeding of Fe^{2+} (at t= 0 min) and two feeding of H_2O_2 (at t=0, 5 min)	223	36	84
150	50	125	One feeding of Fe^{2+} and H_2O_2 (at t=0, 10 min)	295	47.2	84
			Two feeding of Fe^{2+} and H_2O_2 (at t=0, 10 min)	300	33	89
			Three feeding of Fe^{2+} and H_2O_2 (at t= 0,5, 10)	305	27	91
			Initial full feeding of Fe^{2+} (at t= 0 min) and two feeding of H_2O_2 (at t=0, 5 min)	309	62	80

Appendix B Kinetic study

Table B-1 Effect of reaction time on COD removal at different initial oil concentration (operated at the optimum Fenton’s reagent dosages)

cutting oil concentration (mg/l)	**Reaction time (min)**	**COD (mg/l)**	**COD removal efficiency (%)**
50	0	121	0
	0.2	8.8	93
	0.5	9	93
	1	8	93
	5	7	94
	10	8	93
	20	9	93
	30	7	94
	60	8	93
100	0	198.7	0
	0.2	11	94
	0.5	8.8	96
	1	7	97
	5	9.	96
	10	10	95
	20	9	95
	30	8.6	96
	60	8	96
150	0	272	0
	0.2	1	99
	0.5	10	96
	1	5	98
	5	4	98
	10	4	98
	20	7	97
	30	6	98
	60	4	98

Appendix C Residual Fe^{2+} and Fe^{3+} in the Fenton reaction

Table C-1 Amount of residual Fe^{2+} and Fe^{3+} in the Fenton reaction (Fe^{2+}= 200 mg/l and Fe^{2+}/H_2O_2= 1:2.5)

Reaction time (min)	Fe^{2+}= 200 mg/l and H_2O_2= 500 mg/l (Fe^{2+}/H_2O_2= 1:2.5)		
	Total Fe (mg/l)	Fe^{2+} (mg/l)	Fe^{3+} (mg/l)
0	0	200.0	0
0.2	199.6	4.3	195.3
0.5	200	4.3	195.7
1	202.5	4.6	198.0
5	201.1	5.1	196.0
10	201.5	5.1	196.4
15	200.0	5.8	194.1
20	200	5.1	194.9
30	199.9	5.6	194.3
60	200.2	5.8	194.4

Table C-2 Amount of residual Fe^{2+} and Fe^{3+} in the Fenton reaction (Fe^{2+}= 50 mg/l and Fe^{2+}/H_2O_2= 1:2.5)

Reaction time (min)	Fe^{2+}= 50 mg/l and H_2O_2= 125 mg/l (Fe^{2+}/H_2O_2= 1:2.5)		
	Total Fe (mg/l)	Fe^{2+} (mg/l)	Fe^{3+} (mg/l)
0	0	50	0
0.2	50.1	2.2	47.9
0.5	49.9	2.4	47.4
1	50.5	2.9	47.6
5	50.1	3.4	46.8
10	50.3	3.2	47.1
15	50.4	3.8	46.6
20	50.1	3.6	46.5
30	51.0	3.8	47.2
60	50.9	3.8	47.2

Appendix D Discrete Settling

Table D-1 Discrete settling result (Fe^{2+}= 50 mg/l and H_2O_2= 125 mg/l)

Cutting oil concentration (mg/l)	Height (cm)		Time (min)								
			0	3	5	10	20	30	60	90	120
50	32	C	133	127	140	127	113	73	48	40	27
		C/C_0	1	0.95	0.95	0.95	0.85	0.55	0.33	0.3	0.2
		H/t (cm/min)	-	10.67	6.4	3.2	1.6	1.07	0.53	0.36	0.27
100	32	C	160	160	160	150	80	65	40	40	20
		C/C_0	1	1	1	0.94	0.5	0.41	0.25	0.25	0.125
		H/t (cm/min)	-	10.6	6.36	3.18	1.59	1.06	0.53	0.35	0.26
150	32	C	200	200	200	180	180	125	75	56	36
		C/C_0	1	1	1	0.9	0.9	0.625	0.375	0.28	0.18
		H/t (cm/min)	-	10.27	6.16	3.08	1.54	1.03	0.51	0.34	0.26

Table D-1.1 Settling efficiency from discrete settling

(initial oil concentration= 50 mg/l, Fe^{2+}= 50 mg/l and H_2O_2= 125 mg/l)

V_0 (cm/min)	**P_0**	**$1- P_0$**	**$1/V_0$ (cm/min)**	$\int_0^{P0} V_i dP_i$	**Settling efficiency (%)**
0.27	0.2	0.8	3.7	0.027	90
0.36	0.3	0.7	2.78	0.058	86
0.53	0.33	0.67	1.89	0.071	80
1.07	0.55	0.45	0.94	0.247	68
1.6	0.85	0.15	0.63	0.647	55
3.2	0.95	0.05	0.31	0.887	33
6.4	0.95	0.05	0.16	1.276	14
10.67	0.95	0.05	0.09	1.276	6

Table D-1.2 Settling efficiency from discrete settling
(initial oil concentration= 100 mg/l, Fe^{2+}= 50 mg/l and H_2O_2= 125 mg/l)

V_0 (cm/min)	P_0	1- P_0	1/V_0 (cm/min)	$\int_0^{P0} V_i dP_i$	Settling efficiency (%)
0.265	0.125	0.875	3.774	0.017	94
0.353	0.25	0.75	2.831	0.055	90
0.53	0.25	0.75	1.889	0.055	85
1.06	0.406	0.594	0.943	0.179	76
1.59	0.5	0.5	0.629	0.304	69
3.18	0.938	0.062	0.314	1.35	49
6.36	1	0	0.157	1.65	26
10.6	1	0	0.094	1.65	16

Table D-1.3 Settling efficiency from discrete settling
(initial oil concentration= 150 mg/l, Fe^{2+}= 50 mg/l and H_2O_2= 125 mg/l)

V_0 (cm/min)	P_0	1- P_0	1/V_0 (cm/min)	$\int_0^{P0} V_i dP_i$	Settling efficiency (%)
0.26	0.18	0.82	3.896	0.023	91
0.34	0.28	0.72	2.922	0.053	88
0.51	0.375	0.625	1.948	0.094	81
1.03	0.625	0.375	0.974	0.286	65
1.54	0.9	0.1	0.649	0.639	52
3.08	0.9	0.1	0.325	0.639	31
6.16	1	0	0.162	1.101	17.8
10.27	1	0	0.097	1.101	10.7

Table D-2 Discrete settling result (Fe^{2+}= 200 mg/l and H_2O_2= 125 mg/l)

Cutting oil concentration (mg/l)	Height (cm)		Time (min)							
			0	3	7	11	15	20	30	60
50	61	C	380	360	340	300	270	133.3	65	43.3
		C/C_0	1	0.947	0.895	0.789	0.711	0.351	0.171	0.114
		H/t (cm/min)	-	20.33	8.714	5.545	4.067	3.05	2.033	1.017
100			0	3	5	7	11	15	20	30
	61	C	540	360	340	120	110	93.33	50	28
		C/C_0	1	0.667	0.630	0.222	0.204	0.173	0.093	0.052
		H/t (cm/min)	-	20.333	12.2	8.714	5.545	4.067	3.05	2.033
150			0	3	5	8	12	15	20	60
	61	C	480	420	420	380	340	140	46.667	36.667
		C/C_0	1	0.875	0.875	0.792	0.708	0.292	0.097	0.076
		H/t (cm/min)	-	20.333	12.2	7.625	5.083	4.067	3.05	1.017

Table D-2.1 Settling efficiency from discrete settling
(initial oil concentration= 50 mg/l, Fe^{2+}= 200 mg/l and H_2O_2= 2000 mg/l)

V_0 (cm/min)	**P_0**	**1- P_0**	**$1/V_0$ (cm/min)**	$\int_0^{P0} V_i dP_i$	**Settling efficiency (%)**
1.017	0.114	0.886	0.983	0.058	94
2.033	0.171	0.829	0.492	0.145	90
3.05	0.351	0.649	0.328	0.602	85
4.067	0.711	0.289	0.246	1.882	75
5.545	0.789	0.211	0.180	2.261	62
8.714	0.895	0.105	0.115	3.012	45
20.333	0.947	0.053	0.049	3.776	24

Table D-2.2 Settling efficiency from discrete settling
(initial oil concentration= 100 mg/l, Fe^{2+}= 200 mg/l and H_2O_2= 500 mg/l)

V_0 (cm/min)	**P_0**	**1- P_0**	**$1/V_0$ (cm/min)**	$\int_0^{P0} V_i dP_i$	**Settling efficiency (%)**
2.033	0.052	0.948	0.492	0.053	97
3.05	0.093	0.907	0.328	0.156	96
4.067	0.173	0.827	0.246	0.442	94
5.545	0.204	0.796	0.180	0.590	90
8.714	0.222	0.778	0.115	0.722	86
12.2	0.630	0.37	0.082	4.982	78
20.333	0.667	0.333	0.049	5.585	61

Table D-2.3 Settling efficiency from discrete settling
(initial oil concentration= 150 mg/l, Fe^{2+}= 200 mg/l and H_2O_2= 500 mg/l)

V_0 (cm/min)	**P_0**	**1- P_0**	**$1/V_0$ (cm/min)**	$\int_0^{P0} V_i dP_i$	**Settling efficiency (%)**
1.017	0.076	0.924	0.983	0.039	96
3.05	0.097	0.903	0.328	0.081	93
4.067	0.292	0.708	0.246	0.773	90
5.083	0.708	0.292	0.197	2.679	82
7.625	0.792	0.208	0.131	3.209	63
12.2	0.875	0.125	0.082	4.035	46
20.333	0.875	0.125	0.049	4.035	32

Appendix E Reuse of iron sludge

Table E-1 Reuse iron sludge as iron catalyst for the next Fenton process (initial oil concentration= 100 mg/l, the sludge from 50 mg Fe^{2+}/l and H_2O_2= 125 mg/l used in Fenton process)

Reused times	**initial COD (mg/l)**	**Fenton stop reaction at pH7**		**Fenton stop reaction at pH 9**	
		COD at 30 min (mg/l)	**COD removal (%)**	**COD at 30 min (mg/l)**	**COD removal (%)**
0	226	47	79	41	82
1	221	53	76	49	78
2	222	58	74	47	79
3	219	59	73	53	76
4	230	71	69	67	71
5	224	74	67	72	68

Table E-2 Reuse iron sludge for coagulation (initial oil concentration= 100 mg/l, the sludge from 50 mg Fe^{2+}/l and H_2O_2= 125 mg/l used in Fenton process)

Reused times	**initial COD (mg/l)**	**Coagulation at pH7**		**Coagulation at pH 9**	
		COD at 30 min (mg/l)	**COD removal (%)**	**COD at 30 min (mg/l)**	**COD removal (%)**
0	224	49	78	38	83
1	218	87	60	57	74
2	226	97	57	68	70
3	221	102	54	71	68
4	228	110	52	80	65
5	220	108	51	75	66

Table E-3 Residual Fe^{2+} and Fe^{3+} at 1st reuse

Reaction time (min)	**Fe^{2+}= 50 mg/l and H_2O_2= 125 mg/l (Fe^{2+}/H_2O_2= 1:2.5)**		
	Total Fe (mg/l)	**Fe^{2+} (mg/l)**	**Fe^{3+} (mg/l)**
0	46.591	2.796	43.795
0.2	46.495	2.033	44.461
0.5	46.529	2.033	44.495
1	46.921	2.042	44.878
5	45.921	1.612	44.308
10	46.813	1.605	45.208
15	46.539	1.524	45.015
20	46.747	1.509	45.237
30	46.583	1.101	45.482
60	46.988	1.328	45.659

VITA

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