การบำบัดน้ำเสียปนเปื้อนน้ำมันตัดด้วยกระบวนการโคแอกกูเลชันและโซโนเฟนตัน

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตร์มหาบัณฑิต
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TREATMENT OF CUTTING OIL WASTEWATER BY COAGULATION AND
SONO-FENTON PROCESSES

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
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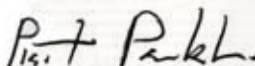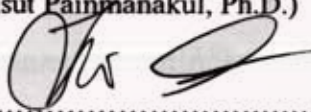|	
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ธนันท์ เฉลิมสินสุวรรณ: การบำบัดน้ำเสียปนเปื้อนน้ำมันตัดด้วยกระบวนการโคแอกกูเลชันและโซโนเฟนตัน. (TREATMENT OF CUTTING OIL WASTEWATER BY COAGULATION AND SONO-FENTON PROCESSES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ.ดร.พิสุทธิ์ เพียรมนกุล, 143 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาความเป็นไปได้ในการประยุกต์ใช้กระบวนการอะคูส-ติคออกซิเดชัน (acoustic oxidation) อันเป็นหนึ่งในกระบวนการออกซิเดชันขั้นสูง (advance oxidation processes) ในการบำบัดน้ำเสียปนเปื้อนน้ำมันตัด (cutting oil wastewater) ที่ยากต่อการบำบัดด้วยวิธีการทั่วไป โดยตัวแปรที่ทำการศึกษาได้แก่ ความเข้มของคลื่นความถี่เหนือเสียง (ultrasonic intensity) อุณหภูมิของปฏิกิริยา ความเข้มข้นน้ำมัน รวมถึงการเพิ่มประสิทธิภาพการออกซิไดซ์ด้วยการเติมสารออกซิแดนท์ชนิดอื่น อาทิเช่น ไฮโดรเจนเปอร์ออกไซด์ การเติมอากาศ และการใช้สารเฟนตันอีกด้วย

ทว่า ผลการทดลองแสดงให้เห็นว่า การใช้อะคูสติคออกซิเดชันเพียงอย่างเดียวนั้นไม่เพียงพอที่จะใช้ในการบำบัดน้ำเสียชนิดนี้ โดยมีสาเหตุส่วนหนึ่งมาจากคุณลักษณะเฉพาะของน้ำเสียชนิดนี้ อย่างไรก็ตาม การใช้สารเฟนตันร่วมกันกับการใช้คลื่นความถี่เหนือเสียงนั้นจะทำให้ได้ประสิทธิภาพการกำจัดซีโอดีสูงถึง 92.3 เปอร์เซ็นต์โดยใช้ความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์เท่ากับ 140 กรัมและสารเฟอร์รัสซัลเฟตในปริมาณ 500 มิลลิกรัมของเหล็กต่อลิตรของน้ำเสีย (mg/L as Fe^{2+}) ซึ่งเป็นปริมาณที่สูง แต่ก็สามารถลดปริมาณเพื่อให้ได้มาซึ่งการกำจัดที่เหมาะสมได้ด้วยการใช้สมการจลนพลศาสตร์ของปฏิกิริยา (reaction kinetic)

นอกจากนี้ งานวิจัยนี้ยังได้ทำการศึกษาความเป็นไปได้ในการประยุกต์ใช้กระบวนการออกซิเดชันขั้นสูงต่างๆ ในการบำบัดน้ำที่ได้จากกระบวนการทำลายเสถียรภาพและรวมตะกอนของน้ำเสียปนเปื้อนน้ำมัน โดยมีจุดประสงค์ในการ (1) ลดสารปนเปื้อนในน้ำทิ้ง และ (2) ลดการใช้สารเคมี โดยพบว่า กระบวนการออกซิเดชันขั้นสูงนั้นสามารถลดซีโอดีได้จนถึงระดับที่ไม่สามารถตรวจวัดได้โดยวิธีการทั่วไป โดยใช้สารเคมีในปริมาณน้อย และสามารถนำไปใช้ได้จริงโดยมีหลักการออกแบบที่มีพื้นฐานมาจากทฤษฎี

สาขาวิชา   การจัดการสิ่งแวดล้อม   ลายมือชื่อนิสิต _____

ปีการศึกษา   2552   ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก _____

5187534720: MAJOR OF ENVIRONMENTAL MANAGEMENT

KEYWORDS : ACOUSTIC OXIDATION /SONO-FENTON OXIDATION / CUTTING OIL WASTEWATER / COAGULATION / REACTION KINETIC

TANUN CHALERMSINSUWAN : TREATMENT OF CUTTING OIL WASTEWATER BY COAGULATION AND SONO-FENTON PROCESSES. THESIS ADVISOR: PISUT PAINMANAKUL, Ph.D., 143 pp.

This study aims to investigate the applicability of acoustic oxidation, which is an advance oxidation processes (AOPs), on the treatment of cutting oil wastewater that could not be easily treated by conventional processes. The effect of physical parameters which are ultrasonic intensity, temperature, and oil concentration, were determined as well as the enhancement effects caused by the addition of other conventional oxidant as hydrogen peroxide, aeration, and Fenton's reagents.

However, the results showed that acoustic oxidation alone is not effective in eliminating COD from the sample, and Fenton reagents should be added in order to enhance the performance. It is also found the process, known as sono-Fenton, could reduce the COD up to 92.3 percent using 140 g/L hydrogen peroxide and 500 mg/l Fe^{2+}. The amount of required chemical is considerably high but could be optimized using reaction kinetic parameters determined.

Additionally, this study investigated the possibility of incorporating advance oxidation processes as the post-treatment of conventional coagulation-flocculation process, which serves two purposes: (1) minimizing constituents in the effluent and (2) reducing chemical usage. In this study, COD of the wastewater was found to be able to reduce from over 2,000 mg/l to the level that is undetectable by the analysis method used in this study. The amount of chemical used is minimal, and the processes could be compared and practically designed on theoretical background.

Field of Study : __Environmental Management__   Student's Signature ....

Academic Year : _2009_................................   Advisor's Signature........................

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CHAPTER I

INTRODUCTION

1.1 BACKGROUND

Since the time of Industrial Revolution, environmental degradation became one of the major problems of global scale. Among them, oily wastewater, which is produced from a wide range of activities from heavy industries to household use, is the one with utmost importance. Oil could contain high amount of aromatic hydrocarbons, some of them are known carcinogens (LaGrega, Buckingham, and Evans, 2001), and most of the rest are suspected. Presence of oil could also cause nuisance by fume and odor, and it is known to pose several problems to conventional wastewater treatment processes (Metcalf & Eddy Inc., 2004).

Normally, oil-water mixture is unstable, and will eventually separate after left alone for a while. However, most oily wastewater exists as oil-in-water emulsion by the presence of surfactant, which could attach to the oil droplets, making it polar and virtually soluble (Aurelle, 1985). In this case, oil droplets are more stable and take longer time to naturally separate. Therefore, various physical and chemical techniques were invented, developed, and applied to make the separation faster and more effective, but it is only the concentration method, not the elimination ones. Such separation processes could too produce oily sludge as the secondary waste that needed to be further handled, managed, and disposed of.

Acoustic oxidation is an emerging technique using hydroxyl radicals (·OH) which are produced by thermolytic bond breakage of water molecule at the extreme condition around collapsing cavitation bubbles. Additionally, volatile substances could be volatilized and thermally destructed within the heated bubbles. The process was proved to be efficient, unselective, simple and clean approach to destruct various kinds of organic substances. Moreover, it is also possible that addition of other conventional oxidants could greatly enhance the process.

This study investigated the possibility of using acoustic oxidation on the treatment of cutting oil wastewater as well as the major factors influencing the oxidation performance. Moreover, prospect of the process to be incorporated as post-treatment for separation process was determined. After that, examples of how the processes could be designed will be given and aspects of different process configurations compared.

1.2 GOAL & OBJECTIVES

1.2.1 To assess the possibility of using acoustic oxidation in the treatment of cutting oil wastewater;

1.2.2 To determine the effects of different physical operating factors (ultrasonic intensity, temperature, and initial oil concentration) on the reaction rate and treatment efficiency of the oxidation process on the treatment of cutting oil wastewater;

1.2.3 To analyze the synergistic effects between acoustic oxidation and other oxidants in terms of reaction rate, reaction kinetic parameters, and removal efficiency;

1.2.4 To investigate the possibility of using acoustic oxidation as a post-treatment process aimed to increase reuse potential of effluent water

1.3 SCOPES AND LIMITATION

The research will be conducted at Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University.

1.3.1 Wastewater samples were synthesized by diluting concentrated cutting oil with tap water. The concentration used will be 0.1%, 0.5% and 1.0% volume/volume. Such concentrations are selected for the purpose of simplicity in analysis while being close to the ones commonly used in industrial processes (El Baradie, 1996a; 1996b).

1.3.2 Experiments were performed in batch-basis.

1.3.3 The operating factors studied are ultrasonic intensity, operating temperature, and initial oil concentration

1.3.4 Effects of the operating factors were represented by the changes of kinetic parameters and treatment efficiency of the process.

1.3.5 Amount of oil were represented by chemical oxygen demand (COD), and the changes occur within the liquid phase will be tracked using oxidation-reduction potential (ORP) probe.

1.3.6 Synergistic effects with other oxidants were studied by adding hydrogen peroxide at different dosages and injecting oxygen by air bubbling at different gas flow rates.

1.3.7. Acoustic oxidation was modified into sono-Fenton by adding $FeSO_4$. Roles of factors which are pH, Fe^{2+}/H_2O_2 ratio, and H_2O_2 dosage were determined.

1.3.8 Conventional coagulation process were used to represent physicochemical separation processes for experiments using acoustic oxidation as post-treatment

1.3.9 Factors of coagulation to be determined are pH, chemical dosage, and mixing condition

1.4. EXPECTED BENEFITS

1.4.1 Acoustic oxidation would be proved for its applicability and practicability for the treatment of cutting oil wastewater as well as other types of wastewater containing organic constituents

1.4.2 Theoretical kinetic model could possibly be developed, incorporated, and integrated into more comprehensive continuous-flow reactor model which could aid the design of larger scale.

CHAPTER II

LITERATURE REVIEW

2.1 CUTTING OIL

2.1.1 Characteristics

Cutting oil, a type of metalworking fluids, is widely used in most metalworking operations. It usually serves four main functions: cooling, lubrication, welding resistance, and disposal of metal chip. Importance of each function varies by the requirement of the process; for example, cooling and welding resistance are more important at higher cutting speed while lubrication is preferred at lower speed. Appropriate selection of cutting oil helps lengthen tool life, improve cutting quality, give better surface finish, and provide easier waste control (El Baradie, 1996a; El Baradie, 1996b; Grzesik, 2008). Soluble cutting oil is usually supplied in concentrated form which contains mineral oil, emulsifiers, biocides, and additives. Prior to its use, the concentrated oil is diluted with tap water, giving a highly stabilized white-colored emulsion.

2.1.2 Compositions and functions

Despite the fact that cutting oil is a mixture of various compounds, its components could be grouped by the function they provide as lubricant, coolant, emulsifier, EP agents, biocides, and others additives (El Baradie, 1996a).

- *Coolant*: In general application, cooling action is simply done by letting the fluid flow over the metal and tool surfaces. Having high heat capacity and conductivity, water could adequately fulfill the role. However, water is highly corrosive to most metals, provides low lubricity, and could wash lubricants away from the machine. In some cases where corrosion is concerned, synthetic chemical coolant could be used. Note that cooling is highly important at high cutting speed where great amount of heat is generated.

- *Lubricant*: Normally, lubricants used are mostly mineral oils of which adequate lubricity could fulfills most general requirement. Fatty oils, which are the better lubricant, could also be used. However, fat is highly unstable, and problems of fume and odor could occur within a short time. Synthetic inorganic lubricants too exist, but the use of this type is rather limited to oil-free metalworking fluids. Mineral oils, as lubricant, could acts as anti-corrosion agents as well, and mixing the oil with water combines together the cooling capabilities of water with lubricating and anti-corrosion of oil.

- *Emulsifier*: In order to produce a stable oil-in-water emulsion, emulsifiers should be added to the cutting oil. They could be either separately added or supplied within the concentrated oil. Normally, anionic surfactant is used as the emulsifier, but other types could be used too when need arise; for instance, cationic surfactant could be used when the diluting water has a high presence of metallic ions, which could destabilized the droplets generated by anionic surfactants (Bataller et al, 2004). Oppositely, when the dilution water is too soft, excessive foaming could occur and damage the equipments, and anti-foaming agents should be employed in cases like this.

- *EP agents*: EP (extreme pressure) agents are needed when high cutting speed and cutting force are used. EP agents are either sulfurized or phophorized compounds that could form a thin metallic film when subjected to extreme heat. The film acts as "a barrier" between metal surface and the face of cutting tool, so that no actual contact could take place and damage the tool. However, some highly reactive compounds in the agents could stain the surface of yellow-colored metals such as copper and bronze; in such cases, less reactive EP agents containing elemental sulfur were preferred.

- *Biocides*: In most working conditions, bacterial growth could occur within organic substances, especially when the complex substances were broken down into simpler ones during the uses. It is reported that bacterial growth on old cutting oil emulsion could cause fuming and odor; moreover, the growth further breaks down the organic substances, enabling more growth.

  Normally, biocides are added along with the concentrated oil in order to control such bacterial activities. More than one disinfection compounds, mainly phenolic, are frequently used in order to obtain enhanced microbial controls. Note that, no matter how much biocide were used, microbial growth could still occur due to thermal degradation caused by heat generated during the process (El Baradie, 1996a; Sandin, Mattsby-Baltzer, and Edebo, 1991; Sokovic and Mijanovic, 2001).

- *Others*: Apart from the components noted earlier, other additives could be added to fulfill specific requirement of the process; for example, water softener when the dilution water is extremely hard, buffer solution which prevent extreme pH, humectants, anti-corrosion, and wetting agents to reduce surface tension.

2.1.3 Problems

In addition to the potential to become fuming and odorous, direct contact with cutting oil emulsion could cause dermal aliments, which could be caused by either degraded components or microbial within the emulsion. NIOSH (2007) recommended in one of its survey report that direct dermal contact should be avoided, and dermatitis cases are common in machine operators, apart from other respiratory symptoms. Moreover, phenolic compounds and some degraded organics are classified as either suspected or known carcinogen. Some allergen components are also reported in *Table 2.1*.

Table 2.1 Common allergens in metalworking fluids

Substance	Role	Notes
Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA), and Diglycolamine	Rust-preventing agents Emulsifier	DEA could form N-nitrosamine, a potential carcinogen
Colophonium/Abletic acid	Major components of water-based fluids	
Fragrances	Odor-masking	May contains aromatic hydrocarbons Main exposure pathway is inhalation
Chromium, nickel, cobalt	Contaminant from abrasion of metals	Highly hazardous
Formaldehyde and its releasers	Fluid preservation	
Methyldibromo Glutaronitrile and 2-phenoxyethanol	Fluid preservation	
5-chloro-2-methylisothiazol-3-one/ 2-methylisothiazol-3-one	Additional biocides	
p-Aminoazobenzene	Dye	Uses stopped in 1990

Adapted from Grier and Lessman (2006)

2.1.4 Treatment and disposal

After long use, cutting oil emulsion eventually loses its properties and has to be replaced and disposed of. Despite of different compositions, cutting oil waste in most situations share some common features: it exists as stabilized oil-in-water emulsion containing degraded hydrocarbons, biocides, and other impurities which were accumulated during the use. The emulsion is highly stable due to the requirement of cutting oil that it should give a highly stabilized emulsion upon dilution with water. Therefore, conventional separation methods such as gravity or centrifugal are considered ineffective. The suspended oil droplets were found to be slow to coalesced; in a experiment studying the stability of cutting oil emulsion (Bataller et al, 2004), no significant shift of mass mean diameter could be observed after the emulsion is left alone for seven days.

In general practice, waste containing oil is generally disposed of by incineration, but presence of water in cutting oil waste, which could be as high as 90 - 99%, greatly lowers energy content in the waste. It is usually found that the waste has too much toxicity to be effectively biodegraded partly due to extensive microbial inhibiting actions caused by biocides.

Currently, the primary method employed in the treatment of cutting oil waste is destabilizing the emulsion using metallic salt or strong acid followed by gravity separation. *Figure 2.1* presents the simple separation process in practical use. However, the method is only the concentration of pollutants and gives secondary waste in form of oily sludge, of which the metal content could be as high as 10%. The metal could also be retained within the effluent water along with the dissolved organic pollutants which could not be removed by coagulation (Rizzo et al, 2008).

Studies on the treatment techniques for cutting oil waste were previously conducted. There are two basic types of treatment methods employed. The more studied ones are separation processed using conventional separation techniques modified with process enhancements such as coagulants, while the others are the destruction processes including thermal destruction, chemical oxidation, and biological oxidation. The techniques are described in the following *Table 2.2*.
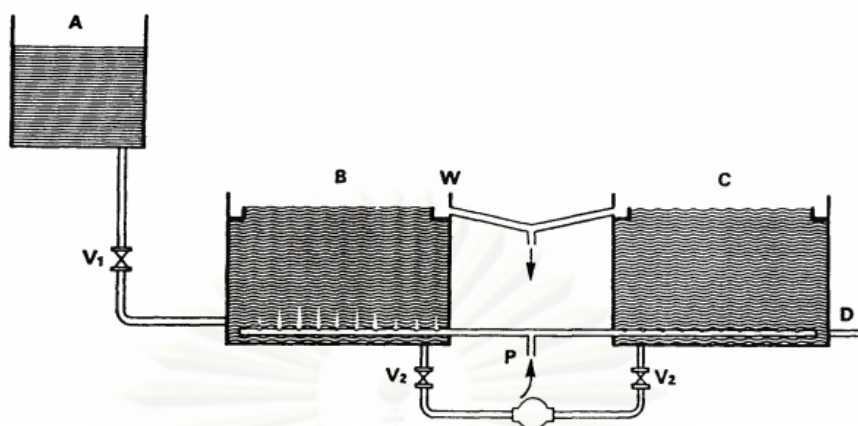
Figure 2.1 *Schematic diagram of simple separation process for cutting oil emulsion*
Source: (El Baradie, 1996a)

Table 2.2 *Technologies proposed to treat cutting oil wastewater*

Technique	Description	Sources
Separation processes		
Coagulation	Using metal salts to destabilize oil droplets	Rios, Pazos, and Coca (1998)
Coagulation and dissolved air flotation (DAF)	Flotation was applied to increase the rising rate of destabilized droplets	Bensadok, Belkacem, and Nezzal (2007)
Electrocoagulation	Similar to coagulation, but the metal ions were produced by electrochemical processes	Bensadok et al. (2008) Kobya et al. (2008)
Two aqueous phase extraction	Using special phase characteristic between solvent/surfactant/aqueous to remove pollutants	Talbi et al. (2009)
Ultrafiltration	The process could separate most suspended substances, including oil droplets	Busca, Hilal, and Atkin, 2003 Chang, Chung, and Han, 2001
Destruction processes		
Biodegradation	Using anaerobic microbe with resistance to toxic substances	Perez et al. (2007)
Supercritical water oxidation	Unique characteristic of water at supercritical point lead to AOPs-like phenomena	Portela et al. (2001)
Sono-Fenton	Combining together ultrasonic irradiation and Fenton's reagents, which are known AOPs	Seo et al. (2007)

As found, each type of proposed processes has some common advantage and disadvantages. For example, separation processes are facing difficulties regarding oily sludge as well as remaining dissolved pollutants. Destruction processes, on the other hand, requires more extreme condition: high energy use, chemical dosage, or sophisticate process control.

It is worth noting that, in most studies mentioned, the effectiveness of such methods is highly varied by the type of cutting oil used. This is due to the fact that cutting oil actually has hundreds, if not thousands, commercial formulas having different proportion of lubricant, coolant, biocides, and additives. Moreover, there are many possible substances with different characteristics that could fulfill such roles. Therefore, treatment of different type of cutting fluid should be separately studied, and great care should be taken when applying the result obtained from one study to another, since it is possible that different types of cutting oil used could give unexpected results.
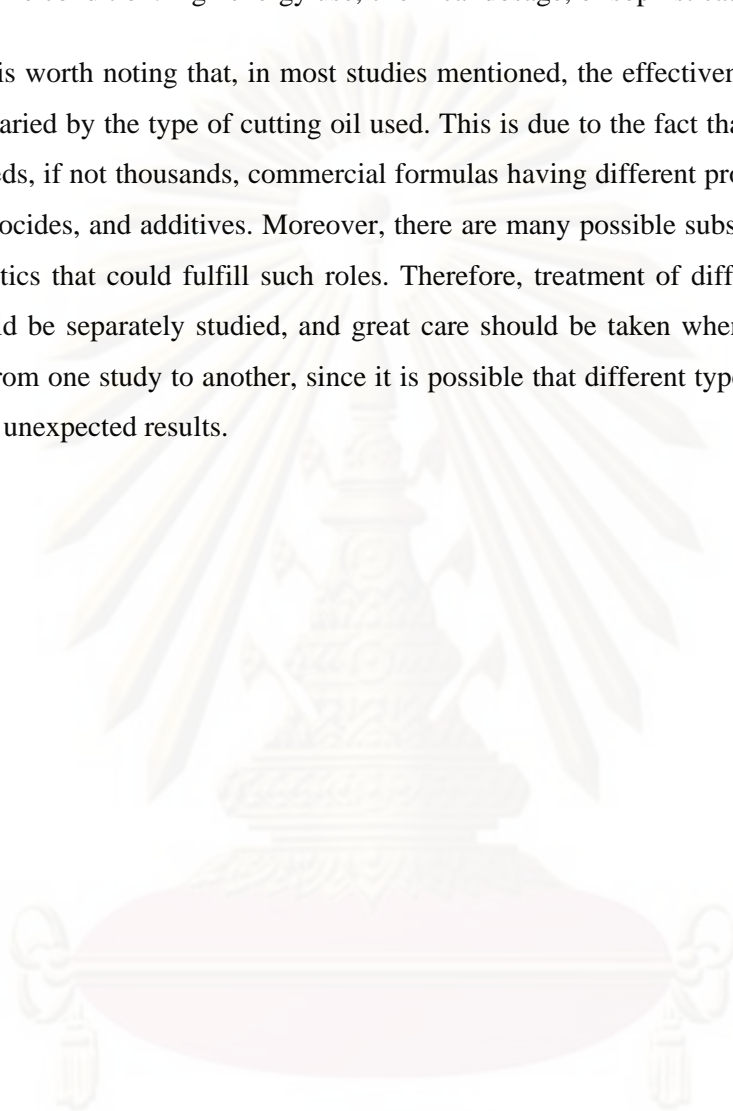
2.2 ADVANCE OXIDATION PROCESSES

Advance oxidation processes (AOPs) are the oxidation processes that based on generation and utilization of reactive free radicals, especially hydroxyl radicals ($\cdot$OH). However, some strong oxidants such as ozone, hydroperoxyl radical ($\cdot$OOH), and free oxygen ($\cdot$O) molecule could also take part in the oxidation. Such free molecules could be produced from conventional oxidants (hydrogen peroxide, oxygen, and ozone) under catalytic actions of UV irradiation, transition metals, electric current, and photocatalysis reagents. The oxidizing potentials of each chemical species are presented in *Table 2.3*. It could be noted from the table that hydroxyl radicals is the strongest oxidant known, second only to fluorine. Examples of combinations that were studied and practically used are shown in *Table 2.4*.

Table 2.3 *Oxidation potential of oxidizing species*

Species	F_2	$\cdot$OH	$\cdot$O	O_3	H_2O_2	$\cdot$OOH	HOCl	Cl_2
E_h (V)	3.06	2.80	2.42	2.07	1.77	1.70	1.49	1.39

Source: Metcalf & Eddy Inc. (2004)

Table 2.4 *Advance oxidation processes and their mechanism*

Process Name	Mechanisms	Sources
Ozone/UV	$O_3 + hv \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2\cdot OH$ $2\cdot OH \rightarrow H_2O_2$	Zhou and Smith (2002)
Ozone/Hydrogen peroxide	$H_2O_2 + 2O_3 \rightarrow 2\cdot OH + 3O_2$	Zhou and Smith (2002)
Hydrogen peroxide/UV	$H_2O_2 + hv \rightarrow 2\cdot OH$	Zhou and Smith (2002)
Fenton Chemistry	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$ $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^+$	Dai et al. (2008)
Photocatalysis	$Ti_2O_2 + hv \rightarrow h_{Ti}^+ + e_{Ti}^-$ $h_{Ti}^+ + H_2O \rightarrow \cdot OH_{Ti} + H^+$ $e_{Ti}^- + O_2 \rightarrow O_2^-{}_{(Ti)}$ $O_2^-{}_{(Ti)} + e_{Ti}^- \rightarrow O_2^{2-}$ $O_2^{2-} + H^+ \rightarrow HO_2$	Zhou and Smith (2002)
Electro-Fenton	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$ $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^+$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $O^2 + 2H^+ + 2e^- \rightarrow H_2O_2$	Jiang and Zhang (2007)

Once generated, hydroxyl radicals could attack organic molecules by four possible means: radical addition, hydrogen abstraction, electron transfer, and radical combination (Metcalf & Eddy Inc., 2004). Note that R is used to represent the organic molecule in this part. After organic compounds are decomposed into simpler entities, it would eventually produce carbon dioxide, water, and additives in elemental form as the end products.

- *Radical addition*: The radical could attacks unsaturated aliphatic or aromatic compounds to produce another compound of less stability that could be further oxidized by oxygen or other species:

$$R + \cdot OH \rightarrow ROH$$

- *Hydrogen abstraction*: The radical could remove a hydrogen atom from organic compound and result in radicalize compound which could initiate a reaction chain including self-propagation of radicals including the production of a peroxyl radical which could react with other organic compounds

$$RH + \cdot OH \rightarrow R \cdot + H_2O$$
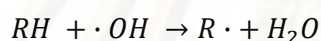
- *Electron transfer*: Hydroxyl radical could take an electron away from the compound or ions to produce either ions of higher valence or free radicals, depends on the valence of original ions.

$$R^n + \cdot OH \rightarrow R^{n-1} + OH^-$$
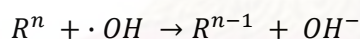
- *Radical combination*: If not consumed by the organic, radicals could be combined together into more stable products.

$$\cdot OH + \cdot OH \rightarrow H_2O_2$$

Moreover, in some certain condition with the presence of some substances, additional pathways could occur; for example, radical-producing chain reactions could occur by the presence of oxygen at supercritical condition (Portela et al., 2001):

$$RH + O_2 \rightarrow R \cdot + \cdot OOH$$

$$R \cdot + O_2 \rightarrow ROO \cdot$$

$$ROO \cdot + RH \rightarrow ROOH + R \cdot$$
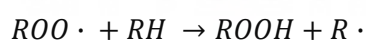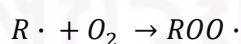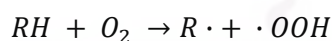
2.3 ACOUSTIC OXIDATION

2.3.1 Acoustic cavitation and sonochemistry

When a body of liquid is irradiated with ultrasonic pressure wave, it could be sheared apart by cycles of rarefaction-compression pressure cycles, producing millions of microscopic *acoustic cavitation* bubbles. Depends on the condition, the bubbles may either maintain their form or collapse within a few milliseconds. During expansion, potential energy is accumulated and then converted into kinetic energy during the collapse. Such rapid conversion of energy results in energy loss as extreme temperature and pressure, which could be as high as 5000 - 8000 K and 1 - 5 MPa (Young, 1999). The condition leads to a number of phenomena such as solid corrosion (pitting), noise emission, mechanical energy losses, luminescence, and unique series of chemical reactions which were called *sonochemical reaction*.

The sonochemical reactions are consists of (1) acceleration of conventional reactions, (2) redox reactions, (3) degradation of macromolecules, and (4) decomposition of organic substances. The first two reactions have been widely applied in preparative chemistry while the other two reactions are previously studied as an alternative treatment method for wastewater containing organic substances; the method is widely known as *acoustic oxidation*, *sono-oxidation*, or *sonochemical oxidation* (Young, 1999).

2.3.2 General Mechanisms

It is proposed that there two possible pathways for acoustic oxidation. First, thermolytic decomposition of water molecules that exist as vapor within the heated bubbles:

$$H_2O_{(g)} +))) \rightarrow \cdot OH + \cdot H$$
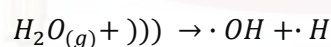
Note that ")))" symbol represents ultrasonic irradiation. ·OH is the second strongest oxidant. Apart from the decomposition that is earlier noted, other reactions that produce hydrogen peroxide (H_2O_2) and hydrogen gas (H_2) could occur:

$$\cdot OH + \cdot H \rightarrow H_2O$$

$$2 \cdot OH \rightarrow H_2O + \cdot H$$

$$2 \cdot OH \rightarrow H_2O_2$$

$$2 \cdot H \rightarrow H_2$$
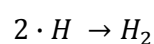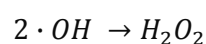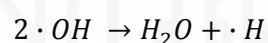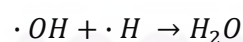
When dissolved oxygen is present, oxygen radical (O°), ozone molecule (O_3), and hydroperoxyl radical ($^\circ OOH$) can be also produced by sonication, but they have far lower redox potentials than hydroxyl radical.

$$O_2 + \cdot H \rightarrow \cdot OOH$$

$$O_2 +))) \rightarrow 2 \cdot O$$

$$\cdot O + \cdot OOH \rightarrow \cdot OH + O_2$$

$$O_2 + \cdot O \rightarrow O_3$$

$$H_2O + \cdot O \rightarrow 2 \cdot OH$$

$$\cdot OOH + \cdot OOH \rightarrow H_2O_2 + O_2$$
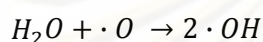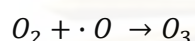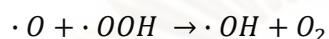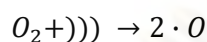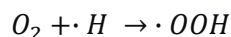
Ozone created could further produce additional radicals via special pathways, including self-decomposition.

$$O_3 + H_2O \rightarrow 2 \cdot OOH$$

$$O_3 + \cdot OOH \rightarrow \cdot OH + 2O_2$$

$$O_3 + H_2O \rightarrow O_3 + \cdot O$$
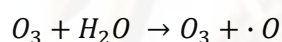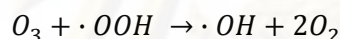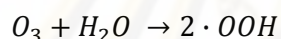
Radicals produced can react with organic substances, change them into radical form, thus enabling them to be easily further oxidized and, finally, mineralized.

Apart from the production of reactive radicals, thermal destruction of volatile organic substances within the heated bubbles could also occur (Jiang, Petrier, and Waite, 2002). The decomposition is generally believed to follow be able to decompose complex molecules into basic hydrocarbon such as C_2H_2, C_2H_4, C_3H_8, or even C_5H_{12} (Lan et al., 2002).

2.3.3 Operating Factors

In studies concerning acoustic oxidation, effects of operating factors such as pH, ultrasonic intensity, ultrasonic frequency, temperature, and other factors, were determined. The effects were found to affect the efficiency and rate of oxidation process to certain different degrees. Greater understanding of such effects was required in order to effectively control these factors for the desired process efficiency and rate.

The result is often reported in the form of pseudo-first order kinetic constant, cavitation yield (amount of substrate destroyed per unit of energy supplied), or removal efficiency. The factors, along with a brief explanation of its effect, are listed in *Table 2.5*.

Table 2.5 *Important factors governing acoustic oxidation*

Factors	Description	Sources
Sonicator types	To date, there are two types of sonicator available: horn type and standing-wave type. The former could produce higher amount of reactive radical and give better rate. The latter provide better uniformity in large liquid volume, giving better oxidation yield.	Jyoti (2003) Yasui (2005)
Ultrasonic frequency	For hydrophilic compounds, higher ultrasonic frequency gives better oxidation rate than the lower ones. No significant different is observed if the compounds are hydrophobic.	Berlan (1994) Petrier (1994) Kidak (2006)
Ultrasonic intensity	Increasing ultrasonic intensity could accelerate the degradation rate and improve the removal efficiency	Jiang (2002) Guo (2005) Naddeo (2007)
Temperature	Temperature of the liquid is not directly related to the reaction rate, but it affects vapor pressure of the liquid which is one of the most important factors governing cavitation process.	Yasui (2005)
Initial concentration	Due to competition from oxidation intermediates, increasing initial concentration greatly lowers the decomposition rate.	Jiang (2002) Maleki (2005) Tang (2006)

Factors	Description	Sources
Ions	Some metal cations (calcium, magnesium, aluminum) could bind acidic substrate, making oxidation ineffective. However, addition of ferrous and manganese ions shows catalytic effect due to their ability to transfer electron.	Kim (2006)
Suspended solid	In some cases, the substrates are sorbed on the particle surface, slowing down the degradation. In other cases, particle could acts as "cavitation seed" by being the bubble creations spot.	Young (1999) Naffrechoux (2000) Kim (2006)
pH	Form of any substrate is highly governed by pH and its pK_a value. It is suggested that the substances in molecular form are easier to be degraded via pyrolytic pathway. The ionic form of substance usually resides within the liquid bulk, making it easier to be degraded via radical pathway.	Maleki (2005) Jiang (2007) Naddeo (2007)

2.3.4 Enhancements

Acoustic oxidation is known to be able to combine with other advance oxidation techniques using other types of oxidant, which are hydrogen peroxide, ozone, ferrous sulfate, and UV irradiation. Moreover, combining acoustic oxidation with uncommon oxidants (oxygen bubbling, copper oxide, barium dioxide) also shows enhancement effects as well. Examples of such combination techniques are given in *Table 2.6*.

Table 2.6 *Examples of oxidant found to enhance the acoustic oxidation rate*

Oxidants	Substrate	Sources
Hydrogen peroxide	Humic substances	Kim (2006)
		Chemat (2001)
	2,4-dinitrophenol	Guo (2005)
	Cyanide	Ioan (2003)
	Microorganisms	Jyoti (2003)
Fenton's reagents	2,4-dinitrophenol	Guo (2005)
	bisphenol A	Ioan (2007)
Copper oxide	2,4-dinitrophenol	Guo (2005)
UV irradiation	Phenol	Naffrechoux (2000)
Ozone	Dimethoate	Liu (2008)
	Microorganisms	Jyoti (2003)
Oxygen bubbling	Cyanide	Ioan (2003)

2.4 REACTION KINETICS

It is generally known that, in addition to reaction stoichiometry, reaction kinetic is another major aspect of chemical reaction, since the former describe *what and how much* chemical species the reaction involves and the latter defines *how fast* the reaction progresses. Basically, every reaction will be eventually complete when adequate time is provided, but it is neither feasible nor time-effective in general practices. Instead, the designed process should be optimized for efficiency, cost, and time, and reaction kinetic could be employed as an optimizing tool in order to effectively design full-scale chemical processes.

2.4.1 Kinetic of homogeneous reactions

The rate of any chemical reaction or the rate of disappearance of substrate, A, could be generally expressed as

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

It could also be expressed on mass basis as:

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

or on concentration basis as:

$$-r_A = \frac{1}{V}\frac{dM_A}{dt} = \frac{dC_A}{dt} = \frac{(concentration\ of\ A\ reducing)}{(time)}, \left[\frac{kg}{m^3 \cdot s}\right]$$

The theory of reaction kinetic describes the rate as the product of two terms, the temperature-dependent and concentration-dependent ones:

$$-r_A = \frac{1}{V}\frac{dM_A}{dt} = \frac{dC_A}{dt} = \begin{bmatrix} temperature \\ dependent\ terms \end{bmatrix} \cdot \begin{bmatrix} concentration \\ dependent\ terms \end{bmatrix}$$

For example,

$$-r_A = \frac{dC_A}{dt} = k_0 e^{-E/RT} \cdot C_A^a$$

The first term exhibit temperature dependency defined by Arrhenius' Law, which will be described in the following part, while the latter term depends mainly on reaction order and mechanism.

2.4.2 Rate of elementary reactions

Any reaction could be classified into two main categories: elementary and nonelementary reaction. Elementary reactions are the ones the kinetic expression corresponds to the stoichiometric, and nonelementary reactions are the opposite.

For instance, considering a reaction:

$$aA + bB \rightarrow R$$

which has a familiar kinetic expression:

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

and another basic reaction:

$$H_2 + Br_2 \rightarrow 2HBr$$
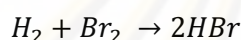
which has a known unique kinetic expression:

$$-r_{HBr} = \frac{d[HBr]}{dt} = \frac{k_1[H_2][Br_2]}{k_2 + [HBr]/[Br_2]}$$

It could be said that the first reaction provided are *elementary* since kinetic expression directly relates to stoichiometry of the given reaction, and the second reaction is *nonelementary* since it is not directly related due to a number of possible reasons, including the "hidden" mechanisms resided within this reaction.

$$Br_2 \leftrightarrow 2Br \cdot$$

$$Br \cdot + H_2 \leftrightarrow HBr + H \cdot$$

$$H \cdot + Br_2 \leftrightarrow HBr + Br \cdot$$
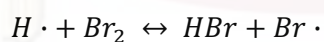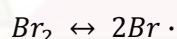
The asterisk sign indicates that they are the undetected short-living intermediates.

Considering a one-way elementary reaction involving only two substances, substrate and product:

$$A \rightarrow B$$

Its kinetic equation could be expressed as:

$$-r_A = \frac{d[A]}{dt} = -k[A]$$

Integrating this equation from $t = 0$ to $t = T$ will result in

$$\log \left(\frac{[A]_T}{[A]_0}\right) = -kT$$

or $\qquad [A]_T = [A]_0 e^{-kT}$

This form of kinetic is commonly called *first-ordered* kinetic which is indicated by the sum of power number.

Additionally, there are also reactions of different orders such as *second* and *third*, which results from elementary reactions involving more than one substances:

Second-ordered

$$2A \rightarrow R, \qquad -r_A = \frac{d[A]}{dt} = -k[A]^2$$

$$A + B \rightarrow R, \qquad -r_A = \frac{d[A]}{dt} = -k[A][B]$$

Third-ordered

$$2A + B \rightarrow R, \qquad -r_A = \frac{d[A]}{dt} = -k[A]^2[B]$$
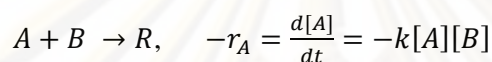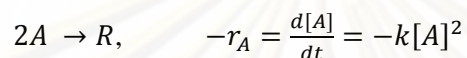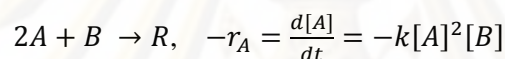
2.4.3 Pseudo first-ordered kinetic

In reactions related to the oxidation of organics where substrate is directly converted into product, kinetic equation could be generally written as:

$$Substrate \rightarrow Product$$
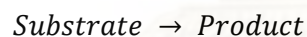
$$r_{Substrate} = {dC_{Substrate}}/{dt} = -k C_{Substrate} C_{Oxidant}$$

Where $C_{Substrate}$ is the concentration of organic substance, and $C_{Oxidant}$ is the concentration of the oxidants such as oxygen molecule or hydroxyl radical. In case of excess oxidant, or when the radicals are kept at constant amount, it could be assumed that concentration of oxidant is another constant, and the equation changes into:

$$r_{Substrate} = {dC_{Substrate}}/{dt} = -k^* C_{Substrate}$$

where

$$k' = k C_{Oxidant,constant}$$

Such relation could be expressed into a general form as:

$$C_t = C_0 e^{-k't}$$

where the *C* term represents substrate concentration.

These derivations and equations are known as *pseudo-first-order* kinetic which was widely applied and reported in studies, especially those on advance oxidation processes (Portela, Nebot, and Martinez de la Ossa, 2001; and others). This is due to the fact that such processes involve multiple substrates, intermediates, oxidants, inherent species, and oxidation end-products as well as many more possible interactions so that deriving the rate equation from actual mechanism is difficult, if not impossible.

Note that such kinetic could only describe the possible trends based on one-step mechanism described in this topic. To define the entire mechanism as a whole, a large and extensive effort should be made, and such efforts lead to more complicated forms of reaction kinetic.

2.4.4 Other types of kinetic

Apart from pseudo first-order kinetic discussed, there are also different type of kinetic used in some studies. Such kinetics were employed since simple first-ordered might not be able to adequately characterize the experiment data obtained, and equations of more complexity were then used.

In the work of Sanchez-Oneto et al. (2008), for example, use two-step pseudo first-ordered kinetic to characterize their obtained result which consists of initial rapid oxidation of substance followed by slower oxidation of produced intermediates. There are too kinetic of other order, as explained by Liu et al. (2008), that ozonation of dimethoate follows nth-ordered kinetic with *n* equals to 1.58.

There are too attempt to use a more detailed kinetic partly derived from actual mechanism. Portela, Nebot, and Martinez de la Ossa (2001) proposed a kinetic model of supercritical of cutting oil waste based on three groups of substances: Substrate, gaseous carbon monoxide as intermediate, and gaseous carbon dioxide as the product. There are too attempts to find the influence of oxidant on the kinetic such as those determined in the work of Sanchez-Oneto et al. (2007).

2.4.5 Temperature-dependent term

According to those described earlier, there are two main components of kinetic expression: temperature-dependent term and concentration-dependent term. According to the equation:

$$-r_A = \frac{1}{V}\left(\frac{dM_A}{dt}\right) = \frac{dC_A}{dt}$$

$$-r_A = \begin{bmatrix} temperature \\ dependent\ terms \end{bmatrix} \cdot \begin{bmatrix} concentration \\ dependent\ terms \end{bmatrix}$$

For example, first-ordered kinetic of simple reaction:

$$-r_A = \frac{dC_A}{dt} = kC_A$$

Term C_A represents the concentration term, while another term, k, is in fact temperature-dependent, as shown in the following equation:

$$k = k_0 e^{-E/RT}$$

where k_0 is called pre-exponential factor and equal to theoretical kinetic constant at 0 kelvin, E is called the activation energy of the reaction, R is the universal gas constant, and T is the reaction temperature. The overall equation is then widely known as *Arrhenius' Law*.

According to the Law, kinetic constant (k) could be increased by increasing reaction temperature, and value of k at any temperature, given k at a specified temperature, could be calculated using:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where k_1 and k_2 are the kinetic constant at temperature T_1 and T_2, respectively.

The equations show the relation between the kinetic constant, k, and temperature, T, but the difference from reaction to reactions lies within the activation energy, E. According to kinetic theory, the activation energy is the minimum amount of energy required to allow the reaction to take place, and its value could be obtained via theoretical calculation, literatures, and experiments of which the details are described in the next part.

2.4.6 Determining reaction kinetic parameters

There are two main methods to determine kinetic parameter, k, of the given dataset obtained from batch-basis reaction: integral and differential method. Each method has its own advantages and disadvantages Integral method is easier to be employed but require that the kinetic form must first be proposed, while differential method is highly subjective but more applicable to determine unknown form of kinetic.

2.5.5.1 Integral method of kinetic determination

Prior to use this method, a kinetic form must be first proposed, and one form that is most common is first- or pseudo first-order kinetics:

$$-r_A = \frac{dC_A}{dt} = kC_A$$

Separating and integrating the expression will results in:

$$\int_{C_{A0}}^{C_A} \left(-\frac{dC_A}{C_A}\right) = k \int_0^t dt$$

or $\qquad -\ln \frac{C_A}{C_{A0}} = kt$

Therefore, if the expressions on the left side of this equation are plotted against time, a linear relation passing the origin with slope equals to k will be obtained.

There are also integral derivations on kinetic of different order, with different expression to be plotted against time. Note that term X_A represent the *conversion* which is the fraction of substance *'A'* that was consumed:

$$X_A = \frac{(C_{A0} - C_A)}{C_{A0}} = 1 - \left(\frac{C_A}{C_{A0}}\right)$$

2.5.5.2 Differential method of kinetic determination

This method is a more direct but subjective way to determine the kinetic constant. It is started by plotting the concentration against time and then creates a curvilinear line passing all of the data coordinate. After that, tangent lines are then drawn to contact each point and its slope measured. The slope, in fact, is equal to $\frac{dC_A}{dt}$ at C_A of the point of contact.

When all pair between $\frac{dC_A}{dt}$ and C_A are obtained, they will be plotted against each other in a separate chart, and observed relation between them is then derived and incorporate directly into the kinetic equation:

$$\frac{dC_A}{dt} = f(C_A)$$

It is also worth noting that this method is vulnerable to human error especially in the process of drawing tangent lines. If available, computer-based algorithm should be instead used to minimize such errors. To making sure, after the kinetic was obtained, it could be integrated to re-check the correctness of the obtained results.

2.5.5.3 Determining temperature dependency of kinetic constant

As described in 2.5.5, kinetic constant, k, highly depends on the temperature of the reaction as indicated by Arrhenius' Law, but what differs from one reaction to another is that activation energy, E, and pre-exponential factor, k_0, are not equal. These two parameters of the reaction should be determined to obtain effective reaction design, especially when reaction temperature is controlled.

In order to obtain k_0 and E, first, multiple experiments must be conducted at different temperature, then, kinetic constant should be determined by either integration or differential method. Resulting values of $\ln k$ could be then plotted against $1/T$ and a straight line that intercept at $\ln k_0$ with slope equals to E/R, as shown in the following derived equations:

$$k = k_0 e^{-E/RT}$$

$$\ln k = \ln k_0 e^{-E/RT}$$

$$\ln k = \ln k_0 + {}^E/_R \left({}^1/_T\right)$$

2.5 REACTOR DESIGN

This part discusses the fundamental of reactor design, which consists of two main ideal types of reactor representing two types of ideal flow. The first, plug flow, is based on the assumption that no longitudinal mixing occur, and the liquid moves as a block and retains its characteristic until it exit the reactor. On the other hand, complete mixed flow, assumes that the liquid is immediately dispersed throughout the liquid body as soon as it enters the reactor.

As a matter of fact, that the flow cannot be possibly ideal, and it rather exhibit combined characteristics behaves partly between two ideals depends on reactor design. Such non-ideal flow is caused by a number of phenomena: short-circuit, diffusion, dead zone, microcurrents, and density currents.

2.5.1 Steady-state plug-flow reactor (PFR)

In plug flow reactor, the composition of substance varies from point to point along the flow path. Considering the mass transfer within a small volume, dV, within the reactor.

$$input = output + disappearance\ by\ reaction + accumulation$$

As it is steady-state, accumulation term is zero, and *Figure 2.2* shows that for substrate *A*:

$$input = F_A$$

$$output = F_A + dF_A$$

$$disappearance = -r_A dV$$
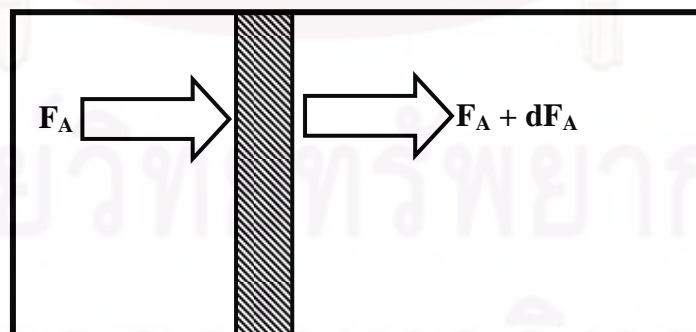
Figure 2.2 *Mass transfer diagram for plug flow derivation*

Substituting these three terms into mass balance equation gives:

$$F_A = F_A + dF_A - r_A dV$$

$$dF_A = r_A dV$$

As the substrate input is equal to the product between concentration and flow rate, assuming that density remains constant, the equation changes into:

$$Q dC_A = r_A dV$$

Exchanging terms and integration will results in:

$$\int_{C_{A0}}^{C_A} \left(1/r_A\right) dC_A = \left(1/Q\right) \int_0^V dV$$

$$\int_{C_{A0}}^{C_A} \left(1/r_A\right) dC_A = V/Q = \tau$$

The term r_A in the above reaction could be substituted with any of the kinetic expression, for example, first-ordered:

$$\int_{C_{A0}}^{C_A} \left(1/kC_A\right) dC_A = \tau$$

$$\ln\left(C_A/C_{A0}\right) = k\tau$$

Except the term of retention time, τ, this is identical to the expression for batch reactor, or it could be easier to imagine that the volume dV is just a travelling batch reactor whose the reaction is allowed to progresses for time equals to τ.

2.5.2 Steady-state mixed-flow reactor (CSTR or CMFR)

Characteristics of this reactor type could be derived using mass balance analysis shown in the following figure and equations. It should be conducted based on a few assumptions, the content within the reactor should be wholly uniform, and the concentration of stream exiting the reactor should be equal to the concentration of the uniform medium within the reactor. The process too must be in steady-state which no time variation is allowed.

$$input = output + disappearance\ by\ reaction + accumulation$$

As it is steady-state, accumulation term is zero, and *Figure 2.3* shows that:

$$input = F_{A0} = C_{A0} Q$$

$$output = F_A = C_{Af} Q$$

$$disappearance = -r_A V$$
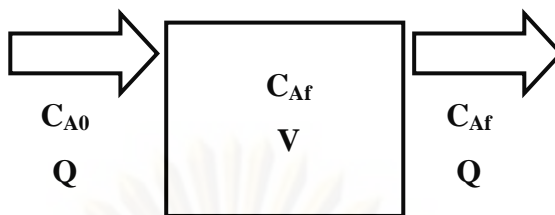
Figure 2.3 *Mass transfer diagram for mixed flow derivation*

Substituting these three terms into mass balance equation gives:

$$C_{A0}Q = C_{Af}Q - r_A V$$

Similar to steps used in plug-flow, the term r_A could be substituted by the kinetic expression, and first-order will be used as the example:

$$C_{A0}Q = C_{Af}Q - kC_{Af}V$$

Exchanging terms will result in:

$$kC_{Af}V = Q(C_{Af} - C_{A0})$$

$$kV/_Q = (C_{Af} - C_{A0})/_{C_{Af}}$$

$$k\tau = 1 - C_{A0}/_{C_{Af}}$$

Note that the equations derived in this part could be used only when the reaction is first-order. Kinetic of other order will produce different final equations.

CHAPTER III

METHODOLOGY

3.1 MATERIALS

3.1.1 Instruments

3.1.1.1 Ultrasonic mixing device

Ultrasonic bath 650LHT supplied by ACME-KORN Co. Ltd., Thailand

Bath size: 6.5 L

Frequency: 20 kHz

Power input: 400 W

Transducers: 4

Figure 3.1 Ultrasonic bath with supplied holder plate

3.1.1.2 pH/ORP meter

EXTECH pH/mV/Temperature meter 4072208 and pH probe

HANNA Standard hydrogen ORP probe

All equipments were supplied by Protonics Intertrade Co.,Ltd.

Figure 3.2 *Temperature/mV/pH meter*

3.1.1.3 Turbidimeter

Lovibond PCCheckit Turbidimeter

Measuring method: Infrared light-scattering method

Measurement range: 0.2 – 2000 NTU

3.1.1.4 Hot air oven

Temperature: 150 °C

3.1.1.5 Jar Test device

Supplied by Metrology Lab Co. Ltd., Thailand

Blades: Six rotating two-blade paddles

Blade width: 75 millimeter

Blade speed: 15 – 300 revolutions per minute

3.1.1.6 Magnetic stirrer

Whatman Bench top hotplate stirrer

Mixing speed: 0 – 1250 RPM

3.1.2 Chemicals

3.1.2.1 Cutting oil

3.1.2.2 Sodium hydroxide (NaOH), 0.1 N

3.1.2.3 Sulfuric acid (H_2SO_4), 0.1 N

3.1.2.4 Hydrogen peroxide, 18%

3.1.2.5 Ferrous sulfate ($FeSO_4$), 15 g/L

3.1.2.6 Aluminum sulfate ($Al_2(SO_4)_3$), 100 g/L

3.1.2.7 Potassium dichromate ($K_2Cr_2O_7$), 0.1 N

3.1.2.8 Ferrous ammonium sulfate (FAS), 0.05 N

3.1.2.9 Concentrated sulfuric acid with silver sulfate catalyst

3.1.2.10 Ferro indicator

3.1.3 Glassware

3.1.3.1 Beaker, 1 liter, 2 EA

3.1.3.2 Beaker, 500 milliliter, 2 EA

3.1.3.3 Beaker, 250 milliliter, 2 EA

3.1.3.4 Beaker, 100 milliliter, 2 EA

3.1.3.5 Pipette, scaled, 25 milliliter, 2 EA

3.1.3.6 Pipette, scaled, 10 milliliter, 2 EA

3.1.3.7 Pipette, scaled, 5 milliliter, 1 EA

3.1.3.8 Pipette, scaled, 1 milliliter, 1 EA

3.1.3.9 Pipette, volumetric, 100 milliliter, 1 EA

3.1.3.10 Pipette, volumetric, 50 milliliter, 1 EA

3.1.3.11 Pipette, volumetric, 25 milliliter, 1 EA

3.1.3.12 Air-displacement auto pipette, 10 milliliter, 1 EA

3.1.3.13 Air-displacement auto pipette, 1 milliliter, 1 EA

3.1.3.14 Burette, scaled, 50 milliliter, 2 EA

3.1.3.15 Volumetric flask, 100 milliliter, 2 EA

3.2 ANALYSIS AND CALCULATION

3.2.1 Chemical Oxygen Demand (COD)

Values of COD in this study were primarily measured by closed reflux titration method (APHA-AWWA, 1998) with the exception in experiments that involve the use of hydrogen peroxide (H_2O_2), which is known to be a major interference of the analysis. The analysis techniques employed in this study to suppress the interference were studied and discussed in Appendix A.

3.2.2 Turbidity

Turbidity, which is another quantifiable parameter of water quality, was measured using a turbidimeter (see 3.1.1.3). Calibration was conducted at every meter start-up using the steps specified by the manufacturer. Measurements were done immediately after sample collection in order to minimize the interference of gas (O_2) bubbles which were produced from the decomposition of hydrogen peroxide.

3.2.3 pH

Values of pH were measured using pH/ORP meter equipped with standard pH probe and metal rod thermometer. The equipment was daily calibrated.

3.2.4 Oxidation-Reduction Potential (ORP)

ORP was measured using pH/ORP meter equipped with standard hydrogen ORP probe. Since one electrode is submerged in hydrogen, no calibration is required.

3.2.5 Temperature

Temperature was measured using built-in thermometer of the ultrasonic bath, but metal rod electronic thermometer may also be used to ensure accuracy.

3.2.6 Removal efficiency of COD (*%COD_{Removed}*)

In this study, COD will mostly be expressed as percentage for the sake of simplicity or when the results of multiple sample concentrations were plotted within the same chart. Therefore, removal efficiency of COD will be defined as:

$$\%COD_{Removed} = 100\% \times \left(1 - {COD_t}/{COD_0}\right)$$

Where $\qquad COD_t = COD \; value \; at \; time \; t, mg/L$

$\qquad\qquad COD_0 = Initial \; value \; of \; COD, mg/L$

In this study, when no specific time is indicated, %COD_Removed will represent final value of
COD where further reduction will not occurs.

3.2.7 Ultrasonic intensity (I)

Ultrasonic intensity is one of the major controlling parameters of ultrasonic
irradiation. It is actually based on the energy expression of pressure wave, as defined by the
following equation (Halliday, Resnick, and Walker, 2005):

$$I = P/A$$

or $\qquad I = \frac{1}{2}\rho v \omega^2 s_m^2$

Where $\qquad \rho = density \; of \; the \; medium, kg/m^3$

$\qquad\qquad v = Sound \; travelling \; speed, m/s$

$\qquad\qquad \omega = Angular \; frequency, radian/s$

$\qquad\qquad s_m = Amplitude \; of \; sound \; wave, m$

Using this equation, intensity of ultrasonic wave could be determined using oscilloscope
coupled with a hydrophone (Hurrell, 2000). However, due to limited equipment availability,
calorimetric measurement will be used in this study.

Calorimetric method of measuring ultrasonic intensity is based on the assumption that
sound energy was completely converted into heat, which in turn raises the temperature of the
medium. The change of temperature could then be tracked and power input could be
calculated:

$$P = {mC_p\Delta T}/{t}$$

Where $\qquad P = Power \; imparted \; into \; the \; liquid \; bulk, watt$

$\qquad\qquad C_p = Specific \; heat \; of \; the \; medium, 4.134 \; kJ/kg \cdot K \; for \; water$

$\qquad\qquad m = Total \; mass \; of \; irradiated \; medium$

$\qquad\qquad \Delta T = Temperature \; changes \; during \; time \; duration, K$

$\qquad\qquad t = Time \; duration, s$

Note that this method produce the energy as power imparted per *unit volume* rather than *unit area*.

3.2.8 Velocity gradient (G)

Velocity gradient, which is a parameter quantifying the intensity of mixing apparatus, could be defined as (Kawamura, 2000):

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

Where

$G = $ Velocity gradient, s^{-1} or $\frac{m/s}{m}$

$P = $ Mixing power imparted to the liquid, W or J/s

$V = $ Mixing volume, m^3

$\mu = $ Kinematic viscosity, cps

3.3 EXPERIMENT SET-UP

3.3.1 Acoustic oxidation

The experimental set-up used in this study can be illustrated in *Figure 3.3*. Four batch reactors, which are 150-ml beakers (1), will be suspended from a holder plate (2) into the bath of an ultrasonic cleaner (3) containing degassed tap water. Each beakers will be immersed to the water depth of 2.5 cm. Prior to ultrasonic irradiation, the medium will be heated and controlled to the desired temperature to ensure that kinetic rate of reaction, k, is not significantly affected by increasing temperature. One beaker, however, will be reserved for measuring the Oxidation Reduction Potential (ORP) as the control system, and a measuring probe will be inserted into it.

Oxidants and reagents to be added into the sample were firstly prepared in a separated vessel, conditions of the sample and reagents were adjusted; the contents of oxidant were then emptied into the reactor, and ultrasonic irradiation was immediately turned on.

Sampling was done by removing a beaker from the bath after specified irradiation time. Entire content in a beaker was collected as a sample to avoid the effect of reaction volume reduction caused by sampling.
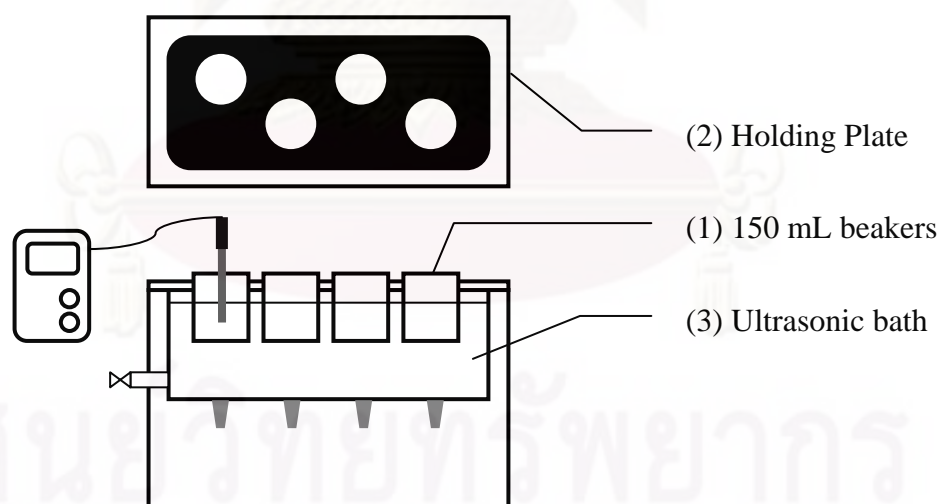
Figure 3.3 Acoustic oxidation set-up

3.3.2 Jar test

Uses of coagulation process to represent physicochemical separation were conducted in a jar test device where a liter of sample was added into each of 1-L beakers, which acts as mixing vessels. The coagulation tests were then conducted using alum ($Al_2SO_4 \cdot 14H_2O$) as coagulant. Subsequent flocculation and sedimentation processes were carried out within the same vessels. pH adjustment was done prior to coagulant addition by 1 N H_2SO_4 and 1 N NaOH.

After the process was completed, samples were then drawn from the bottom of the vessel to be analyzed, and clear portion of the water was then collected to be used in studies on acoustic oxidation as post-treatment process.
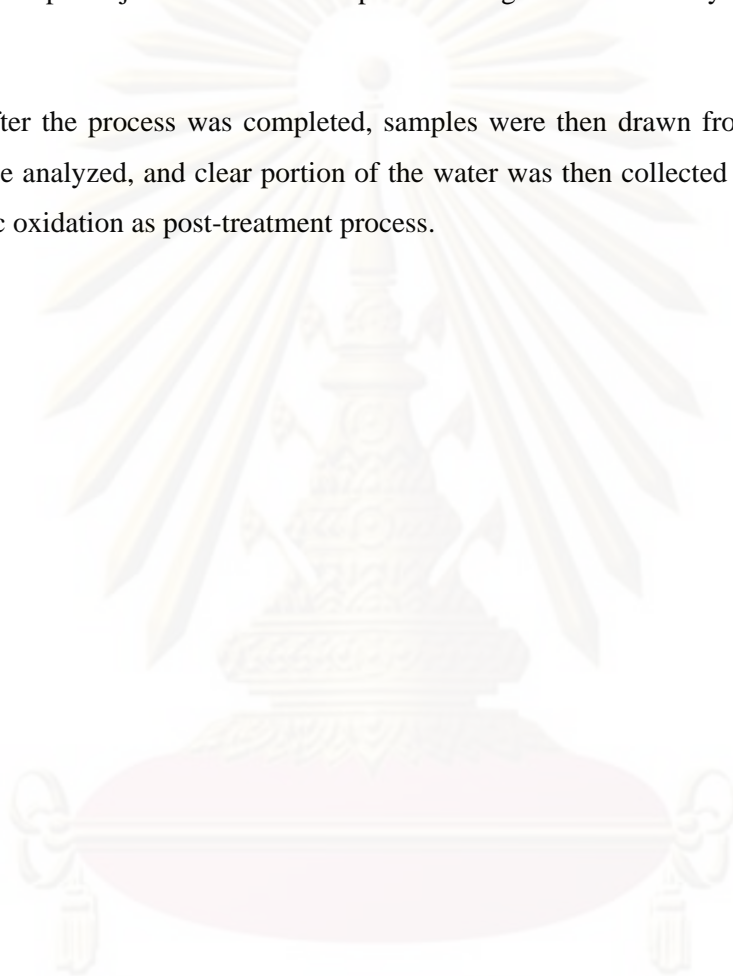
3.4 EXPERIMENT PLANS
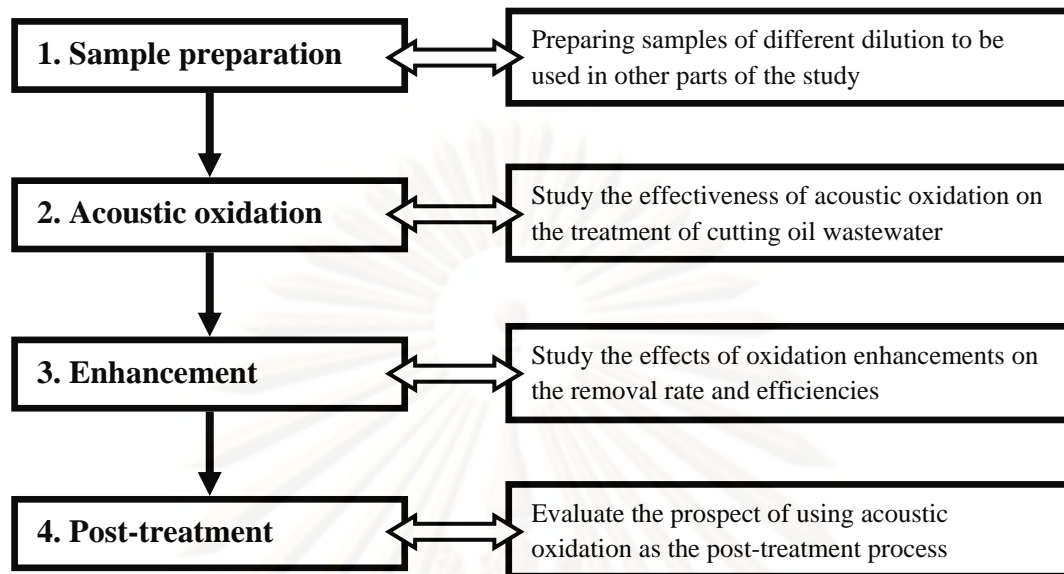
Figure 3.4 Overview of experiments in this study

        In this research, wastewater samples of different dilutions which will be used in oxidation study were synthesized and analyzed for their important parameters which are ultrasonic intensity, oil concentration, and temperature. Then, effectiveness of advance oxidation process and influence of operating factors were determined. After that, effect of oxidation enhancements, which are hydrogen peroxide, air bubbling, and Fenton's reagents were investigated and quantified. Finally, uses of acoustic oxidation and other AOPs as the post-treatment process to eliminate remaining organic substances after using physicochemical separation processes are then studied.

3.4.1 Sample preparation

        Samples of cutting oil wastewater at different dilution ratios were prepared to be used in experiments finding the effects of operating parameters, presence of solid and oxidants. Dilution values used ranges from 0.1% to 1% v/v, which are the typical dilution ratio used in industries (El Baradie, 1996b).

Methods

1. Fill 1, 5, or 10 ml of concentrated cutting oil into 1-litre volumetric flask, and dilute it with tap water to the volume of one litre, giving the representative dilution of 0.1%, 0.5%, and 1.0% v/v.
2. Shake the flask for five minute to ensure uniform mixing.
3. Analyze the sample for COD and pH.

3.4.2 Acoustic oxidation

3.4.2.1 Effect of initial concentration, temperature, and ultrasonic intensity

Methods

1. Prepare the samples of different dilutions
2. Fill 100 ml of sample into a 100-ml beaker.
3. Using the built-in heater, heat the sample to 40, 50 and 60 ˚C.
4. Irradiate the sample using 100, 150, 200, 300, and 400 W power input
5. Samplings were conducted at 1, 5, 10, 15, 30, and 60 minutes of irradiation time, and taken samples were analyzed for COD and turbidity

3.4.2.2 Effect of hydrogen peroxide

Hydrogen peroxide, a widely known oxidant, was added to determine the synergistic effects between acoustic oxidation and other oxidation techniques

Methods

1. Experiment was conducted using 100 ml sample of 0.1% dilution ratio and 400 W of ultrasonic power input.
2. 0.1, 1, 5, and 10 g of hydrogen peroxide (mass basis) was added into the sample prior to irradiation.
3. Oxidation potentials were continuously measured through the oxidation process
4. Samplings were conducted at 1, 5, 10, 15, 30 and 60 minutes of irradiation time, and taken samples were analyzed for COD

3.4.2.3 Effect of air bubbling

Oxygen, which could be simply supplied by air bubbling, was added into the medium to be used as an inexpensive oxidation enhancement. Note that the working volume in this part was 500 mL in order to allow adequate space for aeration equipments.

Methods

1. Experiment was conducted using 500 ml sample of 0.1% dilution ratio and 400 W of ultrasonic power input.
2. 0.3, 0.7, and 1.0 L/min air were continuously bubbled into the sample
3. Samplings were conducted at 1, 5, 10, 15, 30 and 60 minutes of irradiation time, and taken samples were analyzed for COD and turbidity

3.4.3 Sono-Fenton oxidation

FeSO$_4$, known as Fenton's reagent, were added in this step of experiment to increase the oxidizing power of the process.

3.4.3.1 Finding appropriate pH

Fenton and sono-Fenton is widely known to highly dependent on operating pH, so the most appropriate pH would be determined in this part of the study.

<u>Methods</u>
1. Experiment was conducted using 100 ml sample of 0.1% dilution ratio and 400 W of ultrasonic power input.
2. pH was adjusted to 1, 2, 3, 4, and 5 prior to chemical addition
3. 3 g/L of FeSO$_4$ and 140 g/L H$_2$O$_2$ were added into the sample
4. Samplings were conducted at 60 minutes of irradiation time, and taken samples were analyzed for COD and turbidity

3.4.3.2 Finding appropriate Fe^{2+}/H$_2$O$_2$ ratio

Fe^{2+}/H$_2$O$_2$ ratio is a widely accepted operating parameter of sono-Fenton process, as it indicates and alters the mechanism and equilibrium of Fenton oxidation.

<u>Methods</u>
1. Experiment was conducted using 100 ml sample of 0.1% dilution ratio and 400 W of ultrasonic power input.
2. pH was adjusted to appropriate value previously found
3. 10% of hydrogen peroxide were added into the sample
4. 100, 250, 500, 750, and 1000 mg/L of Fe^{2+} were added into the sample
5. Samplings were conducted at 60 minutes of irradiation time, and taken samples were analyzed for COD and turbidity

3.4.3.3 Effects of H$_2$O$_2$ concentration

Not only 1-hour efficiencies, but also kinetic parameters of sono-Fenton process were determined in this part.

<u>Methods</u>
1. Experiment was conducted using 100 ml sample of 0.1% dilution ratio and 400 W of ultrasonic power input.

2. pH was adjusted to appropriate value previously found
3. 1%, 2.5%, 5%, 7.5%, 10%, and 12.5% of hydrogen peroxide were added into the sample
4. Amount of Fe^{2+} added were adjusted to give appropriate ratio previously obtained
5. Samplings were conducted at 1, 2, 5, 10, 15, 30, 45, and 60 minutes of irradiation time, and taken samples were analyzed for COD and turbidity

3.4.4 Coagulation

Objective of this step is (1) to determine the effectiveness of coagulation to compare with AOPs and (2) to produce separated effluent to be further treated in post-treatment advance oxidation processed.

3.4.4.1 Determining appropriate pH

Methods

1. Experiment was conducted using 1 L sample of 0.1% dilution ratio
2. pH was adjusted to 4, 6, 7, 8, and 10
3. 50, 100, and 150 mg/L of alum added
4. Rapid mixing at 100 RPM for 1 minute
5. Slow mixing at 30 RPM for 30 minutes
6. Decanting for 30 minutes
7. Taken samples were analyzed for COD and turbidity

3.4.4.2 Determining appropriate coagulant dosage

Methods

1. Experiment was conducted using 1 L sample of 0.1, 0.5 and 1% dilution ratio
2. pH was adjusted to the value that give the best removal in previous part
3. Different amount of alum added
4. Rapid mixing at 100 RPM for 1 minute
5. Slow mixing at 30 RPM for 30 minutes
6. Decanting for 30 minutes
7. Taken samples were analyzed for COD and turbidity

3.4.4.3 Effects of mixing conditions

Methods

1. Experiment was conducted using 1 L sample of 0.1, 0.5 and 1% dilution ratio
2. pH was adjusted to the value that give the best removal in previous part
3. Optimal amount of alum added into the sample
4. Rapid mixing at 120 - 300 RPM for 0 - 1 minute
5. Slow mixing at 15 - 30 RPM for 5 - 30 minutes
6. Decanting for 30 minutes
7. Taken samples were analyzed for COD and turbidity

3.4.5 Combined process

In this part, use of AOPs to treat separated wastewater was investigated, effluent from coagulation process are used as the influent of these processes, and the selected AOPs to be used are acoustic oxidation with hydrogen peroxide, Fenton oxidation, and sono-Fenton oxidation.

3.4.5.1 Acoustic oxidation with hydrogen peroxide

Methods

1. Effluent from separation process of 0.1, 0.5, and 1.0% were first collected to be used as samples in this part
2. Experiment was conducted using 100 ml sample
3. 1.4, 7.0, and 14.0 g/L of hydrogen peroxide were added to the sample of 0.1, 0.5, and 1.0%, respectively.
4. Ultrasonic was irradiated using 400 W power input
6. Samplings at 15 and 30 minutes
7. Taken samples were analyzed for COD

3.4.5.2 Fenton and sono-Fenton

Methods

1. Effluent from separation process of 0.1, 0.5, and 1.0% were first collected to be used as samples in this part
2. Experiment was conducted using 100 ml sample
3. 1.4, 7.0, and 14.0 g/L of hydrogen peroxide were added to the sample of 0.1, 0.5, and 1.0%, respectively.
4. Different amounts of $FeSO_4$ will be added to maintain Fe^{2+}/H_2O_2 ratio of 3.6:1000

5. Ultrasonic was irradiated using 400 W power input (sono-Fenton) OR sample are mixed with magnetic stirrer (Fenton)

6. Samplings at 15 and 30 minutes

7. Taken samples were analyzed for COD

3.5. STATISTICAL ANALYSIS

Microsoft Excel® with Solver® and Analysis ToolPak® function were used to determine statistical parameters as well as significance in this study. Note that to ensure consistency and reproductivity, the experiments were triplicate and each collected sample was divided into three parts to be separately analyzed.
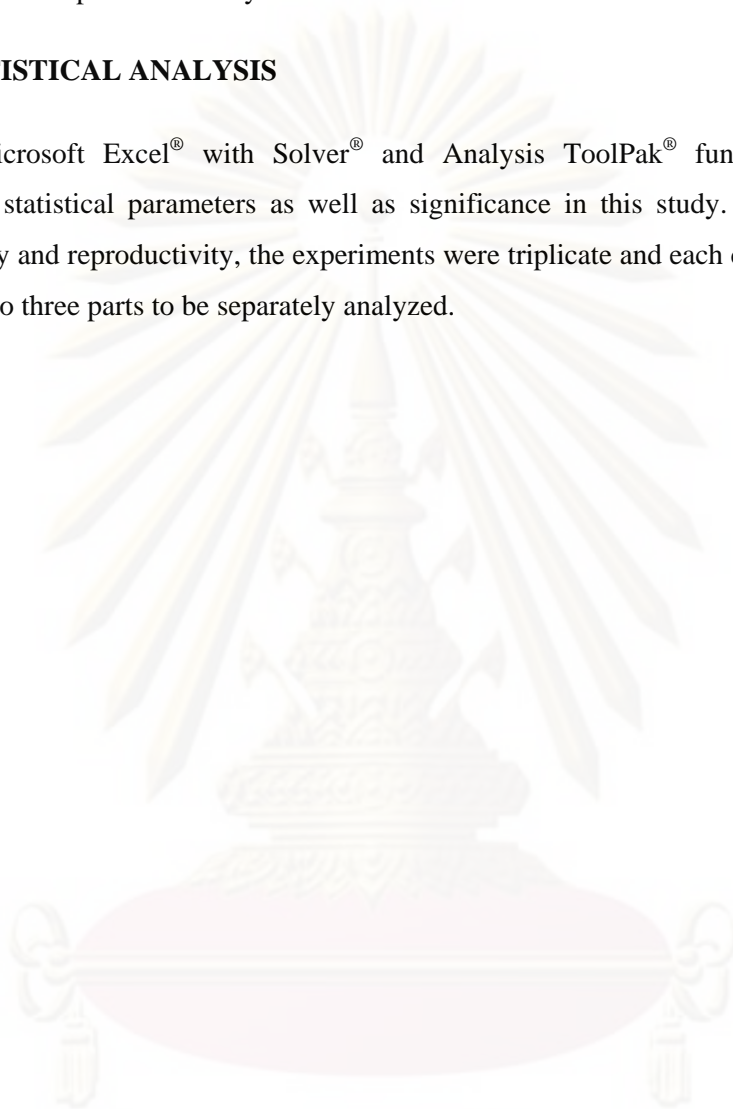
4.1. CHARACTERISTICS OF SYNTHESIZED WASTEWATER

Characteristics and main parameters of the synthesized cutting oily-wastewater were shown in *Table 4.1*. COD values of the each sample were analyzed to be 3.05, 15.53 and 31.0 g O_2/L, respectively. Therefore, the removal efficiencies could be calculated using these values as the baseline. COD values, as analyzed, are highly varied by the nature of the analysis techniques and the waste itself. Note that turbidity value above 2000 NTU cannot be measured due to upper detection limit of the instrument; above that, the sample were diluted to make the turbidity goes below 2,000 NTU, assuming that turbidity linearly rises with oil amount (Rios, Pazos, and Coca, 1998).

Table 4.1 *Parameters of the synthesized sample*

Parameters		Dilution ratio		
		0.1%	0.5%	1%
Droplet size	μm	~1	~1	~ 1
pH		7.4	7.8	7.6
Turbidity	NTU	1,356	7,420	12,200
Viscosity	cps	9.16	-	-
Surface tension	mN/m	47.02	-	-
Initial COD	mg O_2/L	$3,051 \pm 120$	$15,531 \pm 1,271$	$31,000 \pm 5,000$

However, in actual application, cutting oil emulsion might be prepared using higher dilution ratios where as high as 3 – 15% could be used (El Baradie, 1996a; Grzesik, 2008), and different formula compositions could alters these characteristics to some certain degree. These characteristics obtained from other studies were presented in Table 4.2.

It could be seen from the table that characteristic of the emulsion significantly differ from study to study, but it is generally accepted that the emulsions is slow to be naturally destabilized. As found in the experiment of Bataller et al. (2004), negligible shift in distribution range of oil droplets size was observed, even after the emulsion was left alone for 7 days, and mean diameter of the droplets did not anytime exceed 50 nm. Note that this does not apply to the cases of higher dilution (40 – 50%). Such small size is too small to follow the

motion dictated by Stoke's law, and Brownian movement instead dominates (Metcalf & Eddy Inc., 2004).

Table 4.2 Characteristics of cutting oil emulsion obtained from other studies

Sources	Dilution	COD	TOC	pH	Turbidity	Zeta potential
	%	mg/L	mg/L	-	NTU	mV
This study	0.1	3,051	-	7.4	1,356	-
	0.5	15,531	-	7.8	7,420	-
	1.0	31,000	-	7.6	12,200	-
Bensadok (2007)	2	-	-	9.05	19,140	-
	4	-	-	9.21	41,090	-
	6	152,624	-	9.31	52,000	-
	8	-	-	9.41	73,000	-
	10	-	-	9.44	75,000	-
Bensadok (2008)	2	60,282	-	8.63	26,400	-
	4	108,208	-	9.09	41,712	-
	6	116,128	-	9.69	64,125	-
Chang (2001)	*	102,400	28,200	-	-	-
Kobya (2008)	*	17,312	3,155	7.06	15,350	-
Perez (2007)	*	1,049	147.5	6.95	-	-
	*	4,001	211.5	8.30	-	-
Portela (2001)	*	1,770	447	-	-	-
	*	2,882	724	-	-	-
Rios (1998)	4	-	-	-	-	-55, -42

* : Actual wastewater   - : not stated in the literatures

Another thing to be noted from the table is the value of zeta potential, which is a parameter indicating the surface charge of suspended particle in continuous phase. Extreme potential, whether positive or negative, indicate that the suspension is highly stable (Cambiella et al, 2007). As found in the study of Rios, Pazos, and Coca (1998) on coagulation of cutting oil emulsion, initial zeta potential were measured to be -45 and -55 millivolts, which confirmed such stability. Note that zeta potential could be altered by many factors including pH, presence of ions, type of surfactant used in the emulsion. Using this fact,

general method to destabilize the stabilized emulsion are (1) pH adjustment or (2) addition of metal salts coagulants to alter the zeta potential to be as close to zero as possible to eliminate the repulsion force between the particles, or droplets (Kawamura, 2000).
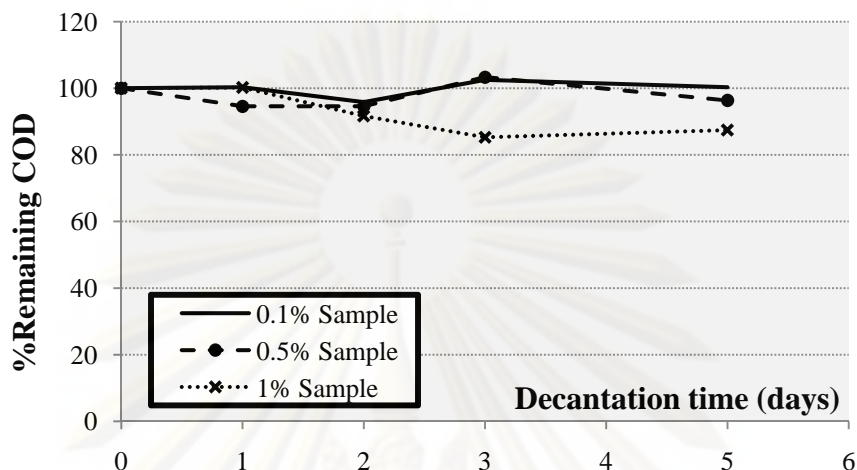
Figure 4.1 %Remaining COD obtained from decantation process

Decantation tests were conducted to confirm the stability of the emulsion used in this study, and the results were shown in *Figure 4.1*. It could be observed from the figure that negligible COD was removed by the process even after five days of decantation, but it is noticeable that COD was comparably reduced when the concentration is 1%, as confirmed by the thin creamy film of oil that could be observed only when this high concentration was used. This may be due to greater probability of droplets collision brought about by greater amount of oil used. This is also confirmed by the finding of Bataller et al. (2004). Additionally, it is practically recommended by cutting oil suppliers that adequate and continuous mixing should be provided to prevent the coalescence of droplets, regardless of oil concentration (El Baradie, 1996b).

4.2. ACOUSTIC OXIDATION

4.2.1. Acoustic oxidation treatment of cutting oil wastewater

Experiments were conducted according to achieve the proposed objectives: to study the effectiveness of acoustic oxidation on the treatment of cutting oil wastewater. Evolution of COD over time during ultrasonic irradiation was reported in *Figure 4.2* using different dilutions. However, no significant reduction of COD could be observed even after the sample was irradiated for five hours, which results in low removal percentages with the maximum value of 8.3%. Moreover, statistical analysis gives that it is highly likely ($p < 0.05$) that the obtained variations were merely caused by random nature of analysis.
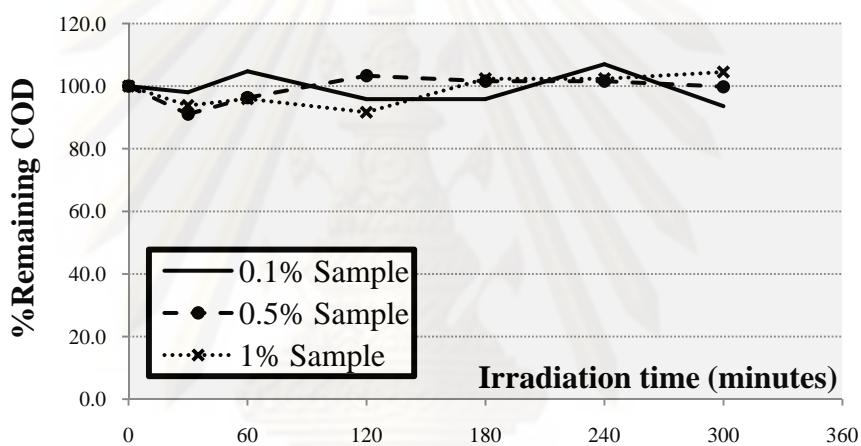
Figure 4.2 *%Remaining COD of the samples at different ultrasonic irradiation time*
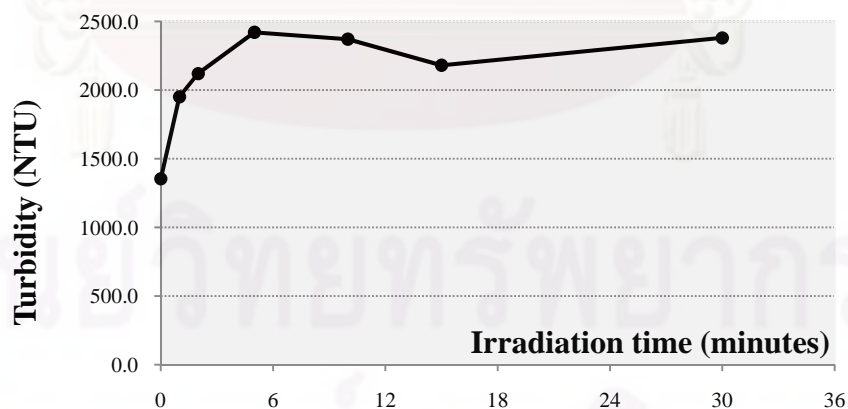
Figure 4.3 *Turbidity of 0.1% samples during ultrasonic irradiation*
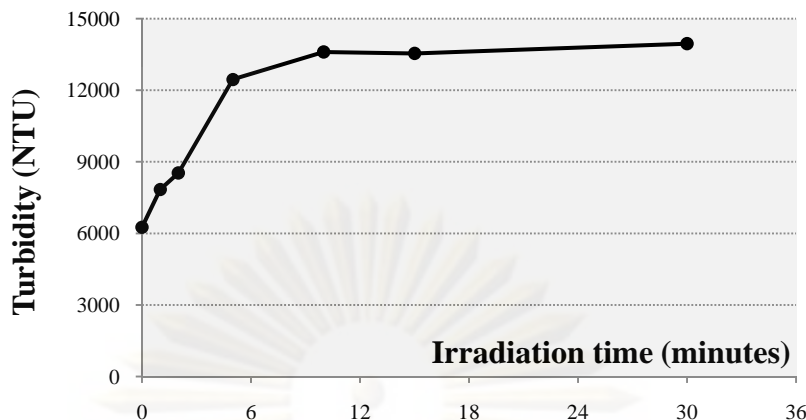
Figure 4.4 *Turbidity of 0.5% samples during ultrasonic irradiation*
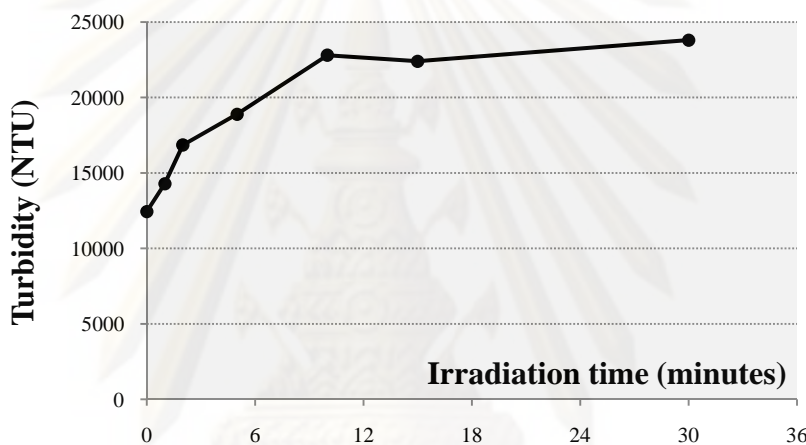
Figure 4.5 *Turbidity of 1.0% samples during ultrasonic irradiation*

Changes of turbidity during the process were too tracked and shown in *Figure 4.3*, *Figure 4.4*, and *Figure 4.5*. It is shown by the figure that the value sharply rises within a few seconds of irradiation and remains stable throughout the studied duration. Such raised could be due to extreme agitation and energy release during the violent collapse of acoustic cavitation bubbles, which could broken the liquid droplets down into a greater number of smaller droplets, which could increase the turbidity (Canselier et al., 2002). It is also worth noting that turbidity rise of sample with higher dilution takes more time to reach the "plateau" than samples with lower dilution, which could possibly due to the fact that there are greater amount of droplets to be broken down.

Apart from those shown, similar low-efficiency results were also obtained when different configuration of ultrasonic intensity and temperature were used. The condition that is theoretically expected to yield the greatest oxidation rate (400 W maximum power input, 60 °C, and 0.1% sample) also gives the same result that COD of the sample was not significantly affected by the ultrasonic irradiation, and heat-induced evaporation tends to be the dominating mechanism of COD removal in such condition, as shown in *Figure 4.6*. As shown, it could be implied that acoustic oxidation alone is not adequate to reduce COD of the sample using the apparatus and condition proposed in this study, and effects of oxidant addition, which is known to greatly enhance the oxidation process, will be studied in the following parts.
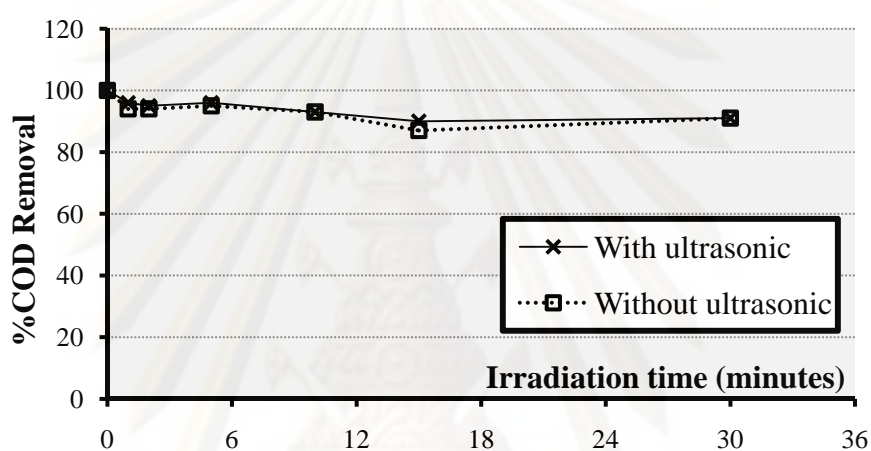
Figure 4.6 *%Remaining COD at different ultrasonic irradiation time using "the best" condition*

4.2.2. Effects of hydrogen peroxide and air bubbling

Due to the finding in the previous part that using only acoustic oxidation was found to be inadequate to eliminate COD value of the sample, effects of the addition of two selected oxidants are studied. The first, hydrogen peroxide, was selected due to its well-known ability to enhance the rate of acoustic oxidation, and the second, air bubbling, was selected due to simplicity and economy.

However, *Figure 4.7* shows that adding hydrogen peroxide could only slightly increase removal efficiency of COD, and the highest value observed is 12.6% using 140 g/L H_2O_2 after one hour of irradiation time on 0.1% sample. The efficiency obtained tends to be lower when the sample concentration increases; one-hour efficiencies, as found in the study, are 12.6% for 0.1% sample, 5.4% for 0.5% sample, and 4.5% for 1% sample. Concentration of the substrate is known to be one of the major factors, since there could be competition for

the radicals between the substrate and the intermediate generated (Jiang, Petrier, and Waite 2002; Maleki et al., 2005; Tang and Liu, 2006; and others).
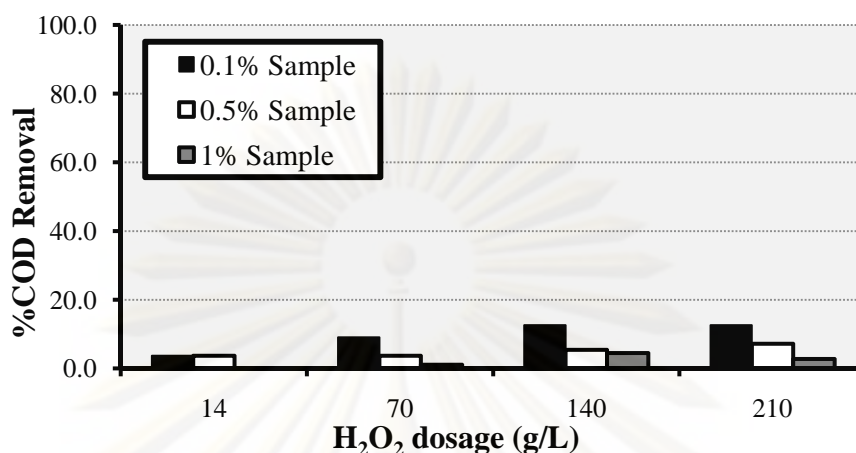
Figure 4.7 *1-hour COD removal efficiencies obtained at different H_2O_2 dosage*

The surprisingly low efficiencies achieved by using both ultrasonic and hydrogen peroxide are in contrast of high removal (60 – 90% removal) found in other studies (Chemat et al., 2001; Ghodbane and Hamdaoui, 2009; Iordache et al., 2003; Kim et al., 2006), but the findings similar to this study could also be observed by Shemer and Narkis (2005) who found that adding hydrogen peroxide did not much improve the efficiency of acoustic oxidation. Moreover, they found that decomposition of hydrogen peroxide occurred at a very slow rate, and the main action of decomposition was done by the action of acoustic oxidation itself.

The accepted mechanism of synergistic effects between hydrogen peroxide and ultrasonic irradiation is the decomposition of hydrogen peroxide molecule, which results in the production of hydroxyl radicals (Jiang, Petrier, and Waite, 2002):

$$H_2O_2 +))) \rightarrow \cdot OH + \cdot OH$$
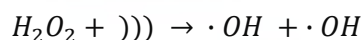
Therefore, lack of hydrogen peroxide decomposition indicates that only a small amount of hydroxyl radicals were produced, and slow degradation rate ensues. Such phenomenon is considered very rare since it is generally accepted that addition of hydrogen peroxide greatly enhanced the rate and efficiency of acoustic oxidation.

Nevertheless, as could be observed in this study, increasing dosage of hydrogen peroxide lead to better COD removal efficiency for marginal amount, though. The efficiency was found to rises from virtually none at 1.4 g/L H_2O_2 to 13.2% at 140 g/L H_2O_2. Afterward, the efficiency slightly changed when 210 g/L H_2O_2 was used. This characteristic was previously observed in most AOPs studies using hydrogen peroxide, that increasing amount

of H_2O_2 beyond a certain value did not lead to further enhancement but decrease the efficiency instead. This could be explained by the fact that excess hydrogen peroxide could too scavenge the hydroxyl radicals generated, producing hydroperoxyl radical ($\cdot OOH$):

$$H_2O_2 + \cdot OH \rightarrow H_2O + \cdot OOH$$
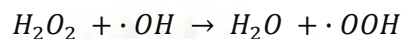
Despite the fact that it is another radical, $\cdot OOH$ have far lower oxidizing power than $\cdot OH$, and could likely be the cause of lower oxidation efficiency (Chemat et al., 2001).

Another oxidant which was observed to be able to enhance the oxidation process is oxygen, which could be simply supplied by air bubbling. However, bubbling lead to no efficiency rise at all, and the obtained change of COD is highly likely to be random error of analysis, as shown in following *Figure 4.8*.
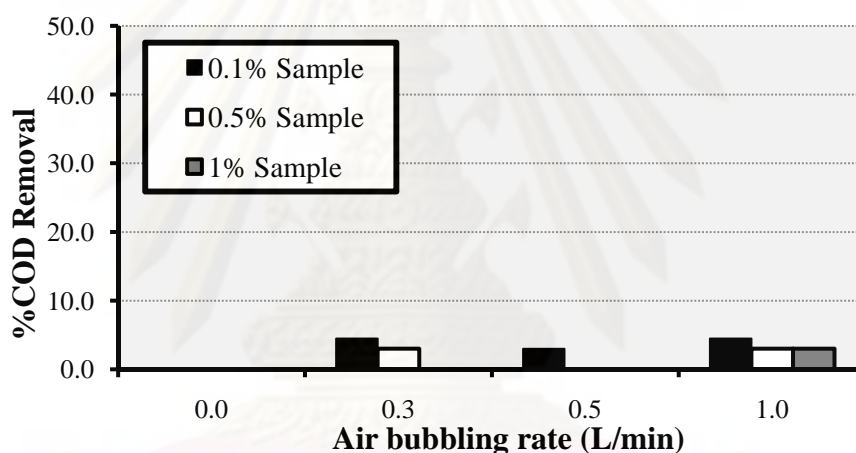
Figure 4.8 *1-hour COD removal efficiencies obtained at different air bubbling rate*

Despite the enhancement observed in the degradation of cyanide ion by Iordache et al. (2003), air bubbling seems not to help at all in this study, which effect of flotation could not even be observed. There are also possibilities that the bubbles could dampen the ultrasonic energy and result in lower occurrence of cavitation (Liu et al., 2008). Moreover, it is apparent that there was virtually no flotation action, which is supposed to be one of expected major removal actions in this experiments, which could be due to two reasons: (1) the bubble is thousands times bigger than the droplets so that it is nearly impossible for bubble and oil droplets to attach together, and (2) agitation caused by ultrasonic gave highly turbulent conditions, which prevent coalescence phenomena of oil droplets induced by the bubble's wake (Moosai and Dawe, 2003).

4.2.3 Oxidation-reduction potential

During the study, value of oxidation-reduction potential (ORP) was measured to investigate the reason of low oxidation efficiency obtained. The measured value was presented in the following *Table 4.3*. It could be clearly seen that ORP of the sample was not changed by acoustic oxidation, which could be explained that hydroxyl radical does in fact exist in very low concentration that is 10^{-12} - 10^{-10} mol/L (Chemat et al., 2001). Such minimal concentration is not enough to significantly affect the oxidizing potential of the whole medium. Instead, the expected mechanism of AOPs relies on the coincidental interaction between the molecules of oxidant and substrate.

Table 4.3 ORP of different reaction mediums

Medium	E_h (mV)
Tap water	242 ± 17
Cutting oil emulsion	265 ± 12
Sample + 14 g/L H_2O_2	293 ± 24
Sample + 14 g/L H_2O_2 +)))	277 ± 13
Sample + 140 g/L H_2O_2	419 ± 31
Sample + 140 g/L H_2O_2 +)))	394 ± 22

4.2.4. Discussion, prospect, and summary

Despite the successful attempts to use acoustic oxidation on the treatment of organic substances in other studies, this study found that acoustic oxidation and its combination with other basic oxidation are not effective methods to treat cutting oil wastewater. The greatest COD removal efficiency achieved is only 13.2%, and acoustic oxidation alone does not lead to any removal at all.

There are several possible reasons of low efficiency observed. First, the concentration of the wastewater sample in this study could be too high to allow effective oxidation. Oil concentration of wastewater sample is 890 mg/L, which is considered high compared to those in other studies; for instances, 1-100 mg/L of phenol (Maleki et al., 2005), 285 mg/L COD equivalent of humic substances (Naffrechoux et al., 2000), and 200 μM of chlorobenzene (Jiang, Petrier, and Waite, 2002). High substrate concentration could lead to competition between the substrates and intermediates for the radicals, which already exists in very low concentration. There are too another possible reason that the first few oxidizing steps involves

only breaking of substances into smaller molecules, according to the work of Nafferchoux et al. (2000) which find that noticeable COD removal could be observed only after the fourth hour of ultrasonic irradiation.

Other possible reason of low efficiencies is the unique characteristic of cutting oil emulsion that a large portion of organic substituent does not exist in dissolved form but as suspended oil droplets surrounded by surfactant molecules (Chang, Chung, and Han, 2001). The droplets act as hydrophilic nonvolatile substance in typical conditions, which make it hard to be volatilized into the heated collapsing cavitation bubbles. Moreover, small size of droplets (<100 μm) cause it to act like particles following Brownian motion that could be easily pushed away by the shockwave generated during bubble collapse from the active high-energy region around the bubbles to the relatively calmer region with fewer amount of reactive radicals.

It is also possible that choice of ultrasonic apparatus in this study play a large part on the obtained results. First, ultrasonic frequency of the bath is considered the lowest in its possible range (20 kHz). Uses of lower frequency favor degradation via pyrolysis pathways, which is ideal for volatile hydrophobic substances, as already discussed (Jiang, Petrier, and Waite, 2002; Kidak and Ince, 2006). Moreover, use of bath with plate sonicator lead to lower energy density in large volume of medium, opposite to high density in small medium volume produced by horn sonicator (Yasui, Tuziyuti, and Iida, 2005).

In order to achieve effective treatment of cutting oil waste, there exist two potential solutions. The first is to increase the oxidizing power of the oxidant used in the process by increasing radical production rate and pathways, or to use physical separation method to reduce the concentration of the waste to the range that was proved to give effective oxidation by other studies. These two solutions will be further investigated in this research. The first solution will be achieved by adding bivalent iron catalyst called Fenton's reagent to accelerate the production rate of hydroxyl radicals, which will be presented and discussed in section 4.3. Regarding the second solution, coagulation process was employed to represent physicochemical separation method, and the obtained results will be presented and discussed in section 4.4. After that, use of advance oxidation processes on the separate water as post-treatment method will be finally investigated in section 4.5.

4.3. SONO-FENTON OXIDATION OF CUTTING OIL WASTEWATER

In this part, Fenton's reagent will be incorporated into acoustic oxidation process for the purpose of increasing the overall oxidizing power of the reaction medium. The combined process, as commonly called *sono-Fenton*, was proved to provide higher rate of radical production than acoustic oxidation and Fenton's chemistry combined (Dai et al., 2008; Ghodbane and Hamdaoui, 2009; Guo et al., 2005, Ioan et al., 2007; Shemer and Narkis, 2005; Zhang et al., 2007).

There are two main important parameters that should be controlled to achieve effective oxidation from Fenton and sono-Fenton process. The first is pH of the medium, where highly acidic condition is common; the second parameter is the ratio between Fe^{2+} and H_2O_2, which greatly varies from study to study. Therefore, pH that gives the greatest removal will be firstly determined, followed by Fe^{2+}/H_2O_2 ratio; after that, the influence of hydrogen peroxide on the oxidation efficiency will be determined to make possible the optimal design where efficiency is not the only single important design goal.

4.3.1. Effects of pH value

In this part, effect of pH was investigated by comparing the efficiency obtained at different pH values, using the condition that was used in the similar study of Seo et al. (2007): 3 g/L $FeSO_4$ and 140 g/L hydrogen peroxide. The result, as illustrated in *Figure 4.9*, shows that as high as 75.1 to 82.5 percent of COD removal could be achieved at pH value between 1.0 and 1.7, which is considered to be extremely acidic. The reasons that extremely low pH used are that (1) pH should be kept low to prevent the precipitation of $Fe(OH)_3$ which induces sweep floc coagulation, and (2) the radical-production step of Fenton chemistry prefers lower pH.

The precipitation of ferric hydroxide, $Fe(OH)_3$, is primarily caused by the fact that solubility of the molecule will be reduced from 1 to 0.01 mol/L, when pH was changed from 1.7 to 2.0 (Sawyer, McCarthy, and Parkin, 2003); Fe^{3+} also exists at a high amount by the oxidation of Fe^{2+}, which is the primary step in Fenton chemistry. High amount of Fe^{3+} and lowered solubility contributes to such precipitation. The precipitate itself could act as sweeping medium in sweep floc coagulation that makes the main removal mechanism to be destabilization-separation rather than advance oxidation, and separation could be clearly observed at pH 2.0, resulting in floating oily sludge and high value of efficiency which is not actually caused by oxidation.
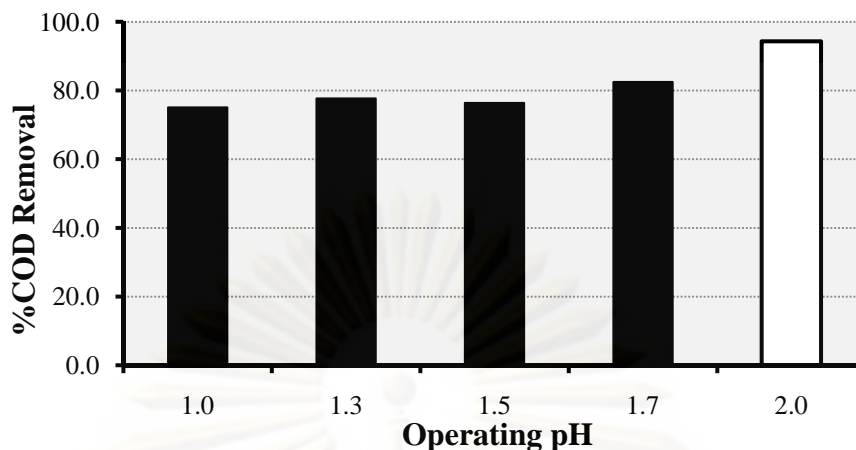
Figure 4.9 *Efficiency of sono-Fenton process obtained at different pH*

Nevertheless, acidic pH is not as unusual, since Fenton chemistry requires lower pH as found in other studies which the best pH are reported in *Table 4.4*.

There are also possibilities that changing pH to acidic regime or the presence of cationic species could destabilize the oil droplets and results in separation (Aurelle, 1985; Bataller et al., 2004). Therefore, another experiment was conducted in order to check whether extreme acidic pH values used or the cation added are the reason of COD removal obtained. The experiment used the same configuration with the absence of hydrogen peroxide and ultrasonic irradiation to ensure that no oxidation would occur.

As shown in *Figure 4.10*, virtually no removal of COD was observed in absence of hydrogen peroxide and ultrasonic irradiation. Despite the fact that presence of metallic cation could destabilize the colloidal system, the amount of ferrous ion added is so great that strong charge reversal could possibly occur (Rios, Pazos, and Coca, 1998). Furthermore, extremely low pH used too contributes to this since it prevents the formation of ferrous and ferric hydroxide that could induce sweep floc coagulation. Note that when pH was raised above 2.0, significantly higher efficiency could be observed due to precipitation of iron, as previously discussed.

Note that, to further suppressed the effect caused by separation mechanism such as gravimetric, flotation, and adhesion, the collected samples were vigorously stirred prior to COD analysis. However, little difference could be observed between stirred and unstirred samples and the margin are smaller than 5%, which showed that oxidation is the dominant mechanism in these experiments conducted.
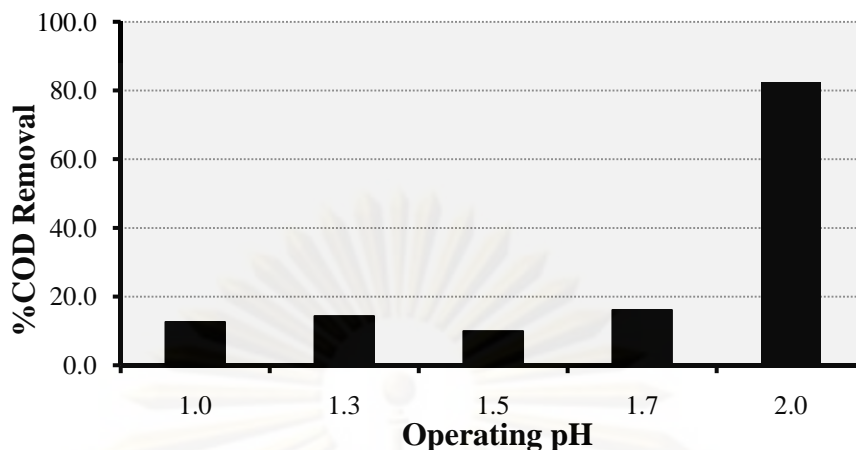
Figure 4.10 *COD removal in absence of radical-producing reagents*

4.3.2. Effects of Fe^{2+}/H_2O_2 ratio

After the optimum value pH, which is 1.7, were obtained, the ratio between ferrous ion and hydrogen peroxide were then determined. This step of the study will make constant the concentration of H_2O_2, which is 140 g/L, and vary the amount of added Fe^{2+} to obtain different ratios. The obtained efficiencies of each ratio were shown in *Figure 4.11*.

Figure 4.11 shows that, initially, the efficiency of sono-Fenton process start rising from nil at Fe^{2+}/H_2O_2 equals to 0.7:1000 until it reach maximum value of 91.3% at Fe^{2+}/H_2O_2 equals to 3.6:1000, or 500 mg/L Fe^{2+} and 140 g/L H_2O_2. After that, the efficiency slowly drops to 82.5% at Fe^{2+}/H_2O_2 equals to 7.1:1000 which is the ratio used in the previous part.
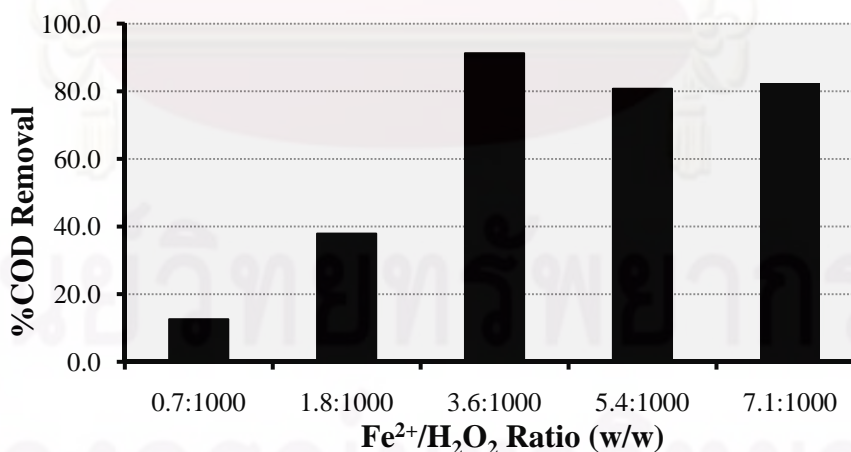
Figure 4.11 *One-hour COD removal efficiencies at different Fe^{2+}/H_2O_2 ratio*

The reason that no removal was observed at low Fe^{2+}/H_2O_2 is that no catalytic decomposition of hydrogen peroxide occurs by inadequate amount of Fe^{2+} (Rizzo et al., 2008). However, value of the "threshold" was found to be highly varies from one study to

another. For example, 600 mg/L in the study of Rizzo et al., which is considerably high compared to 250 mg/L found in this study. Moreover, greater amount of ferrous catalyst would results in greater catalytic activity which means greater rate of radial production.

On the other hand, using high dosage of Fe^{2+} could negatively affect the oxidation process since Fe^{2+} is a known radical scavenger which could reacts with the hydroxyl radical produced, according to the following reaction (Rizzo et al., 2008):

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$$
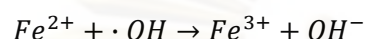
Moreover, excess Fe^{2+} or Fe^{3+} could reacts with unstable radicalized organic compounds, making it stable once again (Shemer and Narkis, 2005):

$$Fe^{2+} + \cdot CX_3 \rightarrow Fe^{3+} + CX_3^-$$

$$Fe^{3+} + \cdot CX_3 \rightarrow Fe^{2+} + CX_3^+$$
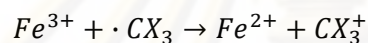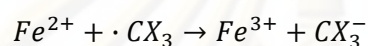
It is also worth noting that the right amount of ferrous ion required for Fenton's oxidation to be effective is highly varies by substances and conditions. The ratios are reported alongside pH in *Table 4.4*.

Table 4.4 Optimum operating pH and Fe^{2+}/H_2O_2 ratio of Fenton in other studies

Source	Wastewater	pH	Fe^{2+}/H_2O_2
Rizzo et al., 2008	Olive mill wastewater	3.0	1,852:15,000
Zhang et al., 2007	C.I. Acid Orange 7	2.0-3.0	3:1*
Ghodbane and Hamdaoui, 2009	Acid Blue 25	1.0	-
Dai et al., 2008	Sulfurized compounds	2.1	1:200
Ioan et al., 2007	bisphenol A	4	1:2.8

*Using iron powder, Fe^0

4.3.3. Effects of H_2O_2/C_{oil} ratio

In this part, amount of hydrogen peroxide will be varied in order to investigate the role of oxidant in sono-Fenton process. Optimum pH, 1.7, and Fe^{2+}/H_2O_2 ratio, 3.6:1000, will be used, and the result will be reported as one-hour-efficiency, as shown in *Figure 4.12*.
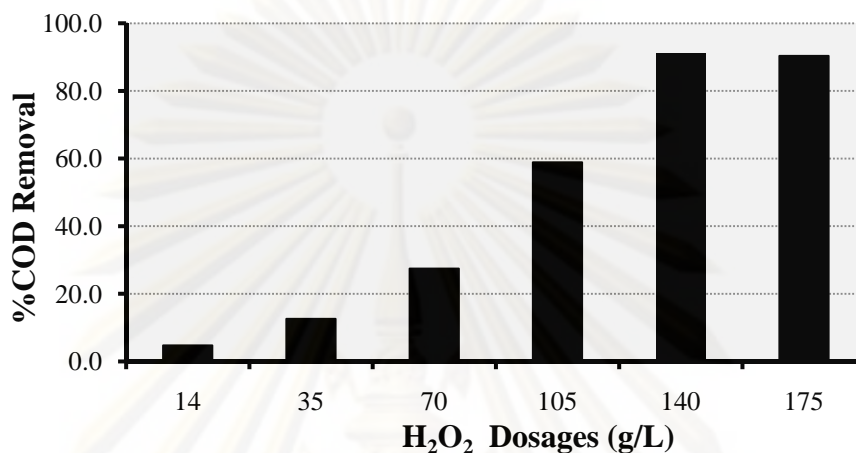
Figure 4.12 *One-hour COD removal efficiencies at different H_2O_2 dosage*

As the result shows, using amount of H_2O_2 lower than 140 g/L gives far lower efficiency; for example, 27.5% and 58.9% removal obtained at 70 and 105 g/L H_2O_2, respectively. Moreover, increasing H_2O_2 dosage above 140 g/L did not lead to noticeable efficiency improvement that dosage of 175 g/L H_2O_2 give 90.4% removal which is close to 91.3% of 140 g/L H_2O_2.

It is previously discussed in *4.2.2* that higher dosage of hydrogen peroxide leads to greater amount of radical production, but radical-scavenging action could occur when excess amount was added. Furthermore, it is suppose that greater amount of hydrogen peroxide are needed in Fenton oxidation, since two molecule of hydrogen peroxide are needed to complete the production cycle of one hydroxyl radical molecule, as opposed to acoustic oxidation where two radical molecules are produced from one molecule of hydrogen peroxide as respectively shown in the following equations:

Acoustic oxidation with hydrogen peroxide

$$H_2O_2 +))) \rightarrow \cdot OH + \cdot OH$$

Fenton's chemistry

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+}$$

$$H_2O_2 + Fe^{3+} \rightarrow \cdot OOH + H^+ + Fe^{2+}$$
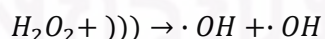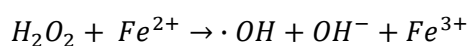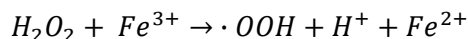
However, as the result shows, sono-Fenton process gives greater removal efficiency than acoustic oxidation at the same amount of hydrogen peroxide. At 140 g/L H_2O_2 acoustic oxidation gave considerably low efficiency, 12.6%, as compared that obtained from sono-Fenton, 91.3%.

It is proposed in studies concerning sono-Fenton oxidation of various organic compounds that sono- and photo-Fenton could regenerate Fe^{2+} from Fe^{3+} by accelerating the sub-reactions shown (Guo et al., 2005):

$$H_2O_2 + Fe^{3+} \rightarrow Fe - OOH^{2+} + H^+$$

Fenton: $Fe - OOH^{2+} \rightarrow Fe^{2+} + \cdot OOH$

Sono-Fenton: $Fe - OOH^{2+} +))) \rightarrow Fe^{2+} + \cdot OOH$
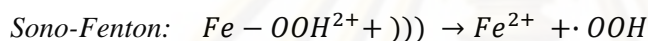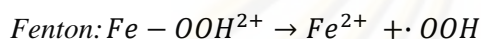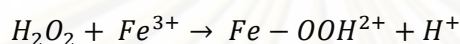
Moreover, energy intensification via ultrasonic or ultraviolet irradiation could regenerate ferrous ion by a unique pathway which does not require hydrogen peroxide (Rizzo et al., 2008):

Photo-Fenton: $H_2O + Fe^{3+} + hv \rightarrow Fe^{2+} + \cdot OH + H^+$

Sono-Fenton: $H_2O + Fe^{3+} +))) \rightarrow Fe^{2+} + \cdot OH + H^+$
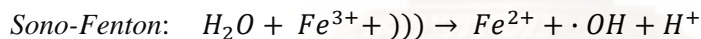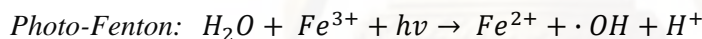
It is worth noting that this pathway produces an additional hydroxyl radical, and these could be the reasons why sono-Fenton oxidation could provide greater efficiency than acoustic oxidation alone.

4.3.4 Reaction kinetic, correlations, and prediction model

Reaction kinetic of sono-Fenton process, which is required to produce an effective process design and recommendation, were determined in this part by plotting COD values of the sample collected over reaction time and kinetic parameters were then derived for different operating conditions.

As an example, COD values obtained when using 375 mg/L Fe^{2+} and 105 g/L H_2O_2 are plotted in *Figure 4.13*. It could be seen that COD exponentially reduce until 15 minutes of reaction time and slightly fluctuate around a certain value afterward. The same trend was also observed by using different conditions, with different reduction rate as well as the value of

final COD. Moreover, this limited exponential reduction was also reported in studies concerning Fenton and sono-Fenton oxidations (Ghodbane and Hamdaoui, 2009; Ioan et al., 2007; Zhang et al., 2007).

The leftover COD found in this study might be the result of refractive organic substances that could not be further oxidized by sono-Fenton process. Such substances could be produced by some undesirable oxidation pathway (intoxication) or dimerization of two radicalized molecules (LaGrega, Buckingham, and Evans, 2000; Portela, 2001a):

Intoxication: $\quad R + \cdot OH \rightarrow R'_{refract}$

Dimerization: $\quad \cdot R + \cdot R \rightarrow R - R$
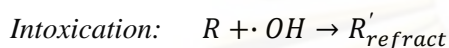
where *R* denotes the organic substances. Moreover, depletion of oxidant were also suspected to be the cause of stable COD, but the bubble production which could be visually observed indicated that decomposition of hydrogen peroxide still occur, and adding more hydrogen peroxide during the process did not lead to any efficiency enhancement.
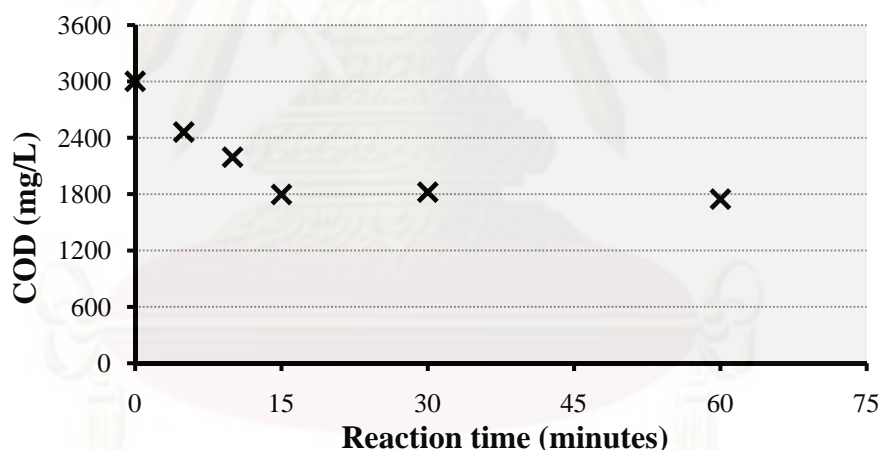
Figure 4.13 *Example of COD reduction, 375 mg/L Fe^{2+} and 150 g/L H_2O_2*

Therefore, it is apparent that conventional pseudo first-ordered kinetic cannot be incorporated into such kinetic, since the most fundamental basis of conventional pseudo first-ordered kinetic is that the reaction should be completed and there should be no substrate left, as contrast to this study's finding (Levenspiel, 1999). Thus, another form of equation should be derived to characterize this result.

Actually, the obtained reduction trend of COD could be separated into two parts, as shown in *Figure 4.14*. The upper part consists of exponential reduction, which is similar to pseudo first-order kinetic, while the lower part stays constant as the reaction progress. Note that the "constant" term is actually indicated by one-hour efficiency that was already presented in previous parts.
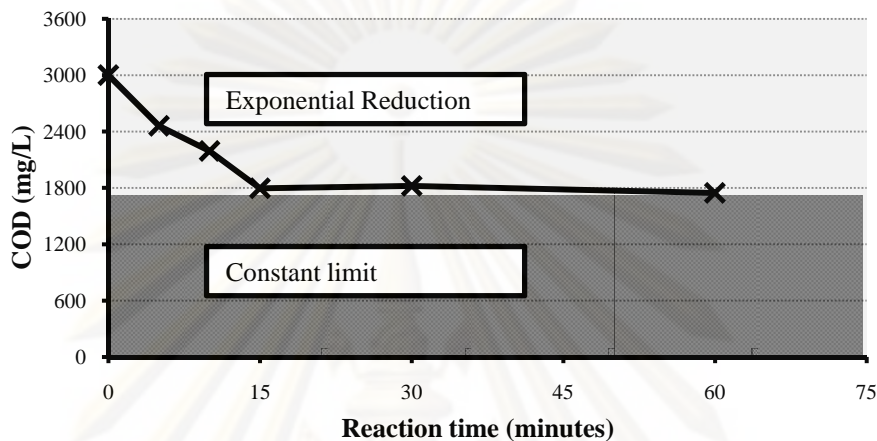
Figure 4.14 *Limited first-order concept of reaction kinetic*

Based on this two-part observation, an equation form could be proposed as:

$$COD_t = COD_f + COD_t^*$$

where $\qquad COD_t = COD\ at\ any\ time, t\ (mg/L\ O_2)$

$\qquad\qquad COD_f = Constant\ COD\ of\ the\ lower\ part\ (mg/L\ O_2)$

$\qquad\qquad COD_t^* = Changing\ COD\ of\ the\ upper\ part\ (mg/L\ O_2)$

COD_t^* is a function of time and initial value of COD_t^*, or COD_i^*:

$$COD_t^* = COD_i^* e^{-kt}$$

where $\qquad COD_i^* = COD_0 - COD_f$

and $\qquad COD_0 = Initial\ value\ of\ COD_t$

Substituting all above relations results in the following equation:

$$COD_t = COD_f + (COD_0 - COD_f)e^{-kt}$$

Or $\qquad COD_t = COD_0 + COD_f(1 - e^{-kt})$

upon assuming that COD_f is obtainable from the given efficiency:

$$COD_f = COD_0 \eta_{COD}$$

where $\qquad \eta_{COD} = 1 - hour\ efficiency\ of\ the\ selected\ condition$

and the equation will become:

$$COD_t = COD_0 + COD_0 \eta_{COD}(e^{-kt} - 1)$$

or $\qquad COD_t = COD_0(1 + \eta_{COD}(e^{-kt} - 1))$

It is worth noting that such equation form is highly similar to concentration-driven mass transfer, where the mass flux is proportional to difference in concentration between two medium. Therefore, two main parameters, k of the exponential part and C_f of the constant part, could be derived from COD-time plot of each operating condition using the method provided in Appendix C. The obtained parameters of each operating condition are reported in *Table* 4.5. Moreover, sample of plot-fitting is shown in *Figure 4.15* using the same example data, and the dotted line represents equation:

or $\qquad COD_t = 3000(1 + 0.582(e^{-0.123t} - 1))$

that is $k = 0.123\ min^{-1}$ and $C_f = 1,742\ mg/L\ O_2$.
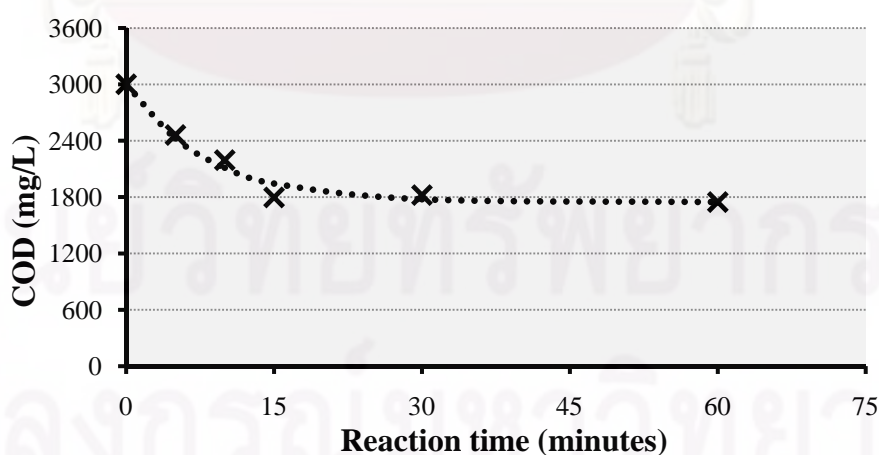
Figure 4.15 *Example of curve-fitting using the proposed kinetic form*

Table 4.5 *Efficiencies and kinetic constants obtained from different studied conditions*

Condition		Efficiency	Kinetic constant
H_2O_2	Fe^{2+}	η_{COD}	k
g/L	mg/L	%	min^{-1}
140	100	12.6	0.104
140	250	37.9	0.115
140	500	91.3	0.148
140	750	80.8	0.124
140	1000	82.5	0.138
35	125	12.6	0.112
70	250	27.5	0.164
105	375	58.9	0.123
140	500	91.3	0.147
175	675	90.4	0.115

It could be seen from the data that while efficiency varies from one condition to another, influence of both H_2O_2 and Fe^{2+} dosage on the kinetic constant was not observed. Values of the kinetic constant were found to be rather random around its average value, which is 0.129 ± 0.019 min^{-1}. This was not unexpected, since all conditions take similar time to reach the final COD value, and the form of this kinetic equation is not normal from the start.

However, there exists a possible trend to be observed, that is the final efficiency tends to linearly increase with increasing H_2O_2 dosage up to 140 g/L, which is tested by Pearson's correlation and found that r-squared value is equals to 0.975, indicating correlation, and the trend equation is:

$$\%\eta_{max} = 0.76[H_2O_2] - 19.3$$

The trend equation will be later used to estimate the maximum efficiency obtained on scaling up of oxidation reactor. Note that when dosage of H_2O_2 is equal to 25.2 g/L, efficiency obtained will be exactly zero. This might indicate the minimum amount of H_2O_2 required for any significant removal to take place.

On the other hand, it is possible that the final value of COD is actually the slowed oxidation rate after bivalent iron (Fe^{2+}) was depleted, since the rate of regeneration reaction (Fe^{3+} to Fe^{2+}) is far lower than the radical-producing reaction (Fe^{2+} to Fe^{3+}). Such characteristic is not uncommon, as it is previously observed in study on supercritical water oxidation where slower rates were obtained during degradation of intermediates, which were produced from rapid degradation of the initial pollutants (Sanchez-Oneto et al., 2007). There was also attempt to apply two-step pseudo-first-ordered kinetic equations to characterize this, but the second step in this study are found to be too obscure to be able to apply kinetic on it.

4.3.5 Analysis of synergistic effects

Synergistic effects, which could be defined as "the effect of a whole entity that is greater than the sum of its parts' effects", are common phenomena in chemistry including oxidation processes, and it is common that using two oxidizing reagents together leads to greater oxidation rate and efficiencies. In many studies in the past, there were attempts to determine and quantify the synergistic effects for comparison, and *"synergistic index"* was often used to express such synergy (Zhang et al., 2007):

$$f = \frac{k_{A+B}}{(k_A + k_B)}$$

where

$f = synergistic\ index, dimensionless$

$k_{A+B} = kinetic\ constant\ of\ combined\ action$

$k_A, k_A = kinetic\ constant\ of\ separated\ action$

As could be seen, f indicates the degree of synergy, and the value above unity indicate the synergistic effects occur, while less than unity indicate prohibition effects.

However, it is obvious that the kinetic of Fenton's chemistry should be firstly determined to be able to obtain the synergistic index. Condition used are 105 g/L H_2O_2 and 375 mg/L Fe^{2+} in absence of ultrasonic irradiation. The results obtained are then plotted alongside the data with the presence of ultrasonic irradiation in *Figure 4.16*.

As could be seen in the figure, final values of COD obtained from Fenton and sono-Fenton oxidation are highly similar, but the difference is that the reduction of sono-Fenton is slightly faster than Fenton alone. It took about 60 minutes for Fenton oxidation to reach the final COD while only 15 minutes are required using sono-Fenton oxidation.
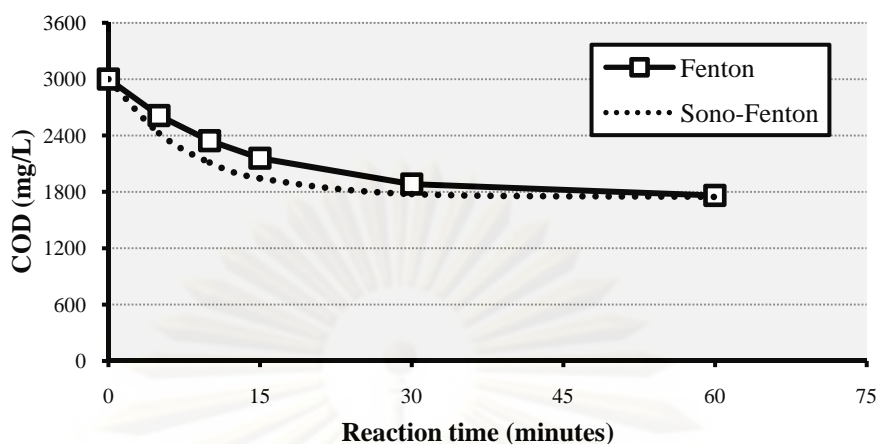
Figure 4.16 *Comparison between COD reduction Fenton and sono-Fenton*

After the kinetic parameter was determined, synergistic index could be then calculated using previous equation and found to be:

$$f = k_{sono-Fenton} \Big/ (k_{Fenton} + k_{Acoustic\ oxidation})$$

$$f = 0.123 \Big/ (0.074 + 0.0) = 1.66$$

Such high value indicates that it is highly synergistic, but it could be argue that kinetic constant term of acoustic oxidation is virtually nil, and ultrasonic irradiation rather act as a catalyst that accelerate the degradation rate, not the oxidation pathway itself.

It is also worth noting that the catalytic action of ultrasonic irradiation is mainly due to greater availability of energy which is, in this case, supplied in the form of extreme temperature and pressure during the collapse of cavitation bubbles. This is rather different from conventional catalyst which helps reduce the required amount of activation energy needed to initiate the reactions (Levenspiel, 1999; Young, 1999).

4.3.6 Discussion, prospect, and summary

The results obtained in this study clearly implied that sono-Fenton oxidation is also an effective process that could be applied to the treatment of cutting oil wastewater, where as high as 90% of COD removal efficiency could be achieved, but there are too costs to be paid as great amount of chemical usage. Hydrogen peroxide dosage that provides the highest removal rate, for example, is 140 g/L, which is considerably high given that the highest commercial concentration is 30% or 420 g/L.

Nonetheless, the kinetic form and parameters derived from experiment data could be used as the designing parameter and guidelines for similar studies on advance oxidation process and the design of larger scale process where optimization is highly important. Additionally, synergistic effects could also be observed between acoustic oxidation and Fenton's reagents which could be further applied in future studies.

However, efficiency and chemical use are not the only important parameters to be used in decision-making process. There are also other aspects and constraints imposed by a number of conditions and regulations; for example, treatment time, sludge productions, energy usage, effluent quality, and others. Therefore, comparisons should be made with the conventional process currently being used in the treatment of cutting oil waste, which is coagulation followed by flocculation and sediment process, and the next part of this research aims to determine and investigate the effectiveness of such processes.

4.4. COAGULATION PROCESS

Effectiveness of coagulation, which is a method currently used in the treatment of cutting oil wastewater, are investigated in this part. Apart from removal efficiency of COD, operating parameter and resulting aspects including chemical dosage, time, and energy used are also determined to compare it with those of sono-Fenton process in previously studies.

4.4.1. Effect of pH

This part investigates the effect of pH value, to find the most appropriate condition for the coagulation of cutting oil emulsion. From *Figure 4.17*, it could be clearly seen that coagulation gives the best removal efficiency at neutral pH, which is the typical range of the emulsion as well as the waste (El Baradie, 1996b).
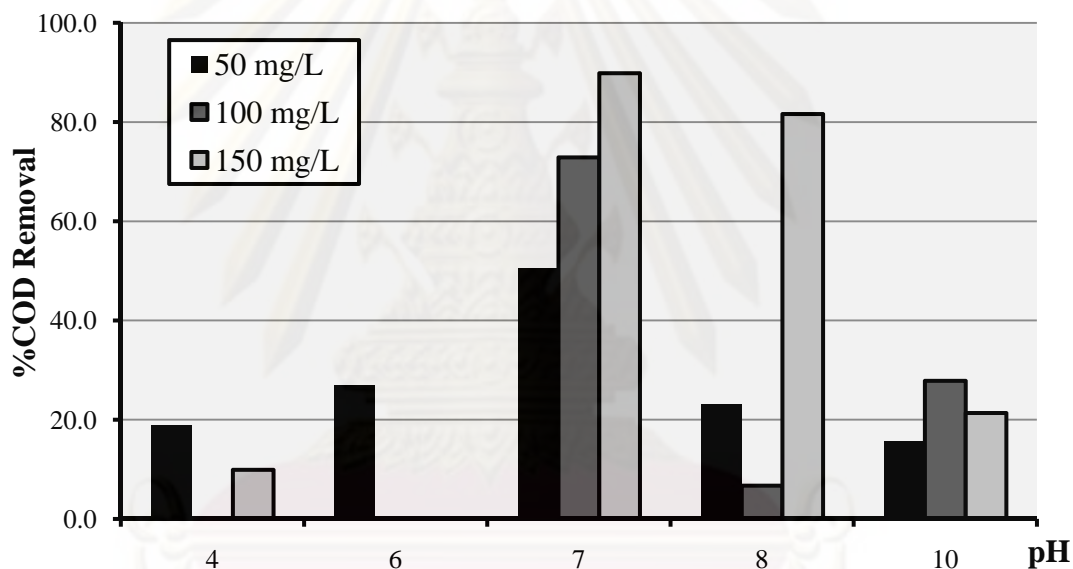
Figure 4.17 *Effect of pH on COD removal efficiency*

It could also be seen from the figure that 150 mg/L alum dosage appears to gives the highest efficiency at neutral pH. Moreover, drop of efficiency which could be observed when pH slightly changed strongly confirms the importance of pH on the coagulation process.

Roles of pH on the process could be explained by the fact that (1) form of aluminum hydroxide widely varies and highly sensitive to the pH value (Reynolds and Richards, 1996). (2) Severe pH also leads to a large amount of either hydroxide (OH⁻) or hydronium (H_3O^+) ions, which could compete for cationic coagulant and anionic surfactant, respectively. Such competition leads to less preferred interaction between the coagulant and the surfactant, thus making the coagulation less effective (Aurelle, 1985).

4.4.2. Effect of coagulant dosage

The efficiencies of coagulation using different coagulant dosage were reported in this part. As shown in *Figure 4.18*, *Figure 4.19*, and *Figure 4.20* the greatest efficiencies were obtained using alum dosage of 150, 400, and 1,000 mg/L for 0.1%, 0.5% and 1% sample, respectively. Note that increasing dosage beyond these values leads to slight decrease of efficiency, which may be the result of ionic re-stabilization effect that is commonly occur at excess coagulant dosage (Kawamura, 2000).
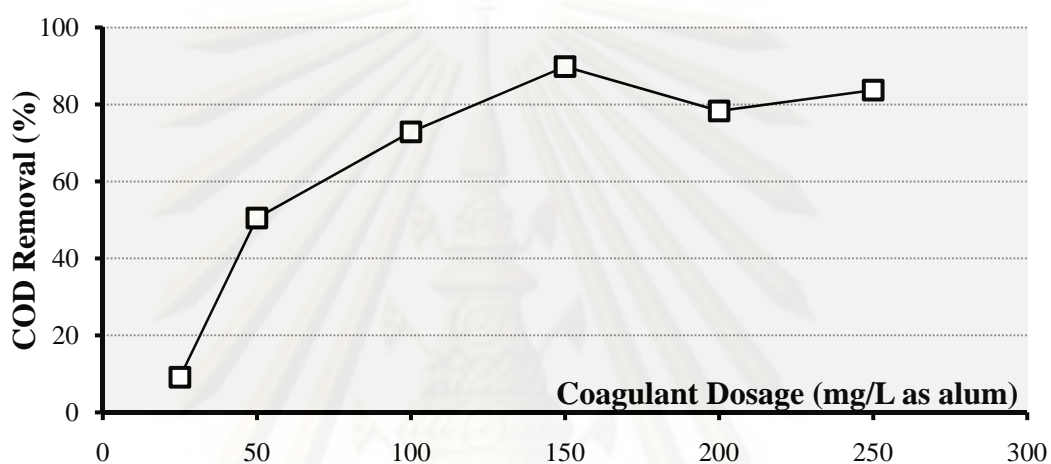
Figure 4.18 *COD removal efficiencies from different alum dosages on 0.1% sample*
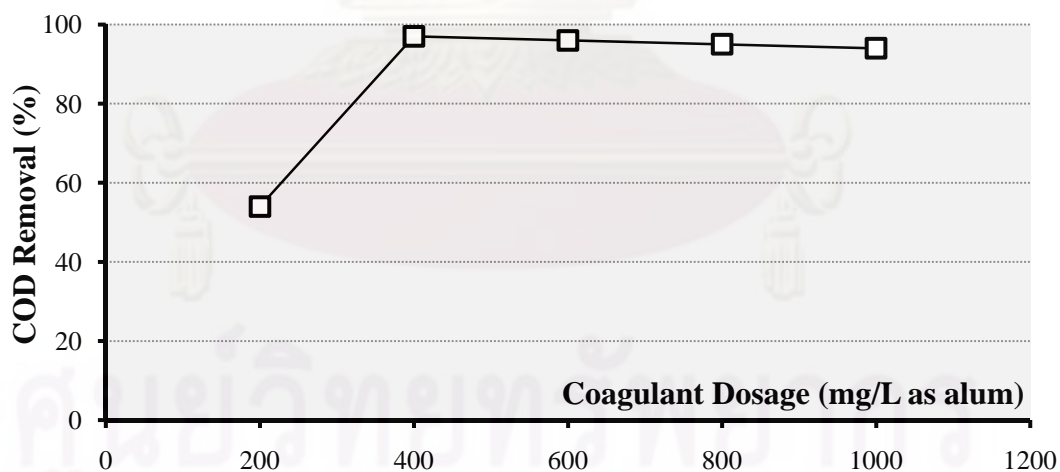
Figure 4.19 *COD removal efficiencies from different alum dosages on 0.5% sample*
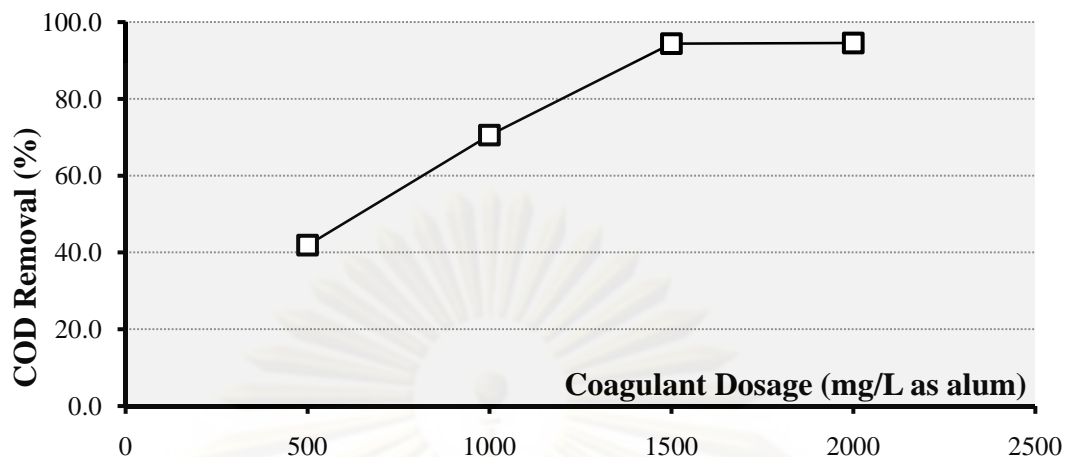
Figure 4.20 COD removal efficiencies from different alum dosages on 1.0% sample

It is also worth noting from the figures that the optimal coagulant dosages seem to be proportional to the oil concentration employed. Moreover, upon plotting the efficiencies with coagulant-oil concentration ratio (C_{Alum}/C_{Oil}) in *Figure 4.21*, highly similar trend could be observed for all concentration, which give a prospect that coagulant-oil concentration ratio could be a potent operating parameter that could be incorporated into a prediction model, but further investigations should be conducted for it to be more widely applicable.
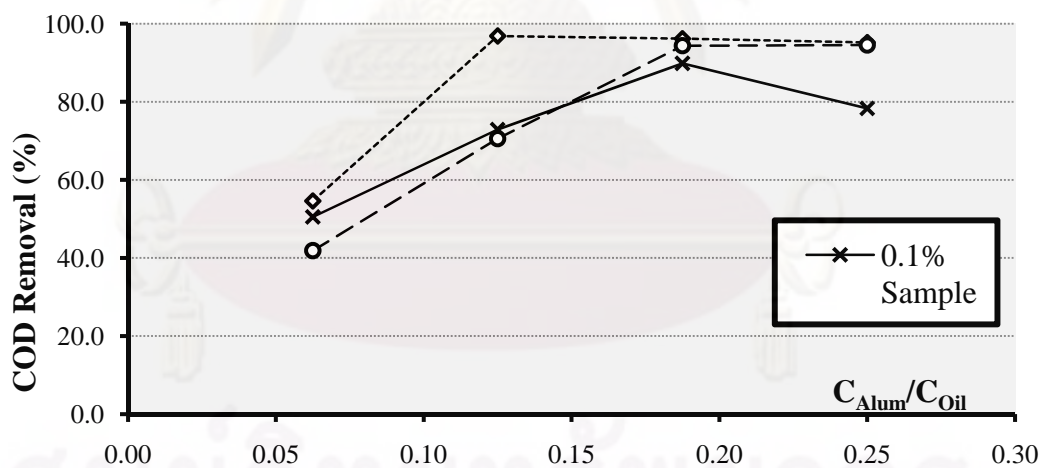
Figure 4.21 COD removal efficiencies at different C_{Alum}/C_{Oil} ratio using different oil sample

4.4.3. Effect of mixing conditions

In this part, effect of mixing condition for both rapid and slow mixing steps of the coagulation-flocculation process was determined. Values of mixing intensity which is expressed as velocity gradient (s^{-1}) at different mixing speeds are reported in *Table 4.6* and *Table 4.7*. However, the velocity gradient used in this study is rather limited due to constraint imposed by the equipment. The obtained results are shown in *Figure 4.22*, *Figure 4.23*, *Figure 4.24*, and *Figure 4.25*.

Table 4.6 *Calculated velocity gradients at different rapid mixing speeds*

Rapid Mixing speed	RPM	120	150	180	210	300
Velocity Gradient (G)	s^{-1}	48.1	67.2	88.4	111.4	190.2

Table 4.7 *Calculated velocity gradients at different slow mixing speeds*

Slow Mixing speed	RPM	15	20	25	30
Velocity Gradient (G)	s^{-1}	2.1	3.3	4.6	6.0
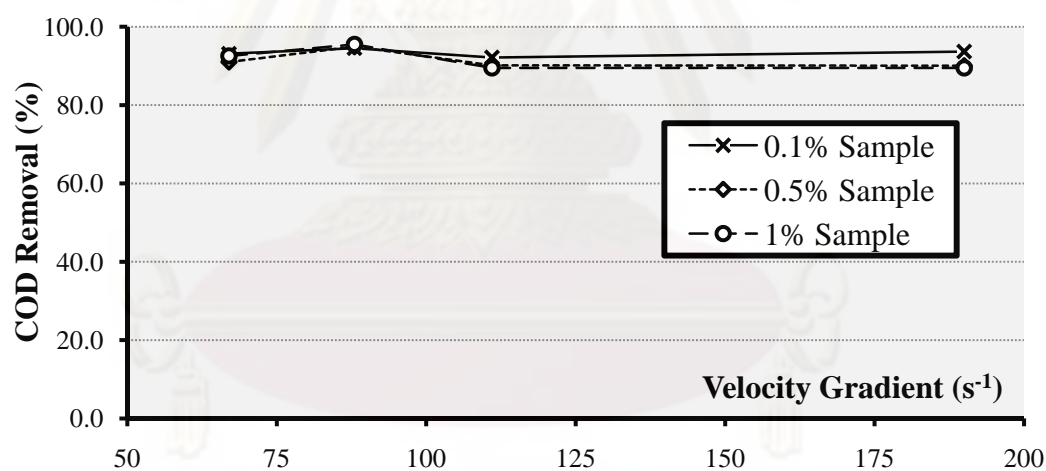
Figure 4.22 *Effect of rapid mix intensity on COD removal efficiencies*
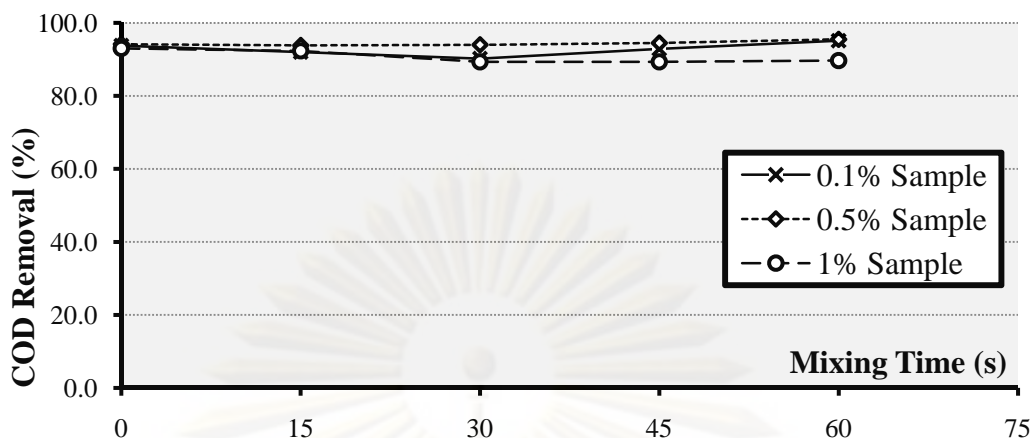
Figure 4.23 *Effect of rapid mix time on COD removal efficiencies*
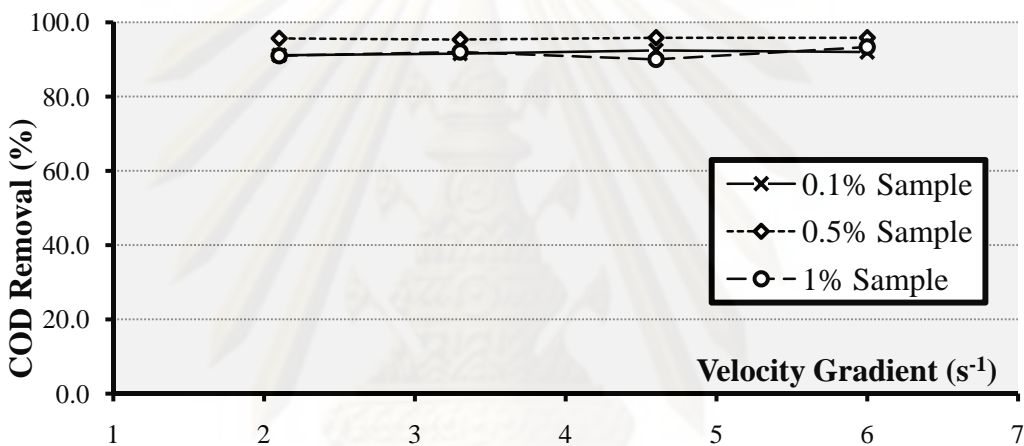
Figure 4.24 *Effect of slow mix intensity on COD removal efficiencies*
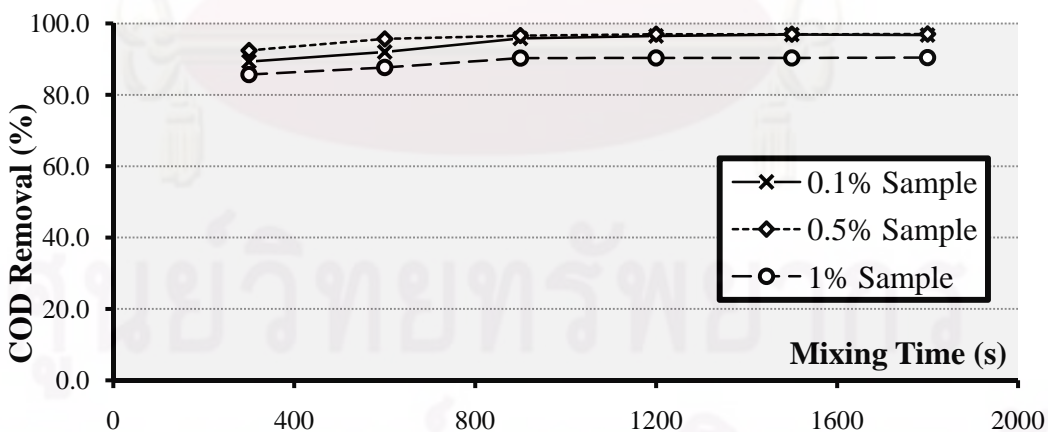
Figure 4.25 *Effect of slow mix time on COD removal efficiencies*

Despite slight difference, the result shows that COD removal efficiency of coagulation process is considerably high, and 90% of COD removal could be expected in most conditions studied. Moreover, only slight changes of efficiency are produced when varying the velocity gradient and mixing time over the studied range. To further investigate this, the efficiency is plotted against $G \times t$ value, which is widely accepted as a process-controlling parameter in *Figure 4.26* and *Figure 4.27*; similarly, the efficiency seems to be not affected by the $G \times t$, as compared to large change that were obtained by varying pH and coagulant dosage in previous part (*4.4.1* and *4.4.2*).
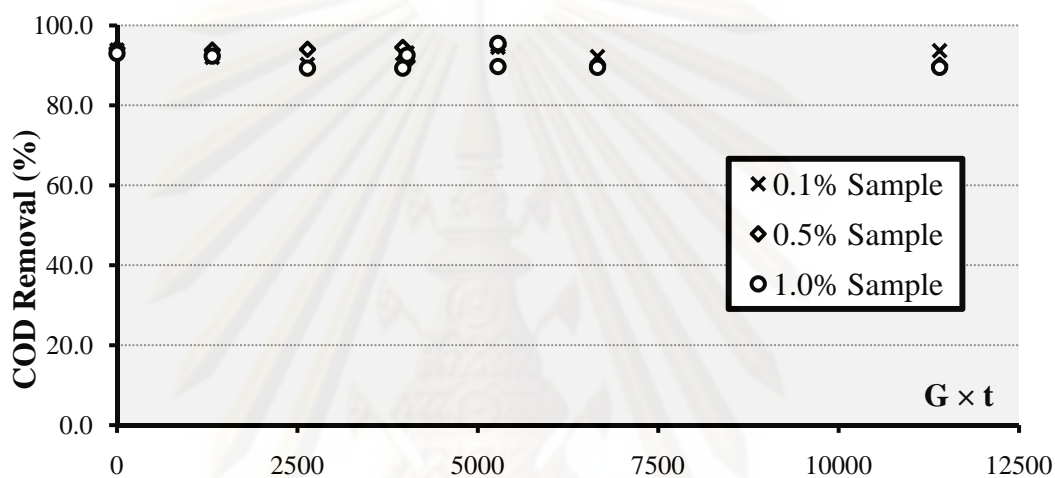
Figure 4.26 *Effect of G × t value of rapid mixing on COD removal efficiencies*
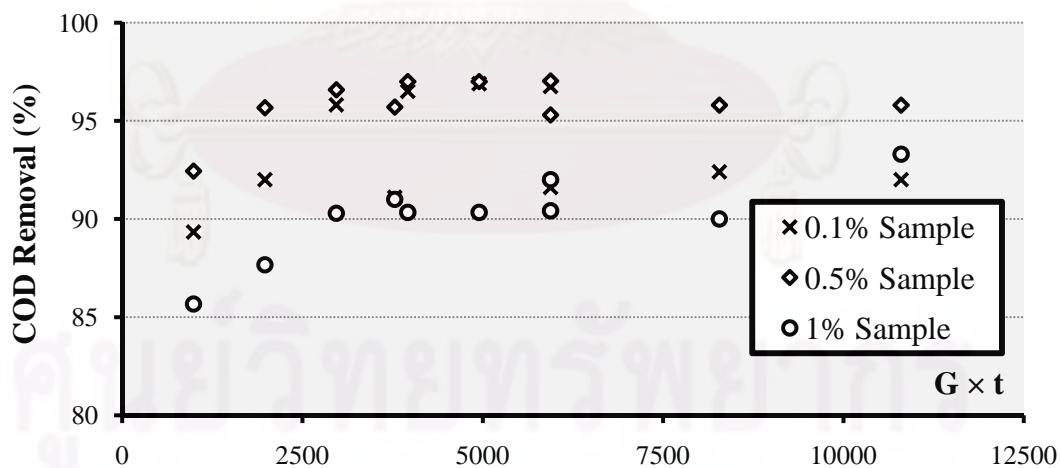
Figure 4.27 *Effect of G × t value of slow mixing on COD removal efficiencies*

Such finding is contrast to the general theory of coagulation that mixing intensity and time of both coagulation and flocculation process are that most important controlling parameters of the processes. This may be due to two main reasons. First, separation of cutting oil emulsion greatly depends on chemical interactions, not the physical ones; small size range of oil droplets causes it to follow Brownian's Motion rather than the motion induced by the mixing force, as described by the equations (Metcalf & Eddy Inc., 2004).

$$l_K = \left(v^3/P_M\right)^{1/4}$$

where
l_K = Kolmogoroff microscale length (m)

v = kinematic viscosity (m^2/s)

P_M = power per unit mass (W/kg)

P_M could be then expressed as

$$P_M = G^2 v$$

where
G = velocity gradient (s^{-1})

v = kinematic viscosity (m^2/s)

Substituting P_M into recent equation gives

$$l_K = \left(\frac{v^2}{G^2}\right)^{1/4}$$

or

$$l_K = \sqrt{v/G}$$

Kolmogoroff microscale length indicates the smallest size of particle that would be affected by mixing of specified velocity gradient. According to the example given in the textbook:

If G = 1000/s and v = 1.003 × 10^{-6} m^2/s at 20 °C, the corresponding value of the microscale length is 31.7 μm, thus, particles smaller than 31.7 μm will not be affected. In fact, if the G value were increased to 10000/s, the corresponding microscale length is 10.0 μm.

For any given range of velocity gradient used and viscosity measured in this study, the smallest particle size that could be affected is 22.4 μm, which is far higher than the average size of oil droplets in this study (<1 μm). Therefore, the major mechanism of the coagulation of cutting oil wastewater should be destabilization by charge elimination followed by coalescing phenomena due to microflocculation and Brownian movement.

The second possible reason that the mixing condition does not affect that coagulation of cutting oil emulsion are that the general coagulation theory was derived from the operation aims for the removal of solid particles which were suspended within natural water. However, the particles in this study are the liquid oil droplets, which behave as elastic deformable particles, follow different mechanism, thus result in different outcome (Moosai and Dawe, 2003).

Nevertheless, despite the fact that physical mechanisms play minimal roles in the coagulation, adequate mixing should be supplied to uniformly disperse the chemical and to allow the coalescence of the larger floc that was produced by microflocculation in the first step.

4.4.4 Discussion, prospect, and summary

In conclusion, destabilizing cutting oil emulsion with coagulation provides high COD removal using small amount of coagulant, and cutting oil wastewater tends to depends on chemical mechanisms rather than the physical ones. The recommended parameters are presented in Table 4.8. Being an efficient process with high removal efficiency (~90%), sludge generated during coagulation, however, could be problematic, since the sludge contains high amount of water content as well as the metal that was added as the coagulant. Remaining COD within the water, too, indicates that there still are remaining residual organic compounded, which leads to two major problems; first, COD values of the resulting water are still not compliance to the industrial effluent standard; second, as found and discussed in most studies on the separation of cutting oil waste, even the most effective separation method could only separate the organic substances that exist as suspended droplets while the dissolved counterparts were left untouched (Bensadok, Belkacem, and Nezzal, 2007; Bensadok et al., 2008; Chang, Chung, and Han, 2001; Rios, Pazos, and Coca, 1998). These dissolved substances vary by some degree due to the cutting oil formula, but the common ones are biocides, EP agents, degraded hydrocarbons, and other additives. Some of them, especially phenolic biocides, are classified as hazardous substances which could cause adverse effect to health or environment, even when they exist at very low concentration (Grier and Lessmann, 2006).

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Table 4.8 *Recommended operating parameters for coagulation process*

Parameters		0.1% Sample	0.5 % Sample	1.0% Sample
pH		7.0	7.0	7.0
Coagulant dosage	mg/L Alum	150	400	1000
Rapid mix				
Intensity	s^{-1}	50 – 200		
Time	S	30 – 60		
Slow mix				
Intensity	s^{-1}	2 – 6		
Time	S	900 – 1800		

4.5 COMBINED COAGULATION-OXIDATION PROCESS

There exist possibilities that advance oxidation processes could be used as the post-treatment process after the emulsion was separated, since the separation process is more effective in the removal of suspended portion of the emulsion while the oxidation is more effective in the destruction of the dissolved counterpart. Moreover, the chemical usage in oxidation processes could also be minimizing the amount of substance to be oxidized could be greatly reduced, and high potential of reusing the separated water could be obtained. Note that several researchers have studied such combination and proved it an effective approach to treat oily wastewater (Chang, Chung, and Han, 2001; Rizzo et al., 2008).

4.5.1 Characteristics of the separation effluent

The effluent water were obtained using 0.1%, 0.5%, and 1.0% samples, which is treated using the recommended mixing condition which is previously determined. Analyzed parameters of the effluents are presented in *Table 4.9*.

Table 4.9 *Parameters of separated emulsion*

Parameters		Samples		
		0.1%	0.5%	1.0%
COD	mg/L	270	750	2600
pH	-	5.2	4.6	4.4
Turbidity	NTU	107	322	865

It could be implied from the table that COD of the effluents are still considered high, especially at high oil concentration where COD of the effluent could be as high as 2,600 mg/L. Also, pH values of the effluent are mildly acidic, which is considered an advantage when using Fenton-based processes that prefer lower pH.

4.5.2 Advance oxidation processes

In this part, three types of AOPs are studied for its effectiveness as the post-treatment of separation processes: acoustic oxidation with H_2O_2, Fenton oxidation, and sono-Fenton. The amount of hydrogen peroxide added are 1.4, 7.0, and 14 g/L for the effluent of 0.1%, 0.5%, and 1.0% sample, respectively. $FeSO_4$ is added at 5, 25, and 50 mg/L to maintain optimal Fe^{2+}/H_2O_2 ratio found in previous part. No effort was made to maintain the pH of the sample, since (1) the sample is already acidic and (2) with lowered dosage of $FeSO_4$, it is not necessary to prevent the precipitation of $Fe(OH)_3$.

Figure 4.28 shows the %COD of the samples after the oxidation is allowed to take places for one hour. It could be seen that all processes employed could effectively reduce COD of the samples so that, for some condition used, no COD could be detected using the standard analysis method. Moreover, after pseudo-first-ordered kinetic constants were derived (shown in Table 4.10), it is apparent that greater initial concentration lead to slower rate while Fenton and sono-Fenton similarly gives faster degradation rate than normal acoustic oxidation.
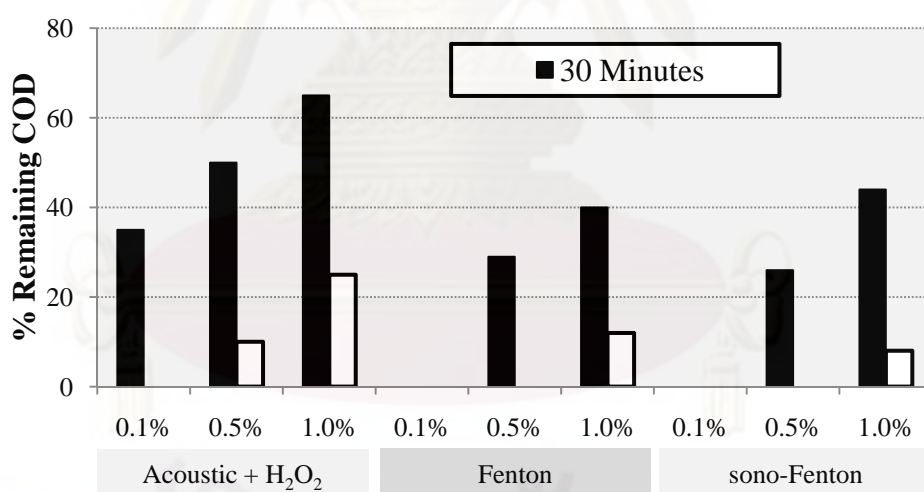
Figure 4.28 *%Remaining COD at different post-treatment processes, conditions, and time*

Table 4.10 *Pseudo first-order kinetic constant of post-treatment AOPs* *(min*$^{-1}$*)*

Initial COD (mg/L)	Processes		
	Acoustic + H_2O_2	Fenton	sono-fenton
270 (0.1%)	0.035	*	*
750 (0.5%)	0.031	0.041	0.045
2600 (1.0%)	0.019	0.032	0.035

*Cannot be determined

4.5.3 Discussion, prospects, and summary

In this part, the combination between separation and advance oxidation processes was investigated. The results showed that the process is considered an effective way to treat cutting oil wastewater as well as suggested some possibilities to be able to treat other type of oily wastewater as well, and great potential of COD-free effluent could be attained using this combination.

It could too be observed from the obtained results that the oxidation in this part does not reduce COD to a certain limit previously observed in *4.3.4*, instead, it could be reduced to undetectable level. As already discussed, organic substances presented within cutting oil wastewater are consisted of two portions: the one that exists as suspended oil droplets surrounded by molecules of emulsifier and the rest of them that is dissolved in aqueous phase. The suspended portion could be removed by separation processes, and it is found in most studies that approximately ten percent of COD remains, even when ultrafiltration was employed (Bensadok, Belkacem, and Nezzal, 2007; Bensadok et al., 2008; Chang, Chung, and Han, 2001; Rios, Pazos, and Coca, 1998). Therefore, it could be proposed that the dissolved portion of organic constituents could easily be oxidized by acoustic oxidation with hydrogen peroxide.

CHAPTER V

COMPARISON AND DESIGN CONSIDERATION

It is found as the research progress that all studied processes were proven to be highly effective for the treatment of cutting oil wastewater; however, each aspect of these processes must be carefully considered in decision making process to achieve the desired treatment goal for different situations.

However, as each treatment process were based on different theory, different mechanism, and different characteristic, a clear baseline must be drawn and used for the processes in question to be equally compared. Unfortunately, this research conducted studies only on batch-based bench scale using small reaction volume, which is not practical.

Normally, to fully grasp the characteristic of any certain process, pilot-scale study should be conducted, but it is highly time and resource consuming. Alternatively, mathematical models based on widely accepted theoretical derivation, could be instead used to simulate and estimate the process's aspects.

This part of the research is an attempt to investigate and determine various aspects of three different processes previously studied: sono-Fenton oxidation, coagulation, and combined process. The mathematical derivations and equations will be explained and illustrated, and the aspects of COD removal efficiency, chemical addition, sludge generation, energy consumption, time taken, and support processes required, will be investigated.

Nevertheless, these equations were derived using *the condition employed in this study*, and variation could be expected when using another condition, e.g. different type and concentration of cutting oil, different ultrasonic apparatuses, etc. Therefore, this part of the study serves only to propose steps and guideline in design processes treating similar kinds of wastewater, and great care should be taken when applying or using these equations and parameters in different situations.

Given a situation where a cubic meter of cutting oil wastewater are generated per day, with concentration equals to 0.1% v/v, containing COD as high as 3,000 mg/L with 1500 NTU turbidity, it requires treatment to reduce such parameters to the level compliance to the regulation.

5.1 SONO-FENTON OXIDATION

5.1.1 Kinetic derivation of reactor design

First of all, it should be noted that as the kinetic derivation of sono-Fenton process found in this study does not exists in general form, therefore, the reactor equations should be specifically derived.

Since it is found that COD reduction rate are proportional to the difference in current COD of the sample, COD_t, and final COD, COD_f, kinetic expression could be written as:

$$r_{COD} = \frac{dCOD}{dt} = -k\left(COD_t - COD_f\right)$$

Considering an ideal steady-state plug-flow reactor with mass transfer diagram in an definite volume dV,

$$Input = Output + Accumulation + Degradation$$

$$Q \cdot COD = Q \cdot (COD + dCOD) + 0 + rdV$$

$$-rdV = Q \cdot dCOD$$

Substituting the rate with the kinetic expression:

$$k\left(COD_t - COD_f\right)dV = QdCOD$$

Exchanging and integration will result in:

$$ln\frac{\left(COD_{out} - COD_f\right)}{\left(COD_{in} - COD_f\right)} = -k\tau$$

or $$\left(COD_{out} - COD_f\right) = \left(COD_{in} - COD_f\right)e^{-k\tau}$$

Note that τ represent the residence time of the reactor which is equal to volume divided by flow rate.

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

By some equation-solving effort, resulting COD of the effluent could be expressed as:

$$COD_{out} = COD_{in}(1 + \eta_{max}(e^{-kt} - 1))$$

where
$$\eta_{max} = 1 - \frac{COD_f}{COD_{in}}$$

Similar steps could also be used to derived an expression on mixed-flow basis

$$Input = Output + Accumulation + Degradation$$

$$Q \cdot COD_{in} = Q \cdot COD_{out} + 0 + rV$$

$$Q \cdot COD_{in} = Q \cdot COD_{out} + 0 + k(COD_{out} - COD_f)V$$

$$COD_{out} = \frac{(Q \cdot COD_{in} + kV \cdot COD_f)}{(Q + kV)}$$

Substituting
$$COD_f = (1 - \eta_{max})COD_{in}$$

$$COD_{out} = \frac{(Q \cdot COD_{in} + kV(1 - \eta_{max})COD_{in})}{(Q + kV)}$$

$$\frac{COD_{out}}{COD_{in}} = \frac{Q + kV(1 - \eta_{max})}{Q + kV} = 1 - \frac{\eta_{max}kV}{Q + kV} = 1 - \frac{1}{\left(\frac{1}{\eta_{max}k\tau} + \frac{1}{\eta_{max}}\right)}$$

Given the situation, a sono-Fenton reactor could be designed using some different configurations; varying the reactor size, for example, will result in different COD, as shown in *Figure 5.1* where obtained effluent COD at different reactor size, for both plug-flow and mixed-flow basis are plotted together. The chemical dosage used is 500 mg/L Fe^{2+} and 140 g/L H_2O_2, which give 87.7% maximum removal efficiency and 0.147 min^{-1} kinetic constant.

As shown in the figure, only 25 L of PFR reactor volume is already adequate to eliminate most COD of the wastewater, and first 50 L of CSTR reactor will lead to 80.1% of reduction, and increasing the volume further to 100 L will lead to only 3.6% of further removal.
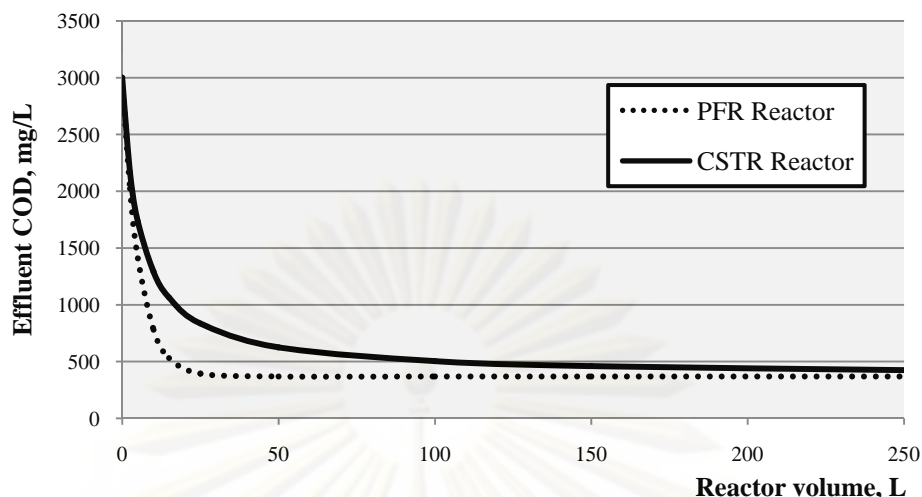
Figure 5.1 *Effluent COD from different reactor volume, 140 g/L H_2O_2, and 500 mg/L Fe^{2+}*

By changing the amount of added H_2O_2 while maintaining Fe^{2+}/H_2O_2 ratio will lead to changes of maximum achievable removal efficiency as previously estimated by the trend equation given in section 4.3.4 (equation predicting η_{max} from H_2O_2 dosage). Using this fact, varying amount of H_2O_2 will lead to different effluent COD shown in *Figure 5.2* and *Figure 5.3*. Note that when changes observed at larger reactor sized are much less than those of smaller reactor; moreover, it could be observed from *Figure 5.1* that minimal further degradation occur when increasing reactor volume beyond a certain point.
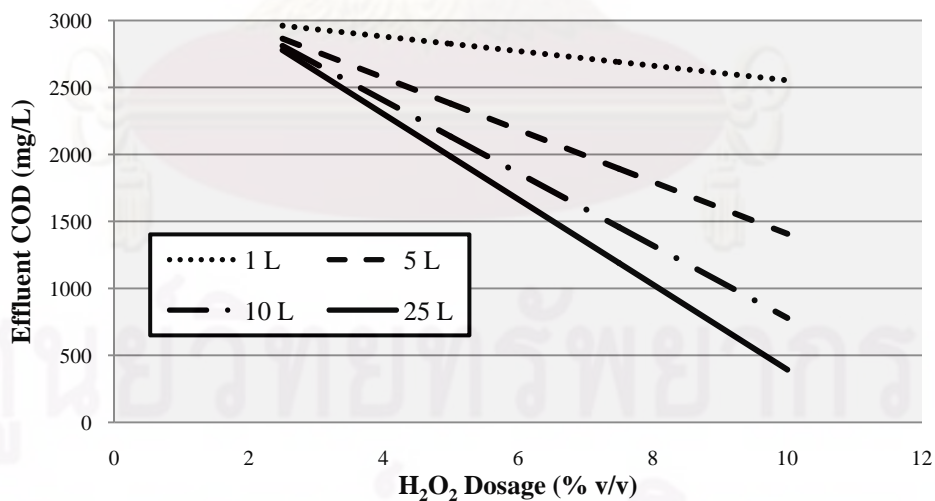
Figure 5.2 *Effluent COD obtained by different reactor size on plug-flow basis*
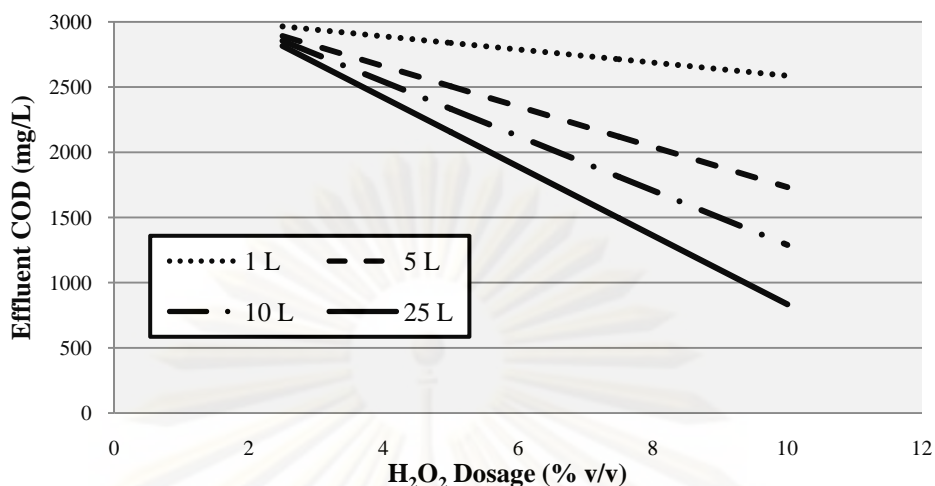
Figure 5.3 *Effluent COD obtained by different reactor size on plug-flow basis*

5.1.2 Energy consideration

Energy consumption during sono-Fenton process could be estimated using the assumption that energy distribution is uniform throughout the medium bulk. In the experiment, volume of the medium bulk is 6 L while total power input is 400 W, which will give power requirement as 66.7 W per liter of working volume. Note that it is possible to linearly increase the kinetic constant by increasing the power density of the ultrasonic irradiation, which could be done be adding more transducer, or reducing the total working volume (Jiang, Petrier, and Waite, 2002; Guo et al., 2005), but the extent of it could not be determined due to constraints imposed by the equipments used.

Since $$P_{Total} = P^*V$$

where $$P^* = Volumetric\ energy\ density = 66.7\ ^W\!/_{liter}\ in\ this\ study$$

$$V = Reactor\ volume$$

As one minute of operation will produce a certain amount of effluent, indicated by flow rate:

$$E_{Volume} = {P^*V}\!/_{Q} = P^*\tau$$

where $$E_{Volume} = Energy\ required\ per\ unit\ volume\ treated, J/L$$

Therefore, it could be clearly seen that total energy consumption depends on only one factor which is retention time of the reactor.

5.1.3 Chemical uses

Chemical uses during sono-Fenton process could be categorized into three main functions: pH adjustment, oxidant, and catalyst. Acid and base are required since the oxidation was found to be effective at extreme pH, and treated water too required to be stabilized to make it eligible to be disposed or for the effectiveness of post-treatment processes. The required amount of oxidant, H_2O_2, and catalyst, $FeSO_4$, could be determined using the reaction kinetic equation where the efficiency is highly dependent on these two parameters.

Due to the fact that hydrogen peroxide and ferrous reagent are kept in acidic regime, little pH adjustment are required to reduce the pH of the sample below 2.0, and approximately one milliliter of 1 N H_2SO_4 are required for 100 mL sample in this study, which is equal to 10 mL/L sample. However, the amount could be highly varies by situations since the characteristics of the wastewater are certainly differs from this study, and the amount of pH adjustment required should be separately determined.

Amount of required hydrogen peroxide could range from 14 to 140 g/L, which is considerably high. For example, when the process requires 140 g/L H_2O_2, 0.5 liter of 30% H_2O_2 solution should be added into a liter of wastewater. The required dosage of hydrogen peroxide oxidant at different supplied concentration to obtain desired concentration is shown in *Figure 5.4*.
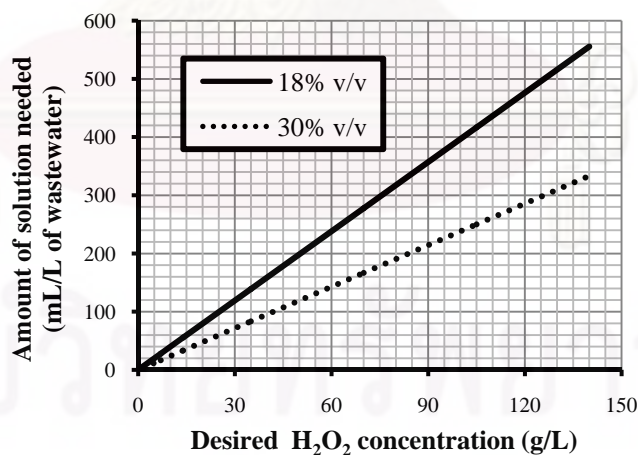
Figure 5.4 *Amount of H_2O_2 solution required per a liter of wastewater to obtain desired concentration*

On the other hand, $FeSO_4$ is usually supplied as solids, but care should be taken when determining the desired dosages, since it could exist in different mineral form, and the actual amount of $FeSO_4 \cdot nH_2O$ required to obtain the desired amount of Fe^{2+} could be obtained by multiplying it with factors given in *Table 5.1*.

Table 5.1 *Mass-based conversion factors between forms of FeSO₄ and Fe²⁺*

Forms	Formulae	$FeSO_4 \rightarrow Fe^{2+}$	$Fe^{2+} \rightarrow FeSO_4$
Anhydrous*	$FeSO_4$	0.37	2.71
Szomolnokite	$FeSO_4 \cdot H_2O$	0.33	3.04
Rozenoite*	$FeSO_4 \cdot 4H_2O$	0.25	4.00
Siderotil	$FeSO_4 \cdot 5H_2O$	0.23	4.32
Ferrohexahydrite	$FeSO_4 \cdot 6H_2O$	0.22	4.64
Melanterite*	$FeSO_4 \cdot 7H_2O$	0.20	4.96

*Common

Note that the amount of oxidant and catalyst to be added should be determined using kinetic and trends discussed in previous part.

5.1.4 Design

After aspects were considered, sono-Fenton as a treatment process could be designed. The reactor to be used will be based on mixed-flow basis, given that ultrasonic irradiation itself could provide intensive mixing. Selected reactor volume to be used is 50 liter, amount of chemical to be used are 140 g/L H_2O_2 and 500 mg/L Fe^{2+}, which will result in 80.6% of COD reduction, and the effluent is expected to contain 625 mg/L of COD. Lower effluent COD, 369 mg/L, could be obtained by changing the reactor to operate on plug-flow basis, but the design would be more complicate due to constraint of ultrasonic transducer installation and operation.

Since the selected reactor volume is 50 L, its retention time could be calculated along with the energy requirement.

$$\tau = V/Q$$

$$\tau = \frac{50 \, L}{(1000 \, L/day)(1/24 \, day/hours)(1/60 \, hour/minutes)}$$

$$\tau = 72 \ minutes$$

Energy requirement per unit volume of wastewater treated:

$$E_{Volume} = P^*\tau$$

$$E_{Volume} = (66.7 \ W/L)(72 \ minutes)(60 \ seconds/minutes)$$

$$E_{Volume} = 288.1 \ kJ/L \approx 0.08 \ kWh/L$$

Chemical used will be supplied as 30% H_2O_2 and $FeSO_4 \cdot 7H_2O$, and it could be found from the chart (*Figure 5.4* and *Table 5.1*) that approximately 300 mL of H_2O_2 solution and 2.5 g of solid $FeSO_4 \cdot 7H_2O$ should be added into a liter of wastewater to obtained the desired H_2O_2 and Fe^{2+} concentration. Moreover, since there is 1,000 liter of wastewater to be treated in a day, daily consumption of H_2O_2 solution and solid $FeSO_4 \cdot 7H_2O$ should be 300 liters and 2.5 kg, respectively.

However, it is apparent that the treatment goal has not been yet achieve, since COD of the effluent is equal to 625 mg/L which still exceed 120 mg/L regulated standard. Therefore, use of post-treatment process, especially biodegradation, is highly necessary, but the chemical dosages during sono-Fenton still pose problems to subsequent processes. The effluent will be acidic, contains great amount of metallic ions, and hydrogen peroxide which is highly toxic to microorganism and could easily foul biodegradation process.

Nevertheless, adjusting pH to neutral regime could alleviate such problems, as (1) the acidic condition could be neutralized, (2) increasing pH lead to precipitation of iron salts, and (3) hydrogen peroxide will be less stable and self-decomposition will be rapid. Thus, water-retaining basin should be coupled between the pH adjustment and post-treatment process to make sure that iron salts are completely precipitate and hydrogen peroxide mostly eliminated.

Table 5.2 *Parameters and aspects of designed sono-Fenton process*

Parameters and aspects	Description
Wastewater	
Flow rate	1 m^3/day (0.69 L/min)
COD	3,051 mg/L
Reactor	
Reactor size	50 liter
Flow condition	mixed flow (CSTR)
Retention time	72 minutes
Energy	
Energy density	66.7 W/L
Power input	3.34 kW
Energy consumption	288.1 kJ per liter of wastewater
Chemical: H_2O_2	
Required dosage	140 g/L
Daily consumption	300 liters of 30% H_2O_2
Chemical: $FeSO_4$	
Required dosage	500 mg/L of Fe^{2+}
Daily consumption	2.5 kg of $FeSO_4 \cdot 7H_2O$
Chemical: pH adjustment	
Optimal pH	1.7
Output	
Expected effluent COD	625 mg/L
Expected effluent pH	1.7
Support operations	
Post-treatment process	To reduce remaining COD
Conditioning	Adjust pH back to acceptable range
Chemical elimination	Eliminate remaining Fe^{2+} and H_2O_2

30% H_2O_2: 300 mL

$FeSO_4$: 2.5 g

H_2SO_4 (pH)

COD = 3051 mg/L

pH ~ 7

Influent

50 – L sono-Fenton reactor

COD = 625 mg/L

pH ~ 1.7

Effluent

Post-treatment

10% H_2O_2

500 mg/L Fe^{2+}

pH 1.7
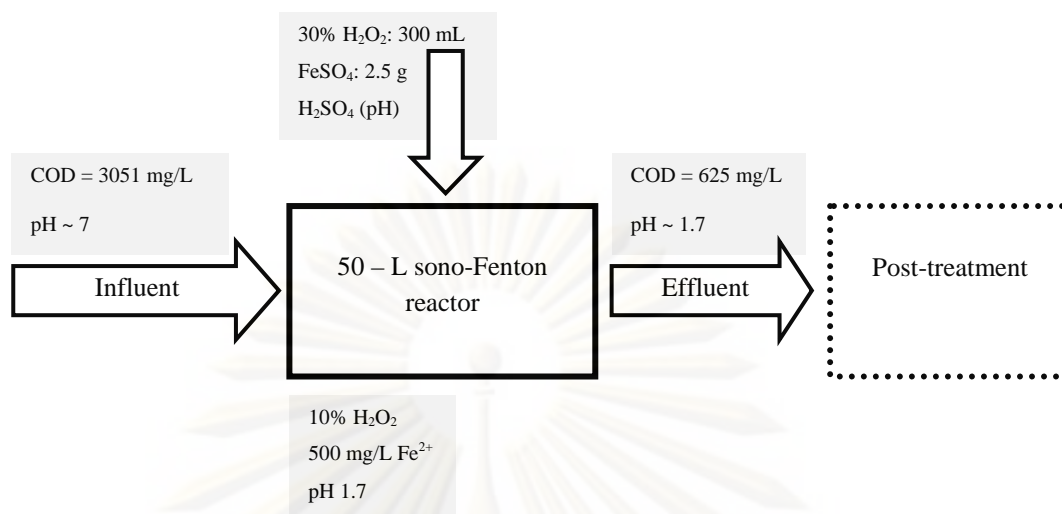
Figure 5.5 *Components of the designed sono-Fenton process*

5.2 CONVENTIONAL SEPARATION PROCESS

In this part, coagulation will be employed as it is one of the simplest physicochemical separation processes.

5.2.1 Energy consideration

For comparison purpose, energy required will be evaluated in this part. The only energy consumption during coagulation, however, is for the mixing. As already previously described, mixing power needed to obtain the adequate mixing could be expressed as

$$P = G^2 \mu V$$

The relation between velocity gradient (G), mixing volume (V), and mixing energy (P) is presented in *Figure 5.6* for rapid mixing and *Figure 5.7* for slow mixing. Ranges used in this study were represented by shaded area. Note that the chart was plotted in logarithmic scale to "linearlize" relations in the charts.

$$\log P = \log(G^2 \mu V)$$

$$\log P = 2 \log G + \log \mu V$$
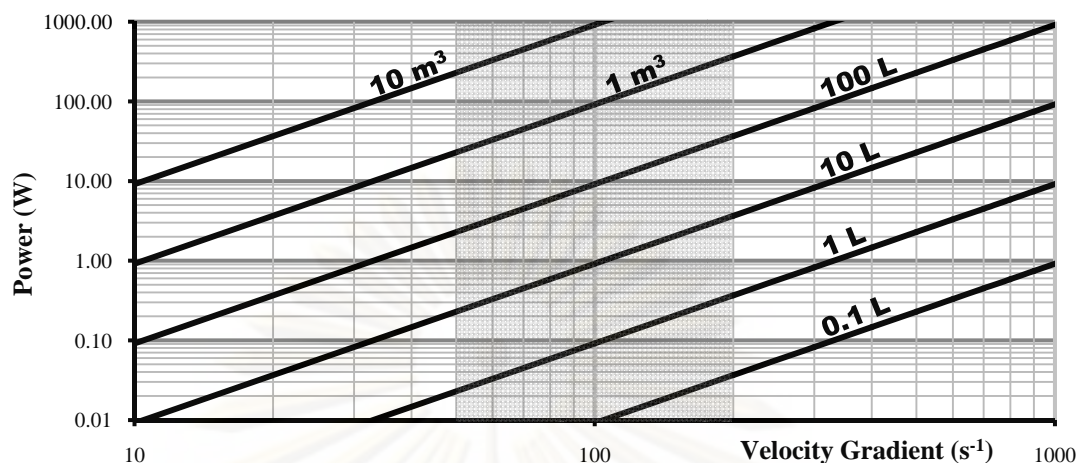
Figure 5.6 *Relation between mixing volume, velocity gradient, and mixing power(rapid mix)*
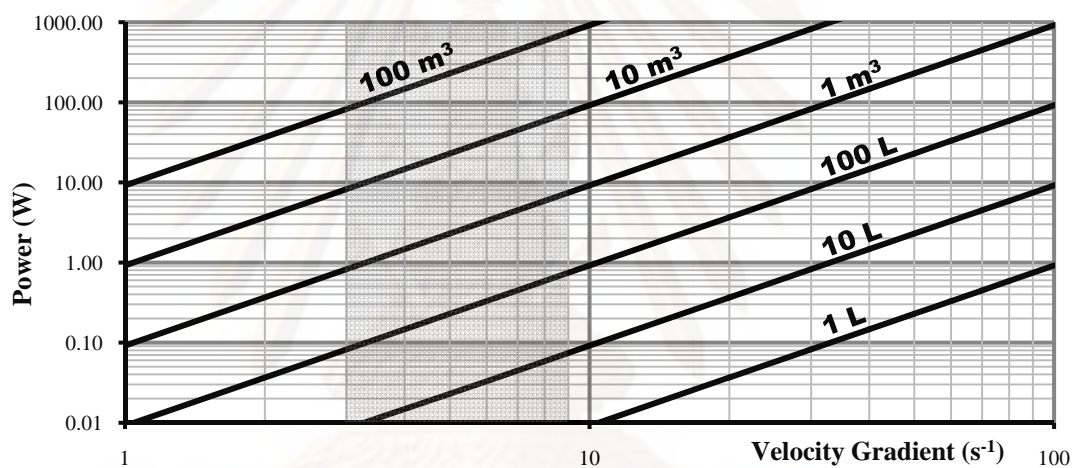
Figure 5.7 *Relation between mixing volume, velocity gradient, and mixing power(slow mix)*

The mixing power itself does not correctly represent total energy consumption, since duration it is being imparted into the liquid also matters. Total energy required (joule or kilowatt-hour) could be obtained as the product between power and time:

$$E = Pt = (G^2 \mu V)t$$

$$E = G^2 \mu (Qt)t$$

$$E = (Gt)^2 \mu Q$$

or $$\log E = 2 \log Gt + \log \mu Q$$

Where E represents the required energy (joule per mixing volume) and Q represents wastewater flow rate (m^3/s). Note that the energy expressed here is those consumed during the

treatment of one mixing volume of wastewater; for example, when mixing volume used is 1 L, the energy here should be expressed as joules per a liter of treated wastewater. Similarly, *Figure 5.8* and *Figure 5.9* presents the energy consumption during mixing with different $G \cdot t$ value and the mixing volume.
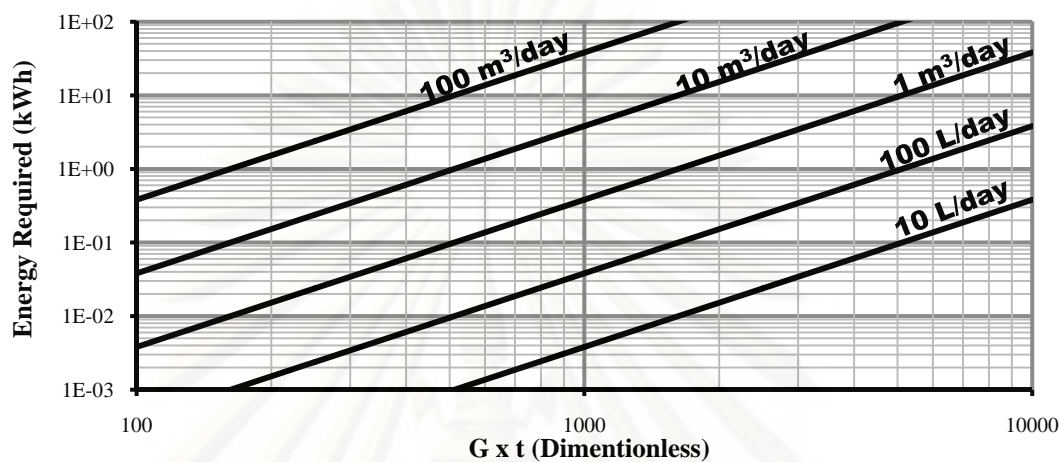
Figure 5.8 *Relation between flow rate, G x t value, and mixing energy (rapid mix)*
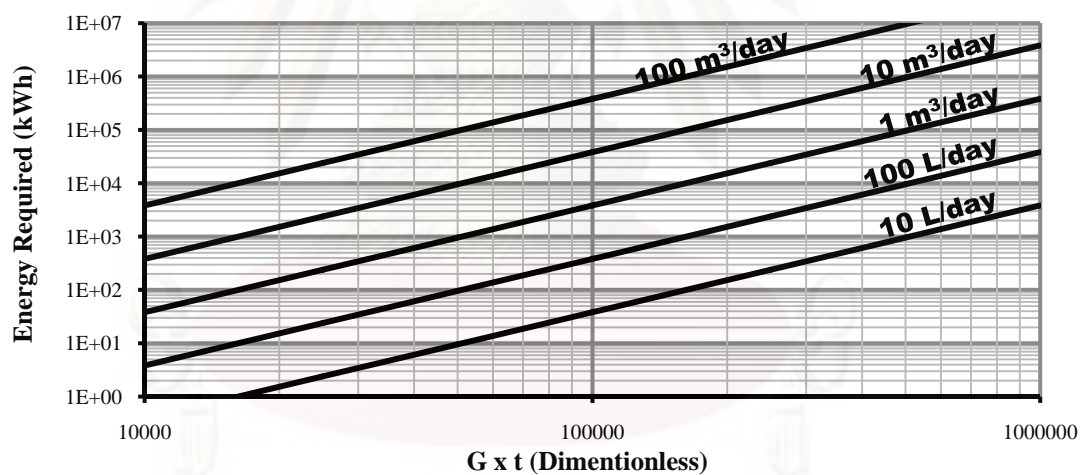
Figure 5.9 *Relation between flow rate, G x t value, and energy requirement of (slow mix)*

Note that the charts presented within this section were derived by assuming that viscosity of the emulsion is 9.16 cps which is the actual value measured from 0.1% sample, and great care should be taken when applying it on other medium of different viscosity.

5.2.2 Design

Using the study's finding and recommended guidelines, conventional coagulation process could be designed. The process consists of rapid mixing, slow mixing, and decantation. Each of the process would be separately determined and designed.

First of all, coagulation will be conducted within a mixing tank with mixing time equals to one minute and velocity gradient used is 100 s^{-1}. These values were previously found to give appreciable removal. From the flow rate given and mixing time indicated, mixing volume could be determined as:

$$V = Q\tau$$

$$V = (1000 \ L/day)\left(\frac{1}{24} \ day/hour\right)\left(\frac{1}{60} \ hour/minute\right)(1 \ minute)$$

$$V = 0.69 \ Liter$$

Given the volume and required velocity gradient, mixing power could be calculated using either the diagram presented or the equation on velocity gradient.

$$P = G^2 \mu V$$

Using either ways, required power is approximately 0.1 W, and energy consumption per unit volume is:

$$E_{Volume} = P/Q$$

$$E_{Volume} = \frac{(0.1 \ J/s)(60 \ s/min)}{(0.69 \ L/min)} = 8.7 \ J/Liter$$

After that, flocculation will be conducted in an adjacent tank, with mixing time of ten minutes and 5 s^{-1} velocity gradients. Using given flow rate and mixing time required, mixing volume could be determined by steps similar to designing rapid mixing process.

$$V = Q\tau$$

$$V = (1000 \ L/day)\left(\frac{1}{24} \ day/hour\right)\left(\frac{1}{60} \ hour/minute\right)(10 \ minute)$$

$$V = 6.9 \ Liter$$

Mixing power and energy too could be obtained using the same method:

$$P_{Mixing} \approx 0.02 \text{ W}$$

$$E_{Volume} = P/Q$$

$$E_{Volume} = \frac{(0.02\,J/s)(60\ s/min)}{(0.69\ L/min)} = 1.7\,J/Liter$$

Total energy required is

$$E_{Volume} = (8.7 + 1.7)\,J/liter = 10.4\,J/Liter$$

Assuming that the mixing equipment is able to convert 60% of its total power consumption into mixing power imparted into the liquid body:

$$E_{Volume,Consumed} = \frac{10.4}{0.6}\,J/liter = 17.3\,J/Liter$$

The energy found is significantly lower than those consumed using acoustic oxidation, which is 15,000 times higher.

Chemical uses will be supplied as 100 g/L alum solution, and 1.5 mL of should be added in to a liter of wastewater to achieve 150 mg/L alum dosage which is known to give effective coagulation. Thus, daily consumption of chemical should be equal to

$$V_{Alum} = (1.5\ mL/liter)(1000\ Liter/day) = 1.5\,L/day$$

which will equal to:

$$M_{Alum} = (1.5\,L/day)(100\,g/L) = 150\,g/day$$

Finally, sedimentation process will be coupled after the flocculation process, using the criteria provided by Kawamura (2000) for sedimentation tanks aimed for removal of flocculated suspended matter. Detention time is selected to be an hour, since the experiment shows that 15 minute is adequate to allow effective sedimentation in 15-cm-high beaker. Therefore, the tank volume would be:

$$V_{Tank} = (0.69\ L/min)(60\ min/hour) = 41.4\,L$$

Selected tank dimension would be 50 cm depth, 25 cm width, and 60 cm long. The length was extended as a precaution. Horizontal flow velocity in the tank will be:

$$v_H = (0.69 \times 10^{-3} \ m^3/min)(0.5 \times 0.25 \ m^2) = 5.5 \times 10^{-3} \ m/min$$

The flow velocity is low enough to maintain laminar flow regime. The overflow rate of this tank will be:

$$v_H = (0.69 \times 10^{-3} \ m^3/min)(0.6 \times 0.25 \ m^2) = 4.6 \times 10^{-3} \ m/min$$

The value is far lower then the recommended criteria, which indicate that, in fact, smaller decantation tank could be used, but space should be allowed for installation of operation appurtenances.

Too, as the result shown, treatment goals may not yet be fulfilled, since separation process could remove only the suspended portion of pollutants. Therefore, post-treatment process should be employed, but care should be taken in process design since some remaining compounds could be highly toxic to microorganism, especially fluid preservation and biocides.

Moreover, amount of oily sludge generated by separation processes too should be concerned since there should be handling and management facilities as well as disposal method. Assuming that 10% of wastewater volume is removed along with the sludge, 0.1 L of oily sludge will be produced from a liter of wastewater, and daily production of such sludge will be 100 L.

Table 5.3 *Parameters and aspects of designed conventional coagulation process*

Parameters and aspects	Description
Wastewater	
Flow rate	1 m^3/day (0.69 L/min)
COD	3,051 mg/L
Rapid mixing	
Tank size	0.7 liter
Velocity gradient	100 s^{-1}
Mixing power	0.1 W
Mixing time	1 minute
Gt	6000
Slow mixing	
Tank size	7.0 liter
Velocity gradient	5 s^{-1}
Mixing power	0.2 W
Mixing time	10 minute
Gt	3000
Sedimentation	
Tank dimension	25 cm width
	60 cm long
	50 cm deep
Horizontal velocity	5.5 mm/min
Overflow rate	4.6 mm/min
Chemical: Alum	
Required dosage	150 mg/L as alum
Daily consumption	150 g of solid alum
Chemical: pH adjustment	
Optimal pH	7.0
Output	
Expected effluent COD	270 mg/L
Expected effluent pH	~7
Daily sludge generation	100 liters

Parameters and aspects	Description
Support operations	
Post-treatment process	To reduce remaining COD
Conditioning	To adjust characteristics to compliance
Sludge handling	Store and stabilize generated oily sludge

150 mg/L alum

COD = 3051 mg/L

pH ~ 7

Influent

0.7 L rapid mixing tank

7 L slow mixing tank

75 L sedimenta-tion tank

COD = 270 mg/L

Effluent
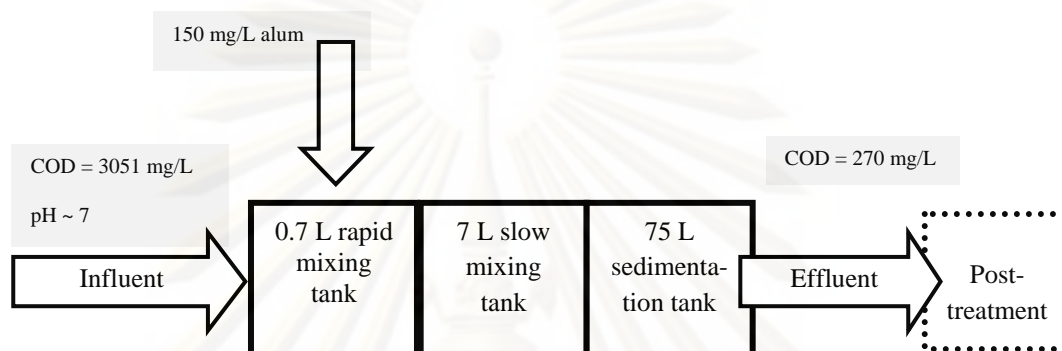
Post-treatment

Figure 5.10 *Components of designed coagulation process*

5.3 ADVANCE OXIDATION PROCESSES AS THE POST-TREATMENT

As separation processes could remove only suspended portion of organic compounds, post-treatment process should be employed in order to eliminate all remaining organic substances within the separated water. Biodegradation is the one most commonly used, but it might not be appropriate for this type of wastewater, since it could contains substances toxic to microorganism. Therefore, this part of the study will propose advance oxidation process as an alternative post-treatment method. Note that acoustic oxidation with hydrogen peroxide was selected to be the AOPs here, since it is the simplest configuration, given that only single reagent (H_2O_2) is required while it still could completely oxidize the remaining pollutants.

The oxidation process selected will be acoustic oxidation with 1.4 g/L hydrogen peroxide, which will results in pseudo-first-order kinetic constant of 0.035 min^{-1}, as previously estimated. Wastewater being oxidized may contains COD as high as 270 mg/L, and expected COD of the effluent was plotted against reactor volume in *Figure 5.11*.
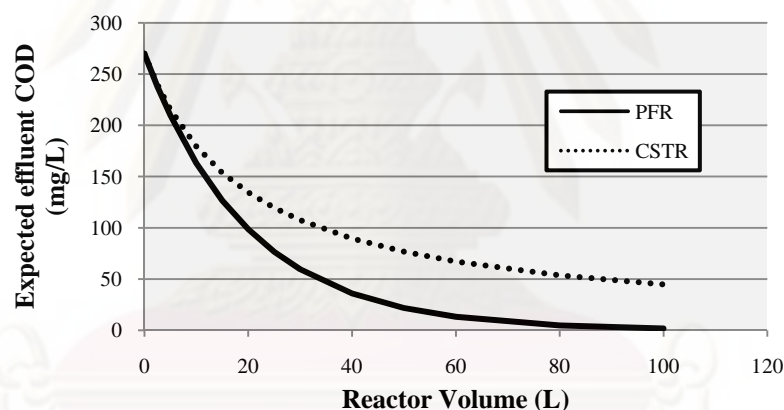
Figure 5.11 *Expected COD of the effluent of post-treatment AOPs*

It could be seen from the figure that only 40 L of reactor volume is already adequate to reduce COD of the wastewater below 100 mg/L, which complies with the regulation. Moreover, it is also possible to further increase the volume to 80 L to obtain further removal, where COD nearly reach undetectable level for PFR and approximately 50 mg/L for CSTR.

As the design of PFR sonochemical reactor is certain to be more complex, 80-L CSTR reactor will be used, and the expected COD of the effluent will be 54 mg/L.

After that, energy requirement per unit volume of wastewater treated could be calculated using steps similar to sono-Fenton:

$$E_{Volume} = P^*V/_Q$$

$$E_{Volume} = \frac{(66.7\,W/L)(80\,L)(60\,s/min)}{(0.69\,L/min)} = 464\,kJ/L$$

When both energy consumption of separation process and AOP post-treatment are combined together, total energy consumption is:

$$E_{Total} = E_{Separation} + E_{Oxidation}$$

$$E_{Total} = 17.3\,J/L + 464\,kJ/L = 464\,kJ/L$$

which is considerably higher than *288.1 kJ/L* of sono-Fenton oxidation.

Only chemical used in this process is 1.4 g/L hydrogen peroxide, which could be achieved by adding approximately 6 mL of 18% H_2O_2 or 3.5 mL of 30% H_2O_2 into a liter of wastewater. If 18% H_2O_2 was selected, daily consumption of chemical would be 6 L of H_2O_2 and an amount of pH adjustment as a conditioning step prior to disposal or reuse.

Note that the reactor size and energy requirement of this design process are still considered high, and these could be reduced by using instead Fenton or sono-Fenton of greater kinetic constants.

Table 5.4 *Parameters and aspects of post-treatment by acoustic oxidation*

Parameters and aspects	Description
Wastewater	
Flow rate	1 m^3/day (0.69 L/min)
COD	270 mg/L
Reactor	
Reactor size	80 liter
Flow condition	mixed flow (CSTR)
Retention time	116 minutes
Energy	
Energy density	66.7 W/L
Power input	53.4 kW
Energy consumption	464 kJ per liter of treated wastewater
Chemical: H$_2$O$_2$	
Required dosage	1.4 g/L
Daily consumption	6 liters of 18% H$_2$O$_2$
Output	
Expected effluent COD	54 mg/L
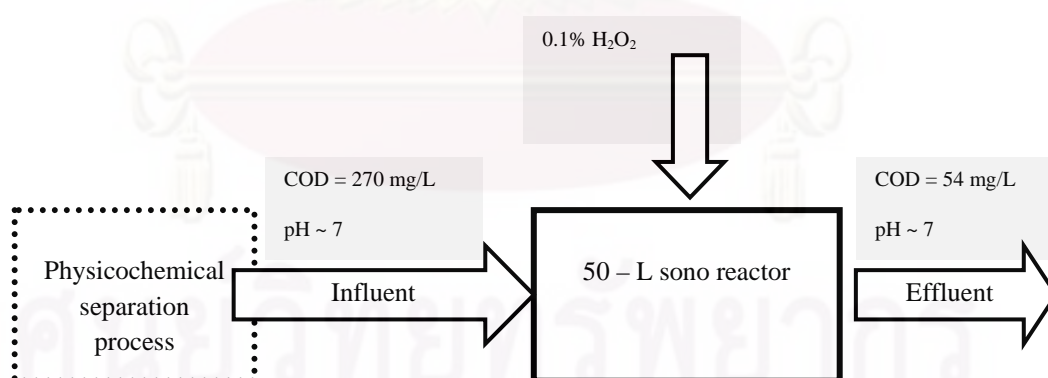
Figure 5.12 *Components of designed post-treatment by acoustic oxidation*

5.4 PROCESSES COMPARISON

After all important aspects of the methods proposed were investigated, they could be then summarized and shown in *Table 5.4*. It could be implied from the table that while sono-Fenton oxidation is simpler and does not produce sludge, it consume great amount of chemical and energy compared to those in conventional coagulation process. It resulting wastewater are still not legally acceptable, and post treatment and conditioning are still required.

On the other hand, it is highly possible to use acoustic oxidation as a post-treatment process to completely mineralize leftover COD after separation process, and it could also be seen that while chemical usage is far lower than using sono-Fenton on fresh wastewater, it require larger reactor and greater amount of energy, but these could be reduced using other type of AOPs such as Fenton and sono-Fenton with greater oxidation rate. The process too has a merit that little COD was expected in the effluent, enabling it to be reused.

Note that to be able to equally compare the aspects, the processes should be based on the same removal efficiency; however, such comparison is impossible due to difference of characteristics determined in this study. Greatest obtainable removal of sono-Fenton, for instance, is 91.3%, and this value could be lower due to reactor configuration. The removal efficiency of coagulation is somehow stable near 90-95% and not as varied by the conditions as sono-Fenton process. Aim of using combined processes, too, is to *further increase the efficiency* of separation process, and comparing these processes on the same removal baseline would not be as sensible.

Instead, for the sake of normalizing, an alternative version of *Table 5.4* is presented in *Table 5.5*, where the energy consumption is reported as *energy consumed per gram of COD removed*.

Table *5.5* *Comparison of designed processes*

Processes	Components	Effluent COD	Energy required	Daily chemical uses	Support processes
Sono-Fenton oxidation	50-L CSTR reactor	625 mg/L	Ultrasonic: 288.1 kJ/L	300 liter of H_2O_2 2.5 kg of $FeSO_4 \cdot 7H_2O$	Post-treatment process Conditioning Iron precipitation H_2O_2 elimination
			Total: 288.1 kJ/L	**Total: 325 kg/day**	
Conventional coagulation	0.7-L Rapid mixing 7-L Slow mixing 75-L Sedimentation	270 mg/L	Rapid mix: 14.5 J/L Slow mix: 2.8 J/L	0.15 kg of Alum	Post-treatment process Sludge handing Conditioning
			Total: 17.3 J/Liter	**Total: 0.15 kg/day**	
Post-treatment: **Acoustic oxidation**	Coagulation process 80-L CSTR reactor	54 mg/L	Coagulation: 17.3 J/L Ultrasonic: 464 kJ/L	0.15 kg of Alum 6 liter of H_2O_2	Sludge handling Conditioning
			Total: 464 kJ/Liter	**Total: 6.15 kg/day**	

These values are not based on the same removal basis of removal efficiency, since these three processes differ by its inherent nature

Table 5.6 *Comparison of designed processes, normalized*

Processes	Components	Effluent COD	Energy required	Daily chemical uses	Support processes
Sono-Fenton oxidation	50-L CSTR reactor	625 mg/L	Ultrasonic: 121.3 kJ/g	300 liter of H_2O_2 2.5 kg of $FeSO_4 \cdot 7H_2O$	Post-treatment process Conditioning Iron precipitation H_2O_2 elimination
			Total: 121.3 kJ/g COD	**Total: 325 kg/day**	
Conventional coagulation	0.7-L Rapid mixing 7-L Slow mixing 75-L Sedimentation	270 mg/L	Rapid mix: 5.3 J/g Slow mix: 1.0 J/g	0.15 kg of Alum	Post-treatment process Sludge handing Conditioning
			Total: 6.3 J/g COD	**Total: 0.15 kg/day**	
Post-treatment: **Acoustic oxidation**	Coagulation process 80-L CSTR reactor	54 mg/L	Coagulation: 6.3 J/g Ultrasonic: 157.5 kJ/g	0.15 kg of Alum 6 liter of H_2O_2	Sludge handling Conditioning
			Total: 157.5 kJ/g COD	**Total: 6.15 kg/day**	

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS

6.1 CONCLUSIONS

This study determined the effectiveness of acoustic oxidation process on the treatment of cutting oil wastewater, which is difficult to be treated by other methods, but the results showed that acoustic oxidation is ineffective to significantly reduce COD of the wastewater using conditions proposed by this study. Unique characteristic of the waste as well as constraint of the equipments were suspected to be the causes of such ineffectiveness, and it was too found that adding hydrogen peroxide only led to slight removal.

Sono-Fenton process was then employed in order to increase the oxidizing power of the process, and it could be seen that as high as 90 percent of COD could be eliminated from the wastewater. The most appropriate Fe^{2+}/H_2O_2 ratio was found to be 3.6:1000, while increasing H_2O_2 dosage will improve COD removal efficiency to a certain value. There are also another alternative that cutting oil wastewater should be firstly treated by physicochemical separation, then the remaining dissolved compounds would be oxidized by acoustic oxidation processes. COD of the separated wastewater could be reduced to undetectable level using analysis method, giving treated water great potential to be indefinitely reused.

In order to obtain effective designs, kinetic form and equation should be known. It is found that sono-Fenton processes could rapidly reduce COD value to a certain constant value within as short as 15 minutes, but the constant value is varied by the efficiency which highly depends on the dosage of oxidant. In case of acoustic oxidation post-treatment, pseudo-first-order kinetic was instead observed of which is possible to reduce COD to nil, given adequate oxidation time.

Design cases were also made for identical situation, and the aspects of different processes obtained are compared. Apparently, the most economical method is conventional coagulation, but it produces oily sludge needed to be managed. Great amount of energy are required by sono-Fenton and acoustic oxidation post-treatment, but the latter requires far less chemical. Nevertheless, importance of each of the aspects will certainly varies by the required situation, and the process selection should be independently evaluated, using method similar to that used in this study, to make sure that the most appropriate process will be selected.

The conditions that give the greatest and fastest removal of each processes and the obtained efficiency is reported in the following *Table 6.1*.

Table 6.1 *Summarized conditions of processes that give the highest removal*

Process	Condition	COD removal efficiency
Acoustic oxidation	Any	None
Acoustic oxidation + H_2O_2	140 g/L H_2O_2	13.6%
Sono-Fenton	140 g/L H_2O_2 500 mg/L Fe^{2+} pH 1.7	91.3%
Coagulation	150 mg/L alum dosage pH 7	95.2%
Combined process	~90% removal by any separation processes 1.4 g/L H_2O_2 5 mg/L Fe^{2+}	99.9%

6.2 SUGGESTIONS

As already noted during the course of the research, uses of advance oxidation processes in the treatment of high-strength wastewater is energy and chemical intensive. Given the fact that oxidants in action exists only in minimal amount, and it is widely found that greater substrates concentration led to lower oxidation rate. This study suggest that to limit the use of energy and chemicals, acoustic oxidation and other AOPs should be instead employed as a post-treatment measure where complete removal of COD is achievable.

Furthermore, COD analysis of the sample taken during oxidation was subjected to numerous problems due to presence of hydrogen peroxide, a widely known oxidant employed in this study. Efforts and method to eliminate its interference are discussed in *Appendix A* that wholly dedicate to this issue. However, in order to avoid such sophistication, amount of organic substances should be represented by other parameters apart from COD. Note that UV absorbance too will be interfered since organic substances exist as suspended droplets in this study.

As the oxidation progress, there are certain to be intermediates generation via various pathways. It is possible to predict and simulate the process characteristics if the amount and structure of these intermediates are determined, but enormous efforts would be required since the substance itself could contain as much as half a hundred chemical; the composition also varies by thousands of commercial formulas. To make clearer the characteristic of oxidation processes, more complex but generalized kinetic model should be employed; for example, in the work of Portela et al. (2001b), kinetic model based on three substances was incorporated into hydrothermal oxidation, where in fact hundreds of substances in both aqueous and gaseous phase could exists.

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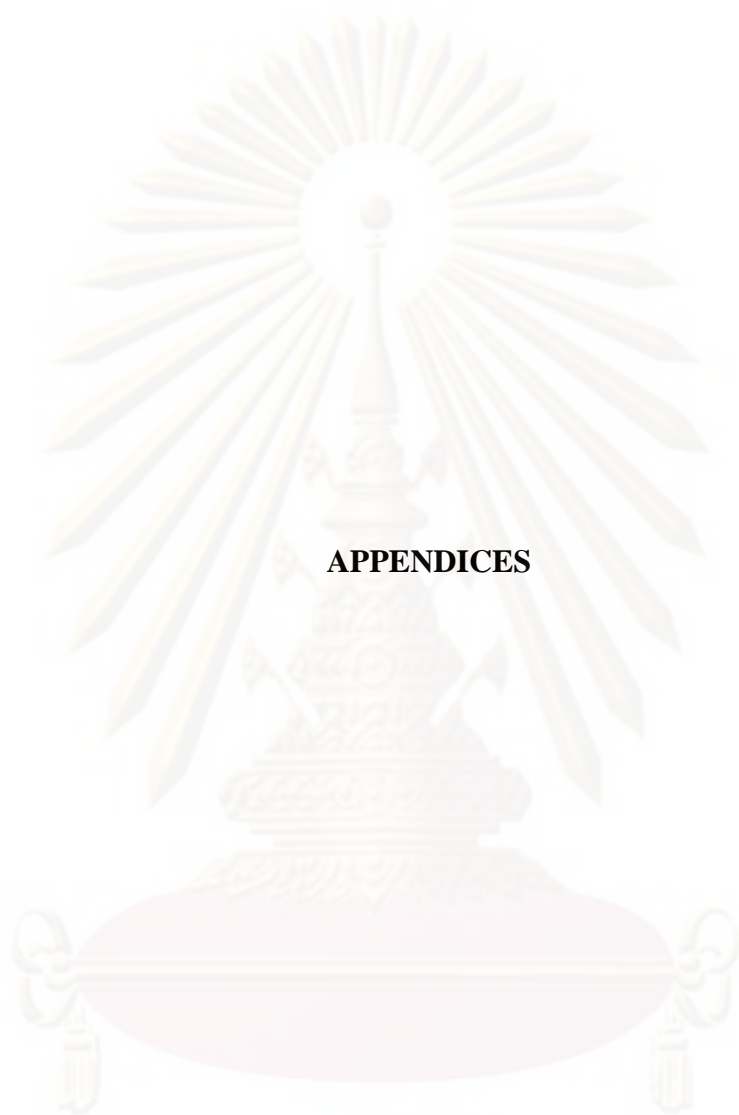
APPENDICES
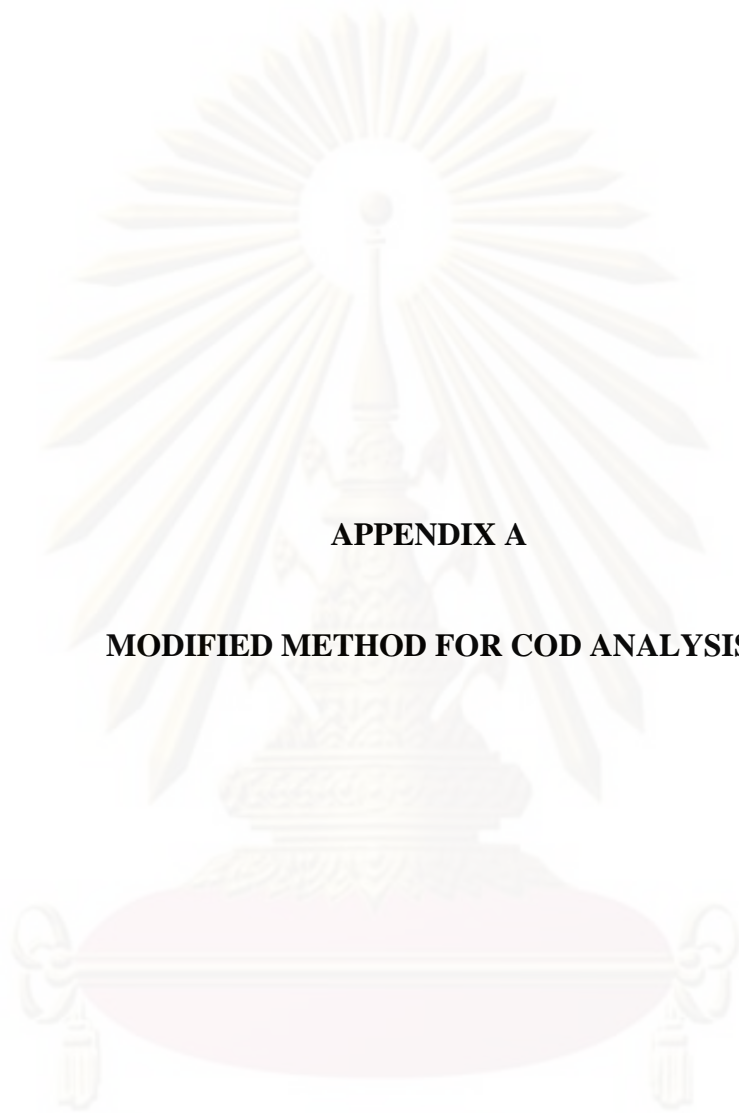
APPENDIX A

MODIFIED METHOD FOR COD ANALYSIS

A.1. Background: interference of hydrogen peroxide

Analysis of Chemical Oxygen Demand (COD) consists of using potassium dichromate ($K_2Cr_2O_7$) to represent actual oxygen molecule on the digestion of oxidizable substances, mainly organics. However, dichromate ions could normally react with inorganic species such as chloride and sulfate. Interference of these two species could be suppressed using mercuric sulfate and sulfamic acid.

On the other hand, hydrogen peroxide, which is used in this study as the primary oxidant, could also react with the dichromate as shown in the following equation:

$$K_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2$$
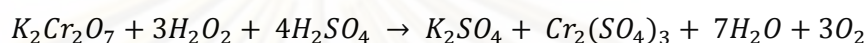
The equation shows that Cr^{6+} ion is oxidized by H_2O_2 into Cr^{3+} ion, which causes greenish color during COD test. Therefore, it could be implied that 1,000 mg/L of H_2O_2 produces 470.6 mg/L of COD value (Kang, 1999). However, as shown in *Figure A.1*, previous experiments found that COD/H_2O_2 ratios are always lower than 0.4706 (Kuo, 1992; Talinli and Anderson, 1992) which may be due to other oxidation pathways in acid condition:

$$H_2Cr_2O_7 + 5H_2O_2 \rightarrow H_2Cr_2O_{12} + 5H_2O$$
$$H_2Cr_2O_{12} + 8H_2O_2 \rightarrow Cr_2O_3 + 9H_2O + 8O_2$$
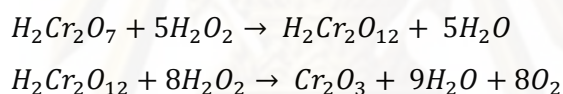
The pathways described give COD/H_2O_2 ratio of 0.108 which could be the cause of lower ratio obtained in actual experiments. Moreover, self-decomposition of hydrogen peroxide could also take place:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$
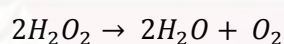
Talinli and Anderson (1992) tested a number of methods to eliminate the interference of H_2O_2 and found that aerating the sample did not help suppressing the interference. Masking agents such as potassium permanganate, sodium thiosulfate, and sodium azide could successfully removed H_2O_2 but cause other interferences instead.
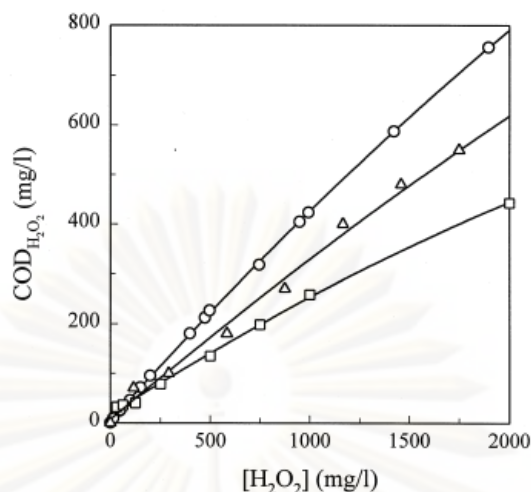
Figure A.1 *COD values of hydrogen peroxide obtained from three studies (Kang, 1999)*
o - *Kang (1999),* □ - *Talinli and Anderson (1992),* Δ – *Kuo (1992)*

A.2 Method A: correlation between hydrogen peroxide and COD

Kang et al. (1998) attempted to determine and eliminate the effect of H_2O_2 addition on the COD value by analyzing COD values of H_2O_2 solution. A second-order linear regression is then plotted, giving a derived equation:

$$COD_{H_2O_2} \ (mg/l) = \ 0.4591[H_2O_2] - (3.24 \times 10^{-5})[H_2O_2]^2$$

where $\qquad [H_2O_2] = concentration \ of \ hydrogen \ peroxide \ (mg/L)$

Using the equation, actual COD values could be calculated from the analyzed ones. The concentration of H_2O_2 could be directly measured by titration with KI, and actual COD value could be simply calculated by:

$$COD_{Actual} \ (mg/l) = \ COD_{Measured} - COD_{H_2O_2}$$

Therefore, to test the applicability this method, additional experiments are conducted in this study by adding 140 g/L hydrogen peroxide into the sample with known COD. Amount of hydrogen peroxide are measured using KI titration, and COD are then measured and corrected using above equations.

The amount of H_2O_2 obtained by KI titration is 124 g/L, which is considered close to the amount added, given that auto-decomposition of hydrogen peroxide could occur. COD value measured is 61.2 g/L oxygen, and COD of hydrogen peroxide that was calculated is

58.35 g/L. Corrected COD is 2.85 g/L or 2,850 mg/L, which is in close proximity of the actual one, 3,051 mg/L.

However, a closer look at the calculation step reveals that only 0.033 mL marginal at FAS titration would change the corrected COD for as high as 1,360 mg/L, which is due to high dilution ratio used. Such margin may be small compared to COD_{Actual}, but it will contribute to over 30% margin of corrected COD. Therefore, the resolution of this analysis method is surprisingly low. Moreover, careful accuracy and precision is vital to obtain actual value, but it is nearly impossible to attain since the titration endpoint of sample containing hydrogen peroxide is highly obscured.

It could be seen that despite the method success to quantify actual value of COD in the sample, this method give surprisingly low resolution of analysis, since COD of hydrogen peroxide contribute to over 90 percent of measured COD. Thus, it could be implied that this method is not appropriate for this study which employ large amount of hydrogen peroxide compared to substrate being oxidized.

A.3 Method B: elimination of hydrogen peroxide

Alternatively, hydrogen peroxide could be eliminated from the sample using different methods. Some methods were proposed and investigated by several groups of researchers, but with different outcome. For example, Talinli and Anderson (1992) who tried eliminating hydrogen peroxide by aeration, but found that aerated sample give the same value of COD as normal sample.

Additionally, it is also possible to accelerate self-decomposition of hydrogen peroxide by (1) increasing pH to neutral regime and (2) heating the sample. Heating is known to be able to induce rapid decomposition so that in many studies hydrogen peroxide was heated to immediately obtain great amount of dissolved oxygen (Portela, 2001a, Sanchez-Oneto et al., 2007).

Similarly, 140 g/L of hydrogen peroxide was added to the sample of known COD. It will be then heated by a hotplate stirrer to 60 $^{\circ}$C for one hour. A sample without hydrogen peroxide was too heated to determine COD reduction via heat-induced evaporation. After heating, COD of the samples will be then analyzed using KI titration correction.

COD analysis of the sample after one hour of heating is 2,720 and 2,811 mg/L for sample with and without hydrogen peroxide, respectively. This indicates that heating could effectively reduce the interference caused by great amount of hydrogen peroxide in the

sample, and all collected sample were heated at 60 $^{\circ}$C for one hour prior to COD analysis in this study.

Note that further degradation could occur during the heating and mixing when using Fenton's reagents where ferrous iron could react with hydrogen peroxide, giving more oxidative hydroxyl radicals. However, this could be prevented by adjusting the pH to neutral regime where Fe^{3+} will precipitate into $Fe(OH)_3$, preventing its catalytic properties.

A.4 Method C: indirect estimation of COD

As there are many samples to be analyzed for COD, and number of available equipments is very limited. Analyzing all the samples using above method consumes great amount of time and chemical reagents. Fortunately, alternative method to estimate COD value of the sample could be established by observing the analyzed parameter during the research.

Turbidity of any oily emulsion was long known to be proportional to amount of oil in the emulsion, since it directly indicates the number of oil droplets in the emulsion (Rios, Pazos, and Coca, 1996). Statistical analysis should be conducted in order to confirm that this two parameters correlates even when the oil emulsion is oxidized. Turbidity and COD of the samples after one hour of oxidation of different conditions are plotted against each other in *Figure A.2*.
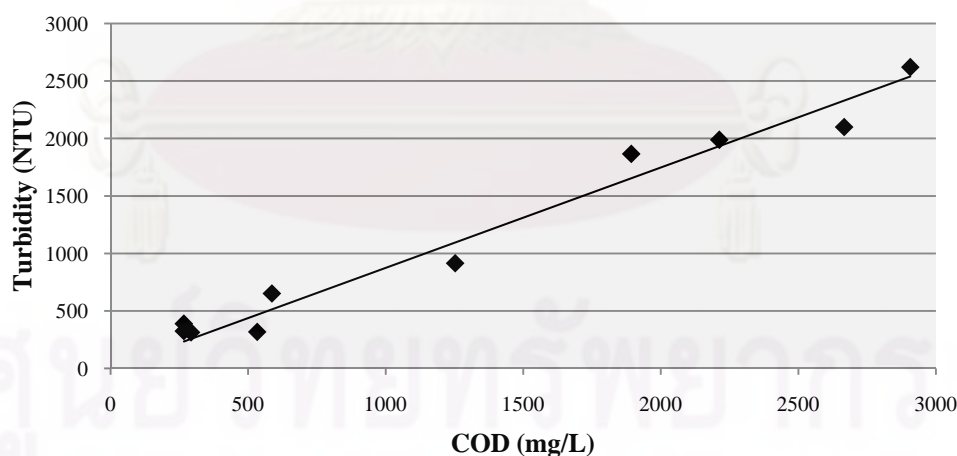
Figure A.2 *Turbidity of oxidized samples with different COD*

The figure shows that these two parameters are highly correlates, and Pearson's regression gave R-squared value equals to 0.970, confirming the correlation. Using this trend, COD of the sample could be then estimated using measured turbidity:

$$[COD] = \left(\frac{1}{0.873}\right)[Turbidity] \approx 1.15[Turbidity]$$

Where $[COD] = COD\ in\ mg/L$

                    $[Turbidity] = Turbidity\ in\ NTU$

This study, however, used this method only for estimating COD values of the sample for kinetic derivation. For the samples that indicate COD removal efficiency, direct analysis was instead used.

It is also worth noting that this estimation will give 2,653 NTU turbidity when COD is equals to 3,051 mg/L. The turbidity value is twice of those measured from "fresh" emulsion which is 1,250 NTU, but it rather close to the turbidity of emulsion irradiated by ultrasonic for a minutes, as previously shown in *Figure 4.3 - Figure 4.5*.
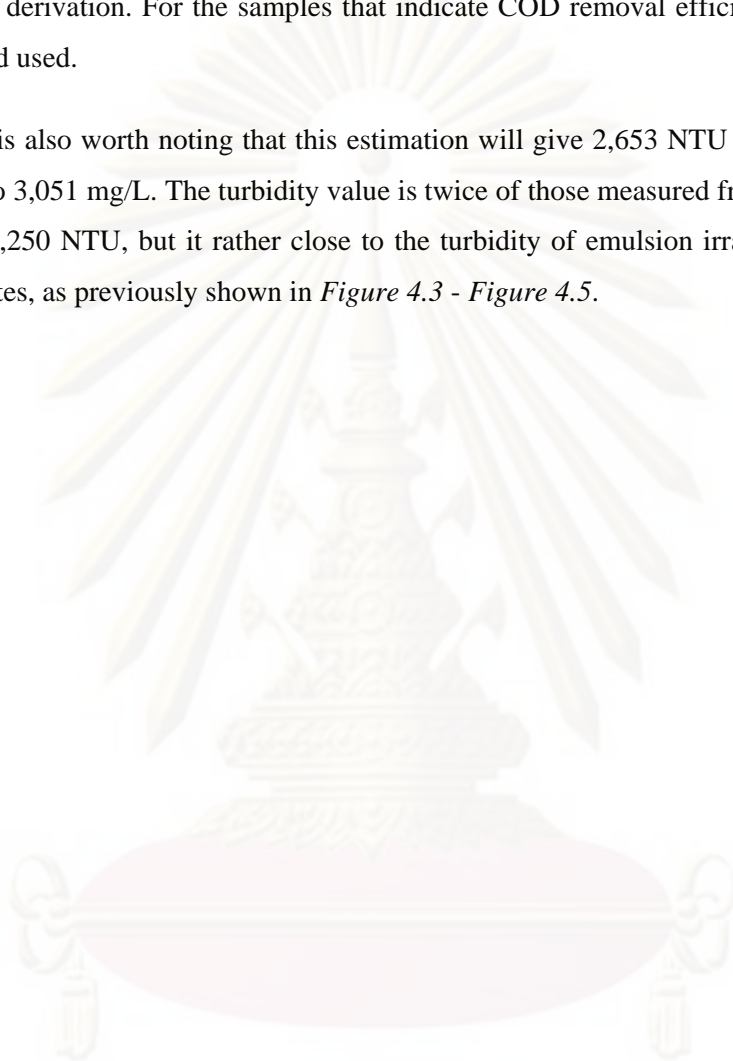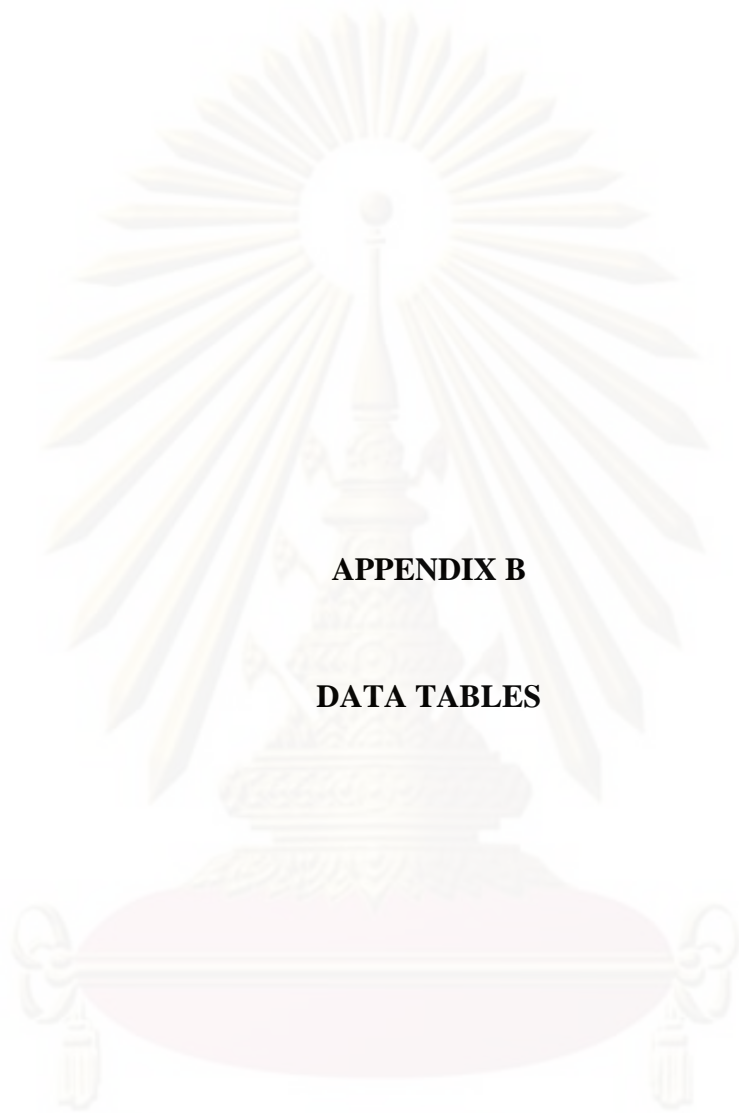
APPENDIX B

DATA TABLES

B.1 Decantation Process

Table B.1 *COD Obtained from Decantation process of 0.1% sample*

Decantation time	COD	%COD
Hours	mg/L	%
0	3051	100.0
1	3060	100.3
2	2924	95.8
3	3128	102.5
5	3060	100.3

Table B.2 *COD Obtained from Decantation process of 0.5% sample*

Decantation time	COD	%COD
Hours	mg/L	%
0	15531	100.0
1	14688	94.6
2	14688	94.6
3	16048	103.3
5	14960	96.3

Table B.3 *COD Obtained from Decantation process of 1.0% sample*

Decantation time	COD	%COD
Hours	mg/L	%
0	31893	100.0
1	31960	100.2
2	29240	91.7
3	27200	85.3
5	27880	87.4

B.2 Acoustic oxidation

Table B.4 *COD and turbidity during ultrasonic irradiation: 0.1% sample*

Irradiation time	COD		Turbidity
Minutes	mg/L	%	NTU
0	3051	100.0	1354
30	3196	98.1	1951
60	2924	104.8	2120
120	2924	95.8	2420
180	3264	95.8	2370
240	2856	107.0	2180
300	2992	93.6	2380

Table B.5 *COD Obtained from Acoustic oxidation process of 0.5% sample*

Irradiation time	COD		Turbidity
Minutes	mg/L	%	NTU
0	15531	100.0	6260
30	14144	91.1	7840
60	14960	96.3	8530
120	16048	103.3	12450
180	15776	101.6	13600
240	15776	101.6	13540
300	15504	99.8	13950

Table B.6 *COD Obtained from Acoustic oxidation process of 1.0% sample*

Irradiation time	COD		Turbidity
Minutes	mg/L	%	NTU
0	31893	100.0	12440
30	29920	93.8	14290
60	30600	95.9	16850
120	29240	91.7	18890
180	32640	102.3	22800
240	32640	102.3	22400
300	33320	104.5	23800

Table B.7 *COD Obtained from Acoustic oxidation process: 0.1% sample, 60 °C, and 400 W*

Irradiation time	COD, with ultrasonic		COD, without	
Minutes	mg/L	mg/L	%	%
0	3051	100.0	3051	100.0
1	2950	96.7	2885	94.6
2	2885	94.6	2831	92.8
5	2925	95.9	2865	93.9
10	2831	92.8	2831	92.8
15	2754	90.3	2654	87.0
30	2775	91.0	2775	91.0

Table B.8 *1-Hour COD removal obtained from acoustic oxidation with H_2O_2*

H_2O_2 Dosage	0.1% Sample		0.5% Sample		1.0% Sample	
g/L	mg/L	%removal	mg/L	%removal	mg/L	%removal
14	2938	3.7	14960	3.7	32096	-0.6
70	2774	9.1	14960	3.7	31552	1.1
140	2666	12.6	14688	5.4	30464	4.5
210	2666	12.6	14416	7.2	31008	2.8

B.3 Sono-Fenton oxidation

Table B.9 *Effect of pH on one-Hour COD value obtained from sono-Fenton oxidation*

pH	COD		Turbidity
	mg/L	%Removal	
1.0	760	75.1	603
1.3	680	77.7	587
1.5	720	76.4	622
1.7	533	82.5	414
2.0	173	94.3	112

Table B.10 *Effect of pH on one-Hour COD value obtained by adding only FeSO$_4$*

pH	COD		Turbidity
	mg/L	%Removal	
1.0	2667	12.6	2222
1.3	2613	14.3	2178
1.5	2747	10.0	2289
1.7	2560	16.1	2133
2.0	533	82.5	114

Table B.11 *Effect of Fe^{2+}/H$_2$O$_2$ ratio on one-Hour COD value obtained from sono-Fenton*

Fe^{2+}/H$_2$O$_2$ ratio	COD		Turbidity
	mg/L	%Removal	
0.7:1000	2667	12.6	2222
1.8:1000	1893	37.9	1578
3.6:1000	267	91.3	222
5.4:1000	587	80.8	489
7.1:1000	533	82.5	444

Table B.12 *H$_2$O$_2$ dosages on one-Hour COD value obtained from sono-Fenton oxidation*

H$_2$O$_2$ dosage	COD		Turbidity
g/L	mg/L	%Removal	
14	2907	4.7	2422
35	2667	12.6	2222
70	2213	27.5	1844
105	1253	58.9	1044
140	267	91.3	222
175	293	90.4	244

B.4 Coagulation of cutting oil emulsion

Table B.13 *Effect of pH on COD removal of coagulation process*

pH	Coagulant dosages					
	50 mg/L		100 mg/L		150 mg/L	
	COD	Removal	COD	Removal	COD	Removal
	mg/L	%	mg/L	%	mg/L	%
4	2474	18.9	3320	-8.8	2749	9.9
6	2231	26.9	3242	-6.3	3432	-12.5
7	1510	50.5	828	72.9	310	89.8
8	2348	23.0	2847	6.7	561	81.6
10	2576	15.6	2202	27.8	2400	21.3

Table B.14 *Effect of coagulant dosage on COD removal of coagulation process, 0.1% sample*

Dosage	COD	%Removal
mg/L	mg/L	%
25	2772	9.1
50	1510	50.5
100	828	72.9
150	310	89.8
200	662	78.3
250	497	83.7

Table B.15 *Effect of coagulant dosage on COD removal of coagulation process, 0.5% sample*

Dosage	COD	%Removal
mg/L	mg/L	%
200	7050	54.6
400	490	96.8
600	594	96.2
800	748	95.2
1000	826	94.7

Table B.16 *Effect of coagulant dosage on COD removal of coagulation process, 1.0% sample*

Dosage	COD	%Removal
mg/L	mg/L	%
500	18020	41.9
1000	9133	70.5
1500	1751	94.4
2000	1694	94.5
2500	12578	59.4

Table B.17 *Effect of rapid mixing conditions on COD removal of coagulation process*

| Velocity Gradient	Time	G x t	%COD Removal		
			0.1%	0.5%	1.0%
s^{-1}	s	s^{-1}	%		
88	0	0	93.8	94.2	93.0
88	15	1326	92.0	93.8	92.3
88	30	2652	90.2	94.0	89.3
88	45	3978	92.9	94.5	89.3
88	60	5304	95.1	95.5	89.7
67	60	4020	93.1	91.0	92.5
88	60	5280	94.5	94.9	95.5
111	60	6660	92.2	90.2	89.5
190	60	11400	93.7	90.1	89.5

Table B.18 Effect of rapid mixing conditions on COD removal of coagulation process

Velocity Gradient	Time	G x t	%COD Removal		
			0.1%	0.5%	1.0%
s^{-1}	s	s^{-1}	%		
2.1	1800	3780	91.1	95.7	91.0
3.3	1800	5940	91.6	95.3	92.0
4.6	1800	8280	92.4	95.8	90.0
6.0	1800	10800	92.0	95.8	93.3
6.0	300	1800	89.3	92.4	85.7
6.0	600	3600	92.0	95.7	87.7
6.0	900	5400	95.8	96.6	90.3
6.0	1200	7200	96.5	97.0	90.3
6.0	1500	9000	96.9	97.0	90.3

B.5 Post-treatment using AOPs

Table B.19 Advance oxidation results of coagulation effluents

Processes	COD values					
	Initial		30 minutes		60 minutes	
	mg/L	%	mg/L	%	mg/L	%
0.1%, Acoustic with H_2O_2			95	35	*	0
0.1%, Fenton's	270	100	*	0	*	0
0.1%, Sono-Fenton			*	0	*	0
0.5%, Acoustic with H_2O_2			375	50	75	10
0.5%, Fenton's	750	100	215	29	*	0
0.5%, Sono-Fenton			195	26	*	0
1.0%, Acoustic with H_2O_2			1690	65	650	25
1.0%, Fenton's	2600	100	1040	40	310	12
1.0%, Sono-Fenton			1144	44	200	8
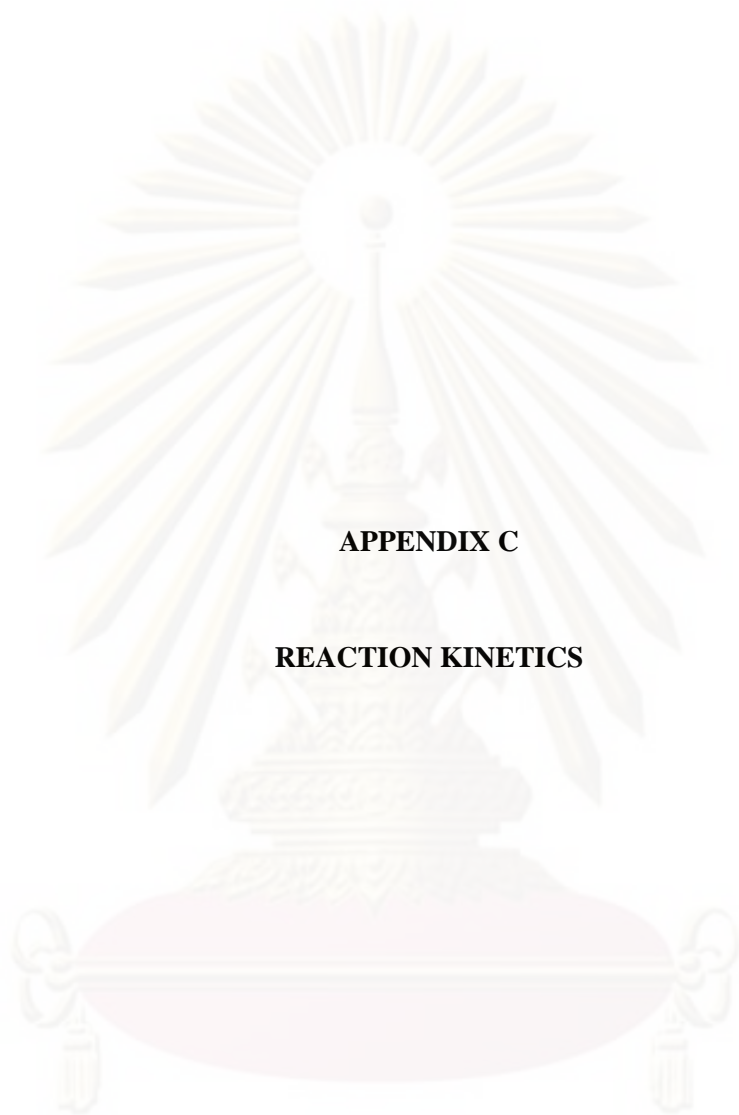
APPENDIX C

REACTION KINETICS

C.1 Methods used to derive kinetic parameters

As the kinetic expression proposed is different form normal ones, special methods apart form plotting in logarithm scale should be employed. The expression to be used is:

$$COD_t = COD_0 + COD_0\eta_{COD}(e^{-kt} - 1)$$

By assuming that maximum removal efficiency could be obtained after one hour of oxidation, removal by that time will be substituted as η_{COD}. After that, trial-and-error method will be employed to find the most appropriate value of k using the target function:

$$f = \sum(COD_{actual} - COD_{calculated})^2$$

While $COD_{calculated}$ will be obtained by substituting value of k into the equation until minimum amount of target function could be achieved. Note that this could be simply achieved using Solver® function which is an add-in of Microsoft Excel®.

C.2 Example

Example of data obtained is shown in *Figure C.1* and *Table C.1*, which is the same set of data shown in the main report.

Table C.1 Data example

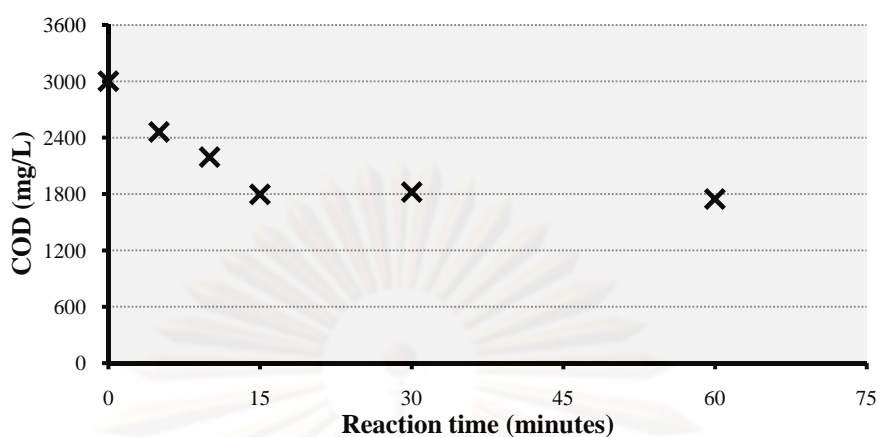| Time	COD
minutes	mg/L
0	3051
5	2460
10	2193
15	1795
30	1822
60	1746

Figure C.1 *Plot of data example*

COD_{calculated} could be then obtained by substituting equations with requires variables. For example, *Table C.2* shows the result obtained when using $k = 0.1$ min^{-1}, and *Table C.3* shows the result using $k = 0.126$ min^{-1}. These steps are then repeated until minimum value of function is obtained.

Table C.2 *Solving step, k = 0.1 min^{-1}*

Time	COD_{actual}	COD_{calculated}	Δ	Δ^2
minute	mg/l	mg/l		
0	3051	3051	0	0
5	2460	2538	78	6010
10	2193	2226	33	1094
15	1795	2037	242	58654
30	1822	1811	-11	122
60	1746	1749	3	10
			SUM	65890

Table C.3 *Solving step, k = 0.126 min^{-1}*

Time	COD$_{actual}$	COD$_{calculated}$	Δ	Δ^2
minute	mg/l	mg/l		
0	3051	3051	0	0
5	2460	2441	-19	360
10	2193	2116	-77	5903
15	1795	1943	148	21948
30	1822	1776	-46	2136
60	1746	1747	1	0
			SUM	30347

BIOGRAPHY

Mr. Tanun Chalermsinsuwan was born on May 30, 1986, in Bangkok, Thailand. Received a Bachelor's Degree of Engineering in 2008 from Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University. He attended the Master's Degree of Science at International Postgraduate Program in Environmental Management, Graduate School, Chulalongkorn University in 2008.