

CERTIFICATION OF APPROVAL

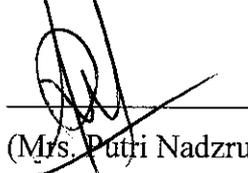
**Removal of Phenol and Benzene Using Photo Fenton Reagent**

By

Syarizan Mustapha

A project dissertation submitted to the  
Chemical Engineering Program  
Universiti Teknologi PETRONAS  
In partial fulfillment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
(CHEMICAL ENGINEERING)

Approved by,



(Mrs. Putri Nadzrul Faizura Megat Khamaruddin)

Main Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2003

I

t  
TD  
897  
.5981  
2003

1. Factory and track  
waste  
2. CHE -- thesis

## CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



---

SYARIZAN MUSTAPHA

## ABSTRACT

Industrial wastewater treatment has become an important issue in countries of the West Asia region, primarily due to the increasing concern associated with environment and health. This project is intended to address one major issue of wastewater management in petroleum refining industry; which is compliance with local EPA on their effluent discharge. Advanced Oxidation Processes (AOP) has the capability of total destruction of many organic pollutants. Particularly, photo-Fenton oxidation has recently emerged as a very promising technology because of its high efficiency and cost-effectiveness compared with other AOPs. The experiments were conducted in a small scale apparatus with constant monitoring of pH, temperature and UV source. In interpreting the result, one important assumption is that the degradation of phenol and benzene is directly related to the level of Chemical Oxygen Demand (COD) reduction, due to no available means to quantitatively determine the final concentration of both pollutants. Among parameters that are crucial to control in the experiment are Fenton reagent ratio, temperature, pH, reaction time and UV irradiation. Based on the experiment conducted, the optimum ratio of Fenton Reagent is  $\text{Fe}:\text{H}_2\text{O}_2=1:25$ , at COD reduction of 53.8%. The optimum temperature for operating photo-Fenton reaction is at  $40^\circ\text{C}$ , at COD reduction of 68%. This generally concludes that operating at higher temperature increases the degradation rate by 26% than operating at ambient temperature. However, trade-off between these parameters is essential for practicality, especially when cost and safety limit are of major elements to be considered in the design of wastewater treatment system. The result however does not portray the overall performance of photo-Fenton process since no direct correlation exists between the extents of COD reduction and photo-degradation rates of the studied compounds. Future recommendations are proposed to further enhance understanding and appreciable towards the photo-Fenton process in degrading refractory compounds. It is hoped that this project will contribute to the development of a new degradation technique in wastewater management.

## **ACKNOWLEDGEMENT**

Upon completing this Final Year Research Project, the author's would like to express her appreciation and gratitude, first of all to ALLAH, God the Al-Mighty, for giving her the strength and ability to carry out all the task and project given.

The author is vastly indebted to many people. First and foremost, sincere gratitude goes to the author's supervisor, Mrs. Putri Nazdrul Faizura Megat Khamaruddin who had been very helpful and supportive throughout this study. Her guidance and stimulating discussion session were greatly appreciated.

My appreciation to all technicians from Chemical Engineering Department, especially to Mr. Zaaba, Mr. Fauzi, Mr. Shaha and Mr. Mahadzir who had been very co-operative in helping and sharing their expertise with the author throughout the project

Million of thanks go to the author's colleagues who had been very supportive and thoughtful in sharing their ideas and support. Finally to the author's parents, love and thank you.

Thank you and may Allah SWT bless all of you.



<b>CHAPTER 3:</b>	<b>MATERIALS AND METHOD</b>	
3.1	Project Approach . . . . .	.25
3.2	Tools and Chemicals Required . . . . .	.27
3.3	Chemicals Preparation	
3.3.1	Preparation of Synthetic Wastewater.	.28
3.3.2	Preparation of Fenton Reagent . . . . .	.29
3.3.3	Preparation of Buffer Solution. . . . .	.30
3.4	Procedure Identification. . . . .	.31
3.5	Chemical Analysis. . . . .	.32
<b>CHAPTER 4:</b>	<b>RESULT AND DISCUSSION</b>	
4.1	Determination of Optimum Fenton Reagent Ratio	
2.1.1	Observations . . . . .	.33
2.1.2	Interpretation of Result . . . . .	.34
2.1.3	Effect of Hydrogen Peroxide Concentration.	.39
2.1.4	Effect of Iron Salt Amount . . . . .	.39
4.2	Determination of Optimum Temperature	
2.2.1	Observations . . . . .	.40
2.2.2	Interpretation of Result . . . . .	.40
2.2.3	Effect of Temperature . . . . .	.43
4.3	Other Parameters Affecting Photo-Fenton Reaction	
2.3.1	Effect of pH . . . . .	.44
2.3.2	Effect of UV Lamp Intensity . . . . .	.44
4.4	Error Justifications . . . . .	.45
<b>CHAPTER 5:</b>	<b>CONCLUSION AND RECOMMENDATIONS</b>	
4.5	Conclusion . . . . .	.46
4.6	Recommendations. . . . .	.47
<b>REFERENCES</b>	. . . . .	.50
<b>APPENDIX A-1:</b>	<b>EXPERIMENTAL RESULT</b>	

## LIST OF FIGURES

- Figure 2.1: Schematic of Chemical Reactions in Photo-Fenton Reaction
- Figure 2.2: Effect of pH on Reaction Efficiency
- Figure 2.3: Typical pH Profile of Fenton Reaction
- Figure 3.1: Experimental Setup for Photo-Fenton Experiment
- Figure 3.2: Equipment Used for COD Analysis
- Figure 4.1: COD Reduction of Photo-Fenton Process (Set 1)
- Figure 4.2: COD Reduction of Photo-Fenton Process (Set 2)
- Figure 4.3: COD Reduction of Photo-Fenton Process (Set 3)
- Figure 4.4: COD Reduction of Photo-Fenton Process as a Function of Temp. (Set 1)
- Figure 4.5: COD Reduction of Photo-Fenton Process as a Function of Temp. (Set 2)

## LIST OF TABLES

- Table 2.1: Relative Oxidation Power of Some Oxidizing Species
- Table 2.2: Reaction Rate Constants of Ozone vs. Hydroxyl Radical
- Table 2.3: H<sub>2</sub>O<sub>2</sub>/ozone/UV Treatment of BTEX and MTBE
- Table 2.4: Treatment of BTX (Pilot Plant Data Treating 3 Gpm with 120 minutes Retention Time)
- Table 2.5: Comparison of AOP Cost for a 650 Gpm Operating System
- Table 2.6: COD Reduction with H<sub>2</sub>O<sub>2</sub>/Ozone/UV
- Table 2.7: Parameter Limits of Effluent of Standards A and B
- Table 2.8: Sources of Pollutant in Petroleum Refinery
- Table 2.9: Effluent Requirement from Petroleum Refinery

Table 2.10: Physical and Chemical Properties of Phenol

Table 2.11: Physical and Chemical Properties of Benzene

Table 3.1: Equipment and Chemicals for Photo-Fenton Experiment

Table 3.2: Amount of Fenton Reagent Required

Table 4.1: COD Analysis from Photo-Fenton Reaction (Set 1)

Table 4.2: COD Level from Photo-Fenton Reaction as a Function of Temp (Set 1)

### **SPECIFIC DEFINITION AND ABBREVIATIONS**

1	UTP	University of Technology Petronas
2	FYP	Final Year Project
3	SV	Supervisor
4	AOP	Advanced Oxidation Processes
5	UV	Ultra-Violet
6	EPA	Environmental Protection Agency
7	COD	Chemical Oxygen Demand
8	BTEX	Benzene, Toluene, Ethylbenzene, Xylene
9	PCP	Pentachlorophenol
10	MTBE	Methyl Tert-Butyl Ether
11	CPI	Corrugated Plate Interceptor
12	APHA	American Public Health Association
13	AWWA	American Water Works Association
14	WEF	Water Environment Federation
15	PBT	Persistent, Bioaccumulative And Toxic
16	MSDS	Material Safety Data Sheet
17	HPLC	High Performance Liquid Chromatography
18	PPB	Parts Per Billion

# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND OF STUDY

Industries have long discharged their effluents into nearby river, public sewers, and sea, resulting in environmental and health problems. Over the past two decades, environmental regulatory requirements have become more stringent as increased awareness associated with environmental contaminants. Regulatory changes and public concern over the environment are requiring waste contributors to reduce their levels of pollutants in discharge wastewater to extremely low levels. Conventional wastewater treatment technologies, i.e. air stripping, carbon adsorption, biological treatment, have limitations. For example, stripping and adsorption merely transfer contaminants from one medium to another; whereas conventional chemical oxidation has low removal rates for pollutants. Aerobic biological oxidation is limited when the effluent discharges contains substances either refractory to biodegradation, or inhibitory to the bio-culture (Eckenfelder Jr., 1993).

The incapability of conventional wastewater treatment methods to effectively remove many refractory pollutants evidences that new treatment systems are needed. Various methods have been developed over the last 10 to 15 years for a cost-effective and environmental friendly technology for the treatment of industrial wastewater. Chemical treatment methods known as Advanced Oxidation Processes (AOP) are an attractive alternative for the treatment of contaminated ground, surface, and waste waters containing hardly-biodegradable substances. These AOP are useful complements to well established techniques like flocculation, precipitation, adsorption on granular activated carbon, air stripping, combustion, and aerobic biological oxidation.

AOP are capable of completely oxidize organic compounds to carbon dioxide, water and salts. These system are particularly applicable to wastewater treatment situations where low discharge limit must be met, and difficult to treat chemicals are present. Partial oxidation can result in increased biodegradability of pollutants so that residual organic compound can be removed through biological treatment (Bull and Zeff, 1993).

Although AOP are cheaper than combustion or wet oxidation technologies, a serious drawback of AOP is their relatively high operational costs compared to those of biological treatments. However, their use as a pre-treatment step for the enhancement of the biodegradability of wastewater containing inhibitory compounds can be justified when the intermediates resulting from the reaction can be readily degraded by microorganism. Therefore, combinations of AOP as preliminary treatments with inexpensive biological processes seem very promising from an economical point of view.

Photo-Fenton system is one of the most promising AOP techniques for the degradation of organic pollutants in wastewater. The process involves the conventional Fenton reaction with ferrous ions complex and photo-reduction (UV range of 300-400 nm) allowing the production of hydroxyl radical from hydrogen peroxide by using catalytic iron concentrations. UV radiation alone would attack and decompose some organic molecules by bond cleavage and free radical generation, but it usually occurs at a very slow rates. The combination of UV-light and various oxidants can decompose pollutants very effectively.

However, only few AOP have been examined extensively under controlled experimental conditions, for uncertainty of the exact chemical mechanisms. Moreover, the practical applications of AOP have been made largely by equipment manufacturers without prior systematic studies of AOP with the view of understanding their advantages and disadvantages (Munter, 2001). AOP are to be important tools for environmental technology and they must be placed on more scientific and engineering basis.

## **1.2 PROBLEM STATEMENT**

This project is interested in tackling the current environmental issue of treating the industrial wastewater containing significant amount of phenol and benzene. One of AOP technologies, the Photo-Fenton process is adopted as the treatment process to achieve the objective of experimentally degrading refractory pollutant; phenol and benzene.

### **1.2.1 Problem Identification**

The primary products of petroleum refining industry fall into three major categories, fuels, finished non-fuel products and chemical industry feedstock. Many refineries unintentionally released liquid pollutant that includes benzene and its derivative, phenol into ground and surface waters. Accidental discharge of large amount of pollutants occurs due to abnormal operation in refineries and potentially poses major environmental hazard (World Bank Group, 1998).

Section 2.4.3 presents the influent discharge level of petroleum refinery industry along with the compliance level outlined by Environmental Protection Agency (EPA) that must be met. The parameters that shall be experimented in this project are the Chemical Oxygen Demand (COD) reduction of wastewater; and phenol and benzene degradation after treatment with photo-Fenton process.

### **1.2.2 Significance of the Project**

This project is significant as it is commissioned in parallel with a Fenton process with similar wastewater characteristics and operating condition. To some extent, it allows a consistent comparative study to be conducted on the efficiency of treatment within specified scope described above. One area for recommendation is to further expand the scope of study to the operating cost by the usage of hydrogen peroxide, ferrous irons and the energy consumption of UV irradiation. Furthermore, this research has been developed based on the understanding of petroleum refinery industry wastewater compliance problem with local environment authority. The result shall be a bench mark for a new treatment technology for the removal of benzene and phenol in wastewater.

### **1.3 OBJECTIVES AND SCOPE OF STUDY**

The general objective of this research project is basically to gain in depth knowledge and enhance understanding towards one of the Advance Oxidation Process (AOP) available in wastewater treatment.

#### **1.3.1 Relevancy of Project**

With the awareness of discussed matters in the preceding sections, a study has been planned to investigate the efficiency of photo-Fenton reagent to remove benzene and phenol from petroleum refinery based wastewater. Detailed comparative study shall be conducted between experimental results and existing literature available either from individual research papers or relevant books. The specific objectives of this experiment-based project are to investigate the optimum ratio of Fenton reagent concentration; i.e. ratio of  $\text{Fe}^{2+}:\text{H}_2\text{O}_2$  and afterwards, determine the optimum temperature for the operation of photo-Fenton process in the degradation of both pollutants in synthetic wastewater.

One significant feature is the usage of UV light to improve the efficiency of degradation process, and thus comparing the outcome with conventional Fenton process. Basis of experiment, i.e. ratio of phenol and benzene in wastewater, was obtained from general petroleum refinery effluent discharge (World Bank Group, 1998).

The result from this project is hoped to contribute to the development of new technologies in wastewater treatment, specifically in addressing the current problem of petroleum refinery industry; and to provide effective alternative to complement the conventional wastewater treatment technologies.

### **1.3.1 Feasibility of Project within Scope and Time Frame**

The scope of study has been defined to investigate the optimum ratio of Fenton reagent concentration and optimum operating temperature for photo-Fenton process. After thorough literature reading and discussion with SV, detailed experimental procedures have been outlined with laboratory technicians. This is crucial to ensure the availability of equipments and chemical to construct the bench scale application of photo-Fenton process. Basically, the sources of chemical are easily accessible in the laboratory allowing indefinite trial run to be conducted and extensive discussion of result.

Major problem faced as this project progressed is on the determination of optimum operating condition for photo-Fenton process. This is essential to ensure that the experiment is conducted at a suitable environment for the reaction to take place. Student had spent half of the semester to do trial run experiment before specific procedure outlined in identified and dependable experimental result is achieved.

Scope of study has been defined carefully to ensure the aim of completing the project within the specified time frame with the objectives of determining the optimum condition for photo-Fenton process is achievable. Every aspect of photo-Fenton parameters is dealt carefully and the foundation theory is revisited along the duration of the project to ensure the direction is parallel with the purpose of the thesis.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 ADVANCED OXIDATION PROCESS (AOP)

##### 2.1.1 Introduction to AOP

Hazardous wastes from industrial, military and commercial operations represent one of the greatest challenges to environmental engineers. As environmental needs and regulations continue to become more severe, destructive treatment technologies consistent with waste minimization must be developed. Oxidation of organic pollutants present in water is an attractive treatment method if carried to completion, as it results in the ultimate degradation of organic compounds. Unfortunately, oxygen is kinetically too slow to be practical, or require severe conditions of temperature and pressure to achieve complete oxidation (Bull and Zeff, 1993).

On the other hand, AOP offers the most effective way for total destruction of many organic pollutants. AOP are suited for degrading dissolved organic contaminants such as halogenated hydrocarbons (trichloroethane, trichloroethylene), aromatic compounds (BTEX), pentachlorophenol (PCP), nitrophenols, detergents and pesticides. AOP can also be used to oxidize inorganic contaminants such as cyanide, sulphate, and nitrite.

Glaze (1987) defined AOPs as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”. AOP typically involve the generation and use of the hydroxyl radical ( $\cdot OH$ ), a powerful and non-selective chemical oxidant (Table 2.1), to destroy organic compounds (Table 2.2) that cannot be oxidized by conventional oxidants such as oxygen, ozone and chlorine (Munter, 2001). Two types of initial attack are possible:

the  $\cdot OH$  can abstract a hydrogen atom from water, as with alkanes or alcohols, or it can add itself to the contaminant, as in the case of olefins or aromatic compounds.

**Table 2.1: Relative Oxidation Power of Some Oxidizing Species**

Oxidizing Species	Relative Oxidation Power
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, $TiO_2^+$	2.35

Source: Munter, 2001

As a rule of thumb, the rate of destruction of a contaminant is approximately proportional to the rate constant for the contaminant with  $\cdot OH$  radical. From Table 2.2, it is observed that chlorinated alkenes are treated most efficiently because the double bond is very susceptible to hydroxyl attack. Saturated molecules (i.e., alkanes) react at a much slower rate and, therefore, are more difficult to oxidize.

**Table 2.2: Reaction Rate Constants of Ozone vs. Hydroxyl Radical**

Compound	$O_3$	$\cdot OH$
Chlorinated alkenes	$10^3 - 10^4$	$10^9 - 10^{11}$
Phenols	$10^3$	$10^9 - 10^{10}$
N-containing organics	$10 - 10^2$	$10^8 - 10^{10}$
Aromatics	$1 - 10^4$	$10^8 - 10^{10}$
Ketones	1	$10^9 - 10^{10}$
Alcohols	$10^{-2} - 1$	$10^8 - 10^9$

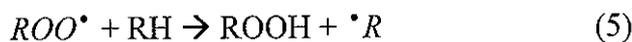
Source: Munter, 2001

UV/oxidation processes combine the use of ultraviolet light (UV) and chemical oxidants such as ozone ( $O_3$ ) and hydrogen peroxide ( $H_2O_2$ ) to destroy organic contaminants in wastewater. In most UV/oxidation processes, high intensity UV radiation is combined with  $H_2O_2$  to oxidize organic contaminants to carbon dioxide and water.

Through direct photolysis, the UV light reacts with the  $H_2O_2$  to generate  $\cdot OH$  which are highly reactive, and is second only to fluorine in relative oxidation potential. The  $\cdot OH$  then attacks the organic molecules resulting in the destruction of the parent organic

compound. The reaction is aided by the direct photolysis of organic molecule in UV light which can break or activate certain atomic bonds making the molecule more susceptible to oxidation. With sufficient oxidation and exposure to UV energy, the reaction by-products are carbon dioxide, water, and inorganic salt. Depending of the chemical structure of the organic molecules, the  $\cdot OH$  reaction pathway can be either addition reactions, subtraction reactions or a combination of both, leading to the mineralized end products.

A common reaction is the abstraction of hydrogen atom to initiate a radical chain oxidation:



The attack by the hydroxyl radical  $\cdot OH$ , in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization of the organic compound. For example, chlorinated organic compounds are oxidized first to intermediates, such as aldehydes and carboxylic acids, and finally to  $CO_2$ ,  $H_2O$ , and the  $Cl^-$ . Nitrogen in organic compounds is usually oxidized to nitrate or to free  $N_2$ , while sulphur is oxidized to sulphate. Cyanide is oxidized to cyanate, which is the further oxidized to  $CO_2$  and  $NO_3^-$  (or  $N_2$ ).

A key advantage for AOP treatment technology is that it is a destruction process (i.e. no toxic by-products are generated in the reaction), as opposed to air stripping or carbon adsorption, for which contaminants are extracted and concentrated in a separate phase. AOP can be applied to the oxidation of chemicals in groundwaters; pre-treatment of hazardous and toxic wastewaters; and post treatment for detoxification depending on the

results desired (Eckenfelder Jr., 1993). Below represent several specific targets of AOP technologies:

- Treatment of toxic organics at low concentration in groundwater;
- Treatment of low volume-high strength wastewaters for detoxification and enhanced biodegradability;
- Treatment of wastewater not normally subject to bio-oxidation, i.e., cyanide and complex metals;
- Detoxification relative to aquatic toxicity following biological treatment.

In general, extensive understanding and research of AOP technologies can give a good opportunity to reduce the pollutants concentration in wastewater from several hundreds ppm to less than 5 ppb. That is why they are called the *water treatment processes of the 21<sup>st</sup> century*.

## 2.1.2 Application of AOP in Industrial Wastewater Treatment

AOP technologies have been implemented in numerous cases commercially, and its utility continues to grow. As the treatment goals become tighter, the use of combined treatment schemes becomes more attractive; instead of being the only treatment system, AOP are effective as pre or post-treatment in a wastewater treatment plant. Next section represents the case study of broader pollutant scope on the applicability of AOP:

### MTBE in Groundwater

The remediation of leaking underground gasoline storage tank sites has created the need for treatment technology for both BTEX compound and oxygenated additives, methyl tert-butyl ether (MTBE). These components are not easily treated with activated carbon, as it contains alkane group that is difficult to treat.

AOP oxidation with H<sub>2</sub>O<sub>2</sub>/ozone/UV showed that the BTEX components were rapidly destroyed to below limits of detection of 5 ppb. At the point of BTEX removal to non-detect level (<5 ppb), 88% of the MTBE was also removed. Continued oxidation demonstrated that non-detectable level of MTBE could also be achieved. The tabulated results are as below:

**Table 2.3: H<sub>2</sub>O<sub>2</sub>/ozone/UV Treatment of BTEX and MTBE**

	O <sub>3</sub> (mg/L)	H <sub>2</sub> O <sub>2</sub> (mg/L)	MTBE ppb	Benzene ppb	Toluene ppb	Xylene ppb	Ethyl- benzene ppb
Raw Water	0	0	8670	10833	7000	4830	806
15 minutes	109	217	7	N/D	N/D	N/D	N/D
30 minutes	218	217	N/D	N/D	N/D	N/D	N/D

Source: Bull and Zeff, 1993

**Table 2.4: Treatment of BTX (Pilot Plant Data Treating 3 Gpm with 120 minutes Retention Time)**

	O <sub>3</sub> (mg/L)	H <sub>2</sub> O <sub>2</sub> (mg/L)	MTBE ppb	Benzene ppb	Toluene ppb	Xylene ppb
Pretreated	0	0	180,000	12,000	23,000	10,000
Effluent	700	700	22,000	<5	<5	<5

Source: Bull and Zeff, 1993

## COD Oxidation in Bio-treatment Effluent

The use of H<sub>2</sub>O<sub>2</sub>/ozone/UV as a pre-treatment step in BOD/COD removal can significantly reduce the overall treatment cost of a wastewater treatment plant. This AOP reduces COD by more than 80% in 20 minutes. Treatment with H<sub>2</sub>O<sub>2</sub>/ozone and ozone/UV resulted in high removal efficiencies but this requires a 50% longer reaction time than H<sub>2</sub>O<sub>2</sub>/ozone/UV, as depicted in Table 2.5. As a result, both capital and oxidant cost for the combination of all three AOP components are less than the cost of the AOP alternatives.

**Table 2.5: Comparison of AOP Cost for a 650 Gpm Operating System**

	Retention Time	H <sub>2</sub> O <sub>2</sub> mg/L	% COD Reduction	\$ Capital	\$/1000 O&M
H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> /UV	20	365	83	1,625,000	\$2.15
H <sub>2</sub> O <sub>2</sub> / O <sub>3</sub>	30	360	69	2,195,000	\$3.39
O <sub>3</sub> /UV	30	360	50	2,415,000	\$3.88

Note: Current biological treatment plant effluent ranged from 26-77 mg/L BOD while the treatment objective is <20mg/L BOD.

Source: Bull and Zeff, 1993

In another COD example, wastewater from a fragrance manufacturer require reduction of COD from 630 mg/L to 250 mg/L. H<sub>2</sub>O<sub>2</sub>/ozone and ozone/UV achieved only 35% and 40% reduction respectively in one hour reaction time. H<sub>2</sub>O<sub>2</sub>/ozone/UV removed 90% of the COD at similar oxidation level and time. Treatment objectives were met within 30 minutes at less than 70% of the oxidant level, as depicted in Table 2.6.

**Table 2.6: COD Reduction with H<sub>2</sub>O<sub>2</sub>/Ozone/UV**

Run	Retention Time	H <sub>2</sub> O <sub>2</sub> mg/L	O <sub>3</sub> mg/L	COD mg/L
1	0	0	0	630
	30	840	0	500
	60	1080	0	410
2	0	0	0	630
	30	0	650	490
	60	0	1320	390
3	0	0	0	630
	30	480	420	140
	60	480	840	63

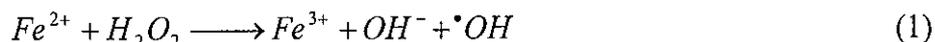
Note: Activated sludge plant effluent varied from 630-800 mg/L COD while the treatment objective is <275mg/L BOD.

Source: Bull and Zeff, 1993

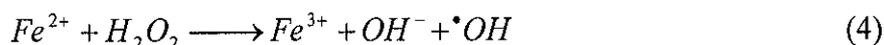
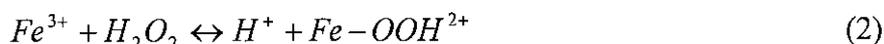
## 2.2 PHOTO-FENTON PROCESS

### 2.2.1 Mechanism of Photo-Fenton Process

The Fenton process was reported by Fenton over a hundred years ago for maleic acid oxidation (Munter, 2001):

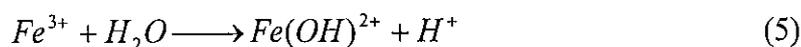


The rate constant for the reaction of  $Fe^{2+}$  with  $H_2O_2$  is high and  $Fe^{2+}$  oxidizes to  $Fe^{3+}$  immediately in the presence of excess amounts of  $H_2O_2$ .  $H_2O_2$  decomposes catalytically by  $Fe^{3+}$  and generates again  $\bullet OH$  according to the reactions:

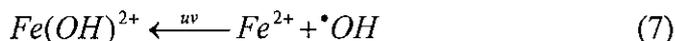


Iron salts act as a catalyst for hydrogen peroxide decomposition. The use of  $Fe^{2+}/H_2O_2$  as an oxidant for wastewater treatment is attractive due to the facts that: i. iron is a highly abundant and non-toxic element, and ii. hydrogen peroxide is easy to handle and environmentally benign. Thus, the Fenton process is very effective for  $\bullet OH$  generation; however, it involves consumption of one molecule of  $Fe^{2+}$  for each  $\bullet OH$  produced, demanding a high concentration of  $Fe^{2+}$ .

When  $Fe^{3+}$  ions exist in the  $H_2O_2/UV$  process, the process is commonly called photo-Fenton oxidation. The Photo-Fenton reaction relies heavily on the UV irradiation to initiate the generation of  $\bullet OH$ . At pH 3, the  $Fe(OH)^{2+}$  complex is formed because of the acidic environment. The mechanism of photo-Fenton process directly follows Fenton process as below:

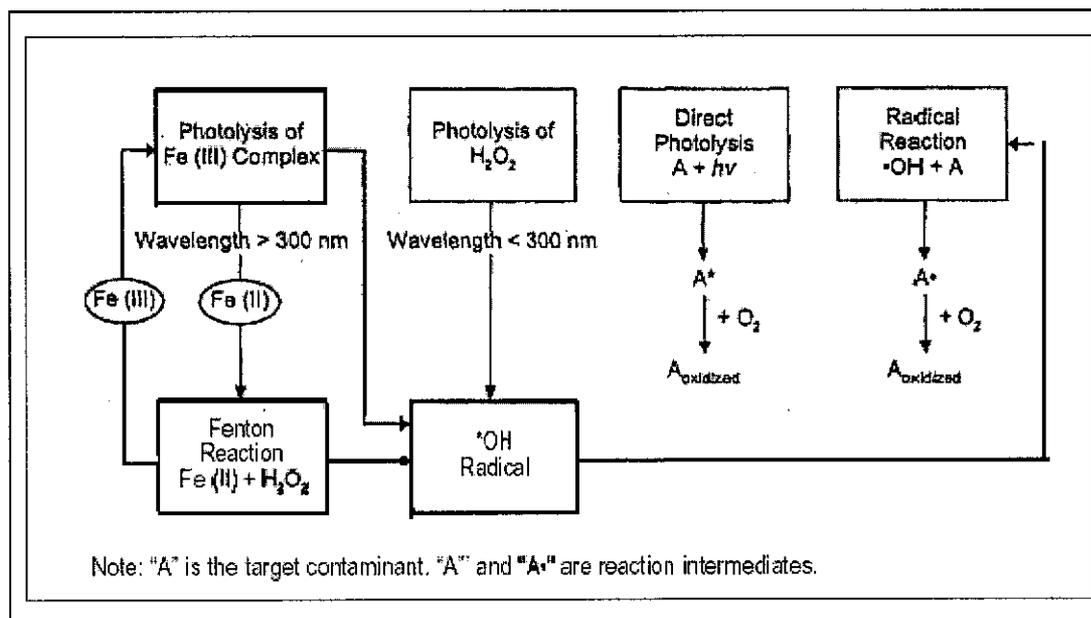


When exposed to UV irradiation, the complex is further subjected to decomposition and will produce  $\cdot OH$  and  $Fe^{2+}$  ions:



It is apparent that the photo-Fenton-type reaction relies heavily on the UV irradiation to initiate the generation of  $\cdot OH$ . If desired, organic pollutants can be mineralized completely with UV/visible irradiation. It has been demonstrated that photo-Fenton's reagent is able to reduce COD and destroy different phenols, nitrobenzene, and herbicides in wastewater. The increased efficiency of Fenton process with UV/visible irradiation is attributed by two main factors:

- ✓ *Photo-reduction of  $Fe^{3+}$* : irradiation of  $Fe^{3+}$  (or  $Fe(OH)^{2+}$ ) produces  $Fe^{2+}$ , which reacts with  $H_2O_2$  generating a second  $\cdot OH$  and  $Fe^{3+}$ , and the cycle continues;
- ✓ *Efficient use of light quanta*: the absorption spectrum of  $H_2O_2$  is below 300 nm and has low extinction coefficient beyond 250 nm. The absorption spectrum of  $Fe^{3+}$  extends to near-UV/visible region and has a relatively large extinction coefficient, enabling photo-oxidation and mineralization by visible light.



**Figure 2.1: Schematic of chemical reactions in the photo-Fenton reaction**

Source: EIA, 1998

## **2.3 PARAMETERS OF PHOTO-FENTON PROCESS**

In conducting the experiment, optimum operating conditions for photo-Fenton process are vital to maximize desirable reaction. The variables directly related to treatment process are the Fenton reagent ratio, temperature, pH, reaction time and UV irradiation.

### **2.3.1 Effect of Hydrogen Peroxide Concentration**

Because of the nonselective effect of  $\cdot OH$ , each oxidation process in series has specific reaction rate and build-up of an undesirable intermediate, which requires sufficient addition of  $H_2O_2$  to push the reaction beyond that point ([www.h2o2.com](http://www.h2o2.com)). Degradation rates increase with  $H_2O_2$  concentration by the effect of the additionally produced  $\cdot OH$  radicals. However, above a certain  $H_2O_2$  concentration, the reaction rate decreases by the progressive increase of the  $H_2O_2$  (Patricia, 2001). Therefore,  $H_2O_2$  should be added at an optimal concentration to achieve the best degradation.

### **2.3.2 Effect of Iron Salt Amount**

Reaction rates of photo-Fenton reaction are generally limited by the rate of  $\cdot OH$  generation, i.e. concentration of iron catalyst. The degradation rates increase with iron salt amount, but after a determined iron concentration, the efficiency decreases. Typical Fe: $H_2O_2$  ratios are 1:5-10wt/wt, though iron levels less than 25-50 mg/L can require excessive reaction times ([www.h2o2.com](http://www.h2o2.com)). Fenton's Reagent is most effective as a pre-treatment tool, where COD's are greater than 500 mg/L due to the loss in selectivity as pollutant levels decrease. Iron dose may also be expressed as a ratio to  $H_2O_2$  dose, which typical ranges are 1 part Fe per 5-25 parts  $H_2O_2$  (wt/wt).

### **2.3.3 Effect of Iron Type (Ferrous or Ferric)**

For most applications, it does not matter whether  $Fe^{2+}$  or  $Fe^{3+}$  salts are used to catalyze the reaction. The catalytic cycle begins quickly if  $H_2O_2$  and organic material are in abundance. However, if low doses of Fenton's Reagent are being used (e.g., < 10-25

mg/L), some research suggests ferrous iron may be preferred. Recycling of iron can be done by raising the pH, separating the iron floc, and re-acidifying the iron sludge.

### 2.3.4 Effect of Temperature

The rate of reaction of photo-Fenton process increases with increasing temperature, with the effect more pronounced at temperatures less than 20°C. However, the efficiency of H<sub>2</sub>O<sub>2</sub> utilization declines as temperatures increase above 40-50°C. Practically, most commercial applications of Fenton's Reagent occur at temperatures between 20-40°C. Applications of Fenton's Reagent for pretreating high strength wastes may require controlled or sequential addition of H<sub>2</sub>O<sub>2</sub> to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when H<sub>2</sub>O<sub>2</sub> doses exceed 10-20 g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well.

### 2.3.5 Effect of pH

The optimal pH occurs between pH 3 and pH 6. The pH value influences the generation of  $\cdot OH$  radicals and thus the oxidation efficiency. For basic pH values, degradation strongly decrease since iron precipitates reducing the Fe<sup>2+</sup> availability. This trend is illustrated in Figure 2.2.

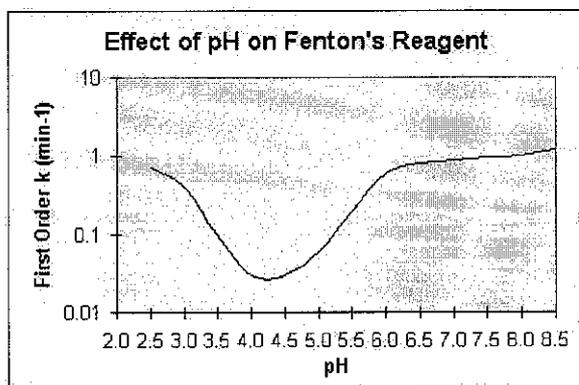
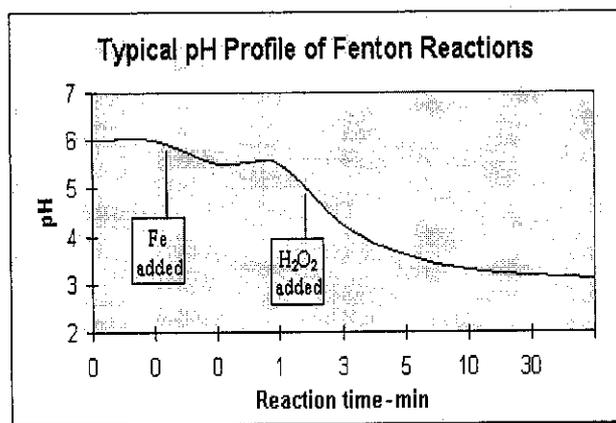


Figure 2.2: Effect of pH on reaction efficiency

A second aspect of pH deals with its shift as the reaction progresses. At initial wastewater pH of 6.0, the following profile is typical of Fenton reactions.



**Figure 2.3: Typical pH Profile of Fenton Reaction**

The first inflection is caused by the addition of  $\text{FeSO}_4$  catalyst which typically contains residual  $\text{H}_2\text{SO}_4$ . This pH change is often monitored to ensure that the reaction is progressing as planned. The absence of pH decrease may mean that the reaction is inhibited and potential hazardous build-up of  $\text{H}_2\text{O}_2$  is occurring within the reaction.

### 2.3.6 Effect of Reaction Time

The time needed to complete a Fenton reaction is dependent upon the parameters discussed above and pollutant level. For simple phenol oxidation (less than 250 mg/L), typical reaction times are 30-60 minutes. For more complex or more concentrated wastes, the reaction may take several hours. Often, observing colour changes can be used to assess the reaction progression. Wastewaters will typically darken upon  $\text{H}_2\text{O}_2$  addition and clear up as the reaction reaches completion.

### 2.3.7 Effect of UV Intensity

The UV spectrum is subjectively divided into three bands: UV-A (315 to 400 nm), UV-B (280 to 315 nm), and UV-C (100 to 280 nm) (Philips Lighting 1985). Of these bands, UV-A and UV-C are generally used in environmental applications. UV-A radiation is also referred to as long-wave radiation, near-UV radiation, or black light. Most UV-A lamps peak emission is at 365 nm, and some at 350 nm. UV-C radiation, which is also referred to as short-wave radiation, is used for disinfection of water and wastewater (US EPA, Dec 1998).

## **2.4 PETROLEUM REFINERY WASTEWATER CHARACTERISTICS**

### **2.4.1 History of Petroleum Refinery**

The petroleum industry began with the successful drilling of the first commercial oil well in 1859, and the opening of the first refinery two years later to process the crude into kerosene. Petroleum refining has evolved continuously in response to changing consumer demand for better and different products. The original requirement was to produce kerosene as a cheaper and better source of light than whale oil. The development of the internal combustion engine led to the production of gasoline and diesel fuels. The evolution of the airplane created a need first for high-octane aviation gasoline and then for jet fuel, a sophisticated form of the original product, kerosene. Present-day refineries produce a variety of products including many required as feedstock for the petrochemical industry (OSHA Technical Manual).

Petroleum refining is the physical, thermal and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished petroleum products. The primary products of the industry fall into three major categories: fuels; finished non-fuel products and chemical industry feed stocks that includes phenol and benzene.

Malaysia itself has six refineries, with a total processing capacity of 514,500 bbl/d. The three largest are the 155,000 bbl/d Shell Port Dickson refinery and the Petronas Melaka-I and Melaka-II refineries, which each have a capacity of 95,000 bbl/d.

The second phase of the \$1.4-billion, 200,000-bbl/d Melaka refinery complex, located about 90 miles south of Kuala Lumpur, commenced operation in August 1998. The 100,000-bbl/d Melaka-II second phase is a joint venture between Petronas (45%), Conoco (40%), and Statoil (15%). This second refinery contains a 62,000-bbl/d vacuum distillation unit, 26,000-bbl/d catalytic cracker, 28,500-bbl/d hydrocracker, 35,000-bbl/d desulfurization unit, and 21,000-bbl/d coker. One of the main purposes of this refinery is to supply gasoline to Conoco's service stations in Thailand and a new line of stations planned for Malaysia (EIA, 2003).

## 2.4.2 Conventional Wastewater Treatment

The wastewater sources in petroleum refinery industry include stripping water, spent caustic solutions, cooling tower and boiler blowdown, and other process-associated water (World Bank Group, 1998). The basic constituents are hydrocarbons, organic materials (phenol, alcohols), sulfuric compounds (sulfide, mercaptan, and sulfate), sodium salts, and suspended solids. Conventional wastewater treatment system adopted three stages separation processes, namely pretreatment, secondary and tertiary treatment.

Pretreatment is the separation of hydrocarbons and solids from wastewater. CPI and settling ponds is used to remove suspended hydrocarbons, oily sludge, and solids by gravity separation, skimming, and filtration. Neutralization of acidic wastewater is done using ammonia, lime, or soda ash; and alkaline wastewater using sulfuric acid, hydrochloric acid, carbon dioxide-rich flue gas, or sulfur. After pretreatment, suspended solids are removed by sedimentation or air flotation; flocculation agents are sometimes added to help separation. Wastewater with low levels of solids may be screened or filtered.

Secondary treatment processes biologically degrade and oxidize soluble organic matter by the use of activated sludge, un aerated or aerated lagoons, trickling filter methods, or anaerobic treatments. Materials with high adsorption characteristics are used in fixed-bed filters or added to the wastewater to form slurry which is removed by sedimentation or filtration. Stripping is used on wastewater containing sulfides and/or ammonia, and solvent extraction is used to remove phenols.

Tertiary treatments remove specific pollutants to meet regulatory discharge requirements. These treatments include chlorination, ozonation, ion exchange, reverse osmosis, activated carbon adsorption, etc. Compressed oxygen is diffused into wastewater streams to oxidize certain chemicals or to satisfy regulatory oxygen-content requirements. Wastewater that is to be recycled may require cooling to remove heat and/or oxidation by spraying or air stripping to remove any remaining phenols, nitrates, and ammonia.

### 2.4.3 Regulation and Environmental Limit

The evolution of petroleum refining from simple distillation to today's sophisticated processes has demand environmental management challenges to protect water from the refinery pollution. Petroleum refineries units generate wastewaters from process operation such as vapor condensation, cooling tower blowdown and stormwater runoff.

*THIRD SCHEDULE*  
*EQA 1974 (Environmental Quality: Sewage and Industrial Effluents)*  
*Regulations 1978*  
*[Regulation 8 (1), 8 (2), 8 (3)]*

**Table 2.7: Parameter Limits of Effluent of Standards A and B**

Parameter	Unit	Standard	
		A	B
Temperature	C	40	40
pH Value		6.0 - 9.0	5.5 - 9.0
BODs at 20°C	mg/l	20	50
COD	mg/l	50	100
Suspended Solids	mg/l	50	100
Mercury	mg/l	0.005	0.005
Cadmium	mg/l	0.01	0.02
Chromium, Hexavalent	mg/l	0.05	0.05
Arsenic	mg/l	0.05	0.10
Cyanide	mg/l	0.05	0.10
Lead	mg/l	0.10	0.5
Chromium, Trivalent	mg/l	0.20	1.0
Copper	mg/l	0.20	1.0
Manganese	mg/l	0.20	1.0
Nickel	mg/l	0.20	1.0
Tin	mg/l	0.20	1.0
Zinc	mg/l	1.0	1.0
Boron	mg/l	1.0	4.0
Iron (Fe)	mg/l	1.0	5.0
Phenol	mg/l	0.001	1.0
Free Chlorine	mg/l	1.0	2.0
Sulphide	mg/l	0.50	0.50
Oil and Grease	mg/l	Not Detectable	10.0

Source: [www.aots.org](http://www.aots.org)

The quantity of wastewater and their characteristics depend on the process configuration. Malaysia's standards are classified into two sets of standards, A and B, according to the river area into which wastewater is discharged. Standard A applies to wastewater discharge upstream from a drinking water intake point, while Standard B applies to discharge downstream from an intake point. Table 2.7 represents the amount of pollutant sourced from petroleum refinery industry.

**Table 2.8: Sources of Pollutant in Petroleum Refinery**

Sources	Pollutant	Approximate Level
Cooling systems	Wastewater generated per ton of crude	3.5-5 m <sup>3</sup>
Polluted wastewater	BOD	150-250 mg/l
	COD	300-600 mg/l
	Phenol	20-200 mg/l
	Benzene	1-100 mg/l
	Heavy metals	0.1-100 mg/l

Source: World Bank Group, 1998

The methods for analyzing water quality are to comply with the Standard Methods for the Examination of Water and Wastewater, jointly published by the American Public Health Association (APHA), American Water Works Association (AWWA), and the Water Environment Federation (WEF). The liquid effluent for direct discharge to offsite surface water should meet outlined specification by local Environmental Protection Agency (EPA), as show in Table 2.8.

**Table 2.9: Effluent Requirement from Petroleum Refinery**

Parameter	Maximum Level
pH	6-9
BOD	30 mg/l
COD	150 mg/l
Phenol	0.5 mg/l
Benzene	0.05 mg/l
Temperature increase	≤ 3°C

Source: World Bank Group, 1998

## 2.5 CHARACTERISTICS OF BENZENE AND PHENOL

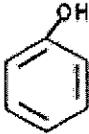
Both phenol and benzene are the major pollutant sourced from petroleum refinery industrial wastewater. Phenol and benzene exposure to human and animals at high concentration are investigated to be tumorigenic, mutagen, reproductive effector (Mallinckrodt Chemicals). Both may be harmful or fatal to contaminated plant and animal-life especially if large amount are released.

### 2.5.1 Phenol

#### Chemical and Physical Properties

Phenol is a colorless-to-white solid when pure; however, the commercial product, which contains some water, is a liquid. It is the simplest member of a class of hydroxyl benzene derivatives, all of which contain a hydroxyl group attached to a benzene ring. Most people begin to smell phenol in air at about 40 parts of phenol ppb of air, and begin to smell phenol in water at about 1-8 parts of phenol per million parts of water.

**Table 2.10: Physical and Chemical Properties of Phenol**

Properties	Information
Chemical formula and molecular structure	$C_6H_6OH$ 
Molecular Weight	94.11 g/mol
Physical state	Crystalline solid liquid (w/8% H <sub>2</sub> O)
Melting / Boiling Point	43°C / 181.8°C
Density at 20°C	1.0545
Solubility : Water at 25°C Organic Solvent(s)	87 g/L Very soluble in alcohol, chloroform, ether, acetone

Source: ATSDR, Dec 1998

#### Production of Phenol

Phenol has been obtained by distillation from petroleum and synthesis by oxidation of cumene or toluene, and by vapor-phase hydrolysis of chlorobenzene. Phenol is used

primarily in the formation of phenolic resins. It is also used in the manufacture of nylon, synthetic fibers and slimicides (chemicals that kill bacteria and fungi in slimes). In 1995, the total annual capacity of phenol production approached 4.5 millions pounds.

### Toxicological and Ecological Hazard

Phenol is a high-priority persistent, bioaccumulative and toxic (PBT) compound. PBT chemicals do not readily break down in the environment, may accumulate in human or ecological food chains through consumption or uptake and may be hazardous to human health or the environment (Ohio EPA, 2002). Once released to the environment, it may present long-term toxic effects to human health and the environment, even if the release was of a small amount. The U.S. EPA has created a priority in its hazardous waste minimization program to reduce the presence of PBT chemicals, promote pollution prevention and avoid the transfer of PBT chemicals across environmental media.

When released into water, this material is not expected to evaporate significantly. When released into water, this material is expected to have a half-life between 10 and 30 days. This material is expected to be toxic to aquatic life. EPA recommends that the level of phenol in surface water (lakes, streams) should be limited to 3.5 mg/L to protect people from drinking contaminated water or eating contaminated fish.

### Conventional Disposal Method

Although the toxicity of phenolic compounds is not as high heavy metals, high concentrations (up to several g/L) often inhibit bacteriological populations in municipal biological wastewater treatment plants. Thus common biological wastewater treatment is not possible. In such cases AOP are a viable alternative. Two commonly applied AOPs that can be powered by sunlight are heterogeneous photocatalysis with titanium dioxide and homogeneous photocatalysis by the photo-Fenton reaction (ATSDR, Dec 1998).

## 2.5.2 Benzene

### Chemical and Physical Properties

Benzene is a colorless liquid with a sweet odor. Benzene evaporates into air very quickly and dissolves slightly in water. Benzene is highly flammable. Most people can begin to smell benzene in air at 1.5-4.7 parts of benzene per million parts of air (ppm) and smell benzene in water at 2 ppm. Most people can begin to taste benzene in water at 0.5-4.5 ppm.

Benzene is the parent substance of the aromatic compounds, a large and important group of organic compounds. It is the first of a series of hydrocarbons known as the benzene series, formed by the substitution of methyl groups, CH<sub>3</sub>, for the hydrogen atoms of the benzene molecule.

**Table 2.10: Physical and Chemical Properties of Benzene**

Properties	Information
Chemical formula and molecular structure	C <sub>6</sub> H <sub>6</sub> 
Molecular Weight	78.11 g/mol
Physical state	Rhombic prisms
Melting / Boiling Point	5.5°C / 80.1°C
Density at 20°C	0.8787
Solubility : Water at 25°C Organic Solvent(s)	0.188% (w/w) Alcohol, chloroform, ether, acetone, oil carbon disulfide, , carbon, tetrachloride, glacial acetic acid

Source: ATSDR, Dec 1998

### Production of Benzene

Currently, benzene is commercially recovered from both coal and petroleum sources. More than 98% of the benzene produced is derived from the petrochemical and petroleum refining industries. These sources include refinery streams (catalytic reformats), pyrolysis gasoline, and toluene hydrodealkylation. Benzene recovered from petroleum and coal sources is used primarily as an intermediate in the manufacture of

other chemicals; i.e. ethylbenzene, cumene, and cyclohexane. Ethylbenzene (55% of benzene production volume) is an intermediate in the synthesis of styrene, which is used to make plastics and elastomers. Cumene (24%) is used to produce phenol and acetone. Benzene is also used for the manufacturing of some types of rubbers, lubricants, dyes, detergents, drugs, and pesticides.

#### Toxicological and Ecological Hazard

Extensive studies have conclusively proven a decrease in hemoglobin, red and white blood cells, platelets and/or changes in the cells upon exposure to benzene (CCOHS, 1995). Effects of varying severity have been demonstrated with both intermittent and continuous exposures to concentrations as low as 10 ppm for 24 weeks.

Benzene can be harmful or fatal to contaminated aquatic plant and animal life. Benzene floats on water, and can potentially form layer which are capable of creating oxygen deprived waterways which can contaminate coastal and shore life (Airgas™ MSDS). Both of these chemical usage and pollution should be reduced wherever possible.

#### Conventional Disposal Method

Benzene-containing wastes, such as commercial chemical products, manufacturing chemical intermediates, and spent solvents, are subject to federal hazardous waste regulations. In the past, landfilling and lagooning were the major methods of disposal of benzene-containing industrial wastes (EPA, 1982). Unfortunately benzene, along with other hazardous contaminants, also leaches into groundwater from the lagooned wastes.

The recommended method of disposal is incineration at elevated temperature to ensure complete combustion. The recommended methods for combustion are liquid injection incineration at a temperature range of 650-1,600°C and a residence time of 0.1-2 seconds; rotary kiln incineration at a temperature range of 600°C and residence times of seconds for liquids and gases, and hours for solids; fluidized bed incineration at a temperature range of 450-980°C and residence times of seconds for liquids and gases and longer for solids (ATSDR, Dec 1998).

## **CHAPTER 3**

### **METHODOLOGY/PROJECT WORK**

#### **3.1 PROJECT APPROACH**

The following phases of research and development have been identified for this project to proceed successfully. Basically, the methodology can be divided into five main stages:

##### **3.1.1 Selection of Project Topics**

The student has been engaged with this stage after the list of Final Year Project (FYP) titles are officially handed to the student for selection process. To relate what she have learnt during Industrial Training, several topics was first proposed to the FYP coordinator and Supervisor (SV) for evaluation on its feasibility in terms of scope and time frame. Thorough discussions have taken place between student and SV regarding the proposed scope of study and method of performing the analysis. The student have involved with many external and internal parties during this stage; such as engineers, industrial practitioners, vendors and technicians.

##### **3.1.2 Project Planning**

After final project title has been awarded, all defined scope of work is outlined along specific time frame to keep track with on-going and planned activities. The planning involves two major activities; the project in larger scale and the experimental work. As the entire data collection merely comes from experimental result, the student is responsible to ensure that the equipments and chemicals required are available upon usage to ensure no interruption during the experimental phase.

A Gantt chart is produced to keep update with the outlined activities and its time frame to avoid delays and behind schedule activities.

### **3.1.3 Literature Study**

In depth understanding of the relevant issues are important since the student has no direct source of gathering the knowledge she require to successfully achieve the objective of this thesis. The study was first carried out by finding the relevant theoretical aspect that will be used as the ground basis for further analysis. The literature review is obtained from established books, articles, and journals. Most information are gathered from Internet and library; i.e. photo-Fenton reaction, petroleum refinery statistics and MSDS. Available research by individuals on related topics serves as a useful reference for basis of comparison.

### **3.1.4 Laboratory Work**

The experiment covers three major stages; groundwork of experiment start-up, determination of optimum Fenton reagent ratio and identification of optimum temperature for photo Fenton reaction. Much of the initial phase involves trial and error to further improve on the procedure to ensure operating in optimum condition. Synthetic wastewater is sampled throughout the reaction for examination of Chemical Oxygen Demand (COD) level. Determination of optimum operating temperature was performed after successfully determining the optimum ratio of Fenton reagent.

### **3.1.5 Data Analysis**

The final tabulated result for this thesis was the optimum Fenton reagent ratio and operating temperature based on the COD reduction level. Experimental results and observations were documented for each set of experiment for detailed analysis and further discussion with SV. Each parameters of photo-Fenton process are analysed in detail to enhance understanding of the reaction to improve on future experiment. It is important to note that no sole references are available for extensive comparison to be conducted since the experimental procedures are unique to this thesis outlined from

proven resources. Among deliverables for data presentation are Weekly Progress Report, Preliminary Report and Second Progress Report.

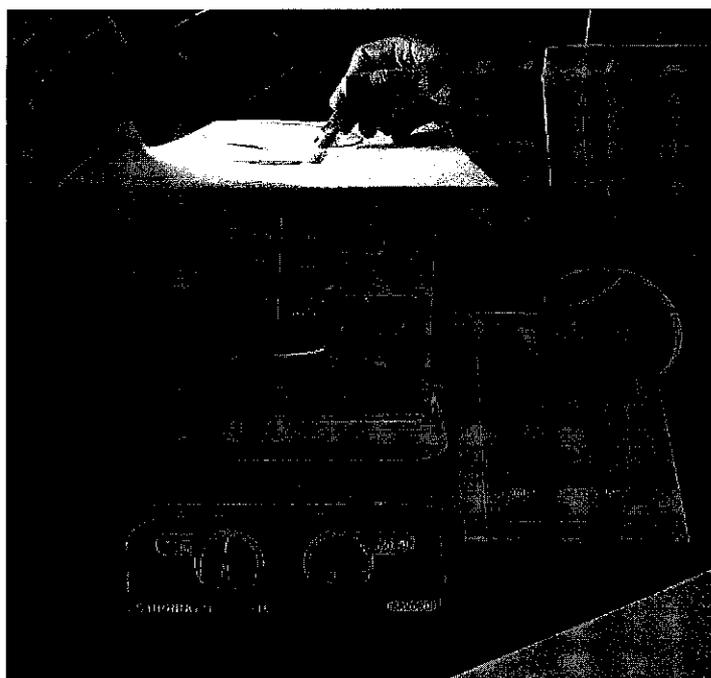
### 3.2 TOOLS REQUIRED

All equipment and chemicals required in the experiment are easily obtainable in the laboratory. The detailed list is summarized in Table 3.1.

**Table 3.1: Equipment and Chemicals for Photo-Fenton Experiment**

Equipment	Chemicals
Hot plate with stirrer	Phenol crystallized
Magnetic stirrer	Benzene solution
Burette (600 mL, 200 mL)	Hydrogen Peroxide 30%
Pipette (10 mL)	FeSO <sub>4</sub> powder
pH Meter	Twice Distilled Water
Thermometer	0.1M NaOH
Study Lamp	0.1M HCL
Micropipette (1-100 $\mu$ L, 100-1000 $\mu$ L)	Buffer solution for pH Meter calibration

Below is the experimental set-up of the bench scale photo-Fenton equipment:



**Figure 3.1: Experimental Set-up for Photo-Fenton Experiment**

### 3.3 CHEMICALS PREPARATION

#### 3.3.1 Preparation of Synthetic Wastewater

All reagents in this experiment were prepared using twice-distilled water (deionized water) with high purity using UltraPure System, with conductivity of 18 mΩ. This is to avoid any contamination of other organic pollutant, i.e. chlorine, fluorides, calcium, heavy metal and small microorganism that normally contained in the tap water.

From Section 2.4, the approximate level of phenol and benzene discharged from petroleum refinery industry is 20-200mg/L and 1-100mg/L respectively. For worst case, phenol and benzene concentration of 200mg/L and 100mg/L is adopted. (www.h2o2.com) stated that the Fenton reagent is most effective as a pre-treatment tool where COD are above 500mg/L. It is determined that that the COD level for the synthetic wastewater composition above is between 600 to 800 mg/L.

The synthetic wastewater was prepared in a 500mL volumetric flask. Fixed concentration of phenol and benzene was adopted for all experiments; 0.1g of crystallized phenol and 56.8μL of benzene. The density of available benzene is 879 kg/m<sup>3</sup>. The calculation of required equivalent volume of benzene is determined as below:

$$V_{benzene} = 50mg \times \frac{m^3}{879kg} \times \frac{1g}{1000mg} \times \frac{1kg}{1000g} \times \frac{1000L}{1m^3}$$

$$V_{benzene} = 56.8\mu L = 60\mu L$$

Micropipette (range 1-100μL) is used to dose from the readily available benzene reagent. Dilution of benzene is avoided since the solubility range of benzene is limited and benzene is extremely volatile, so as to minimize benzene losses during dilution process.

### 3.3.2 Preparation of Fenton Reagent

Hydrogen peroxide and FeSO<sub>4</sub> was used as received without further purification and dilution.

For the preparation of iron catalyst, FeSO<sub>4</sub> powder was used to simplify the calculation. ([www.h2o2.com](http://www.h2o2.com)) stated that i. minimal 3-15 mg/L Fe allows reaction to proceed within reasonable time regardless of organic waste concentration and ii. ratio of Fe:substrate above the minimal threshold, typically 1: 10-50 (w/w), produces the desired end products. The ratio of Fe:substrate of 1:25 is adopted in this experiment. The correlation between pollutants and iron catalyst following the above statement is as follows:

Fe : Phenol → 4: 100 mg	} Total Fe required = 6 mg
Fe : Benzene → 2: 50 mg	

For the amount of H<sub>2</sub>O<sub>2</sub> required, iron dose calculated above may also be expressed as a ratio to H<sub>2</sub>O<sub>2</sub> dose. Typical ranges are 1 part Fe per 5-25 parts H<sub>2</sub>O<sub>2</sub> (wt/wt); the density of H<sub>2</sub>O<sub>2</sub> is 1.11 g/cm<sup>3</sup>. Similar calculation method is applied for other Fe:H<sub>2</sub>O<sub>2</sub> ratio (Table 8). The calculation procedure is as below:

For Fe : H<sub>2</sub>O<sub>2</sub> = 1:5 (wt/wt), → 6 mg of Fe : 30 mg of H<sub>2</sub>O<sub>2</sub>

30%(volume/volume) of 1110 mg/mL H<sub>2</sub>O<sub>2</sub> is 333 mg/mL

Thus 1 mL of solution contains 333 mg of H<sub>2</sub>O<sub>2</sub>. For the required 30 mg of H<sub>2</sub>O<sub>2</sub>,

$$\text{Volume of H}_2\text{O}_2 = \frac{30\text{mg}}{333\text{mg}} \times 1\text{mL} = 0.09\text{mL} = 90\mu\text{L}$$

**Table 3.2: Amount of Fenton Reagent Required**

Chemicals	Amount Required
FeSO <sub>4</sub>	6 mg
Hydrogen Peroxide (30%)	90 μL (Fe:H <sub>2</sub> O <sub>2</sub> =1:5) 180 μL (Fe:H <sub>2</sub> O <sub>2</sub> =1:10) 270 μL (Fe:H <sub>2</sub> O <sub>2</sub> =1:15) 360 μL (Fe:H <sub>2</sub> O <sub>2</sub> =1:20) 450 μL (Fe:H <sub>2</sub> O <sub>2</sub> =1:25) 540 μL (Fe:H <sub>2</sub> O <sub>2</sub> =1:30)

### 3.3.3 Preparation of Buffer Solution

Buffer solution is prepared for three main reasons, which are (1) to maintain the pH of synthetic water at optimum pH of 3 for photo-Fenton reaction; (2) to introduce an acidic pH of 3 at the start of reaction; and (3) to stop the reaction by precipitating the iron catalyst at basic pH of 8. The buffer solutions prepared are 0.1 M of Hydrochloric Acid (HCl) and 0.1 M of Sodium Hydroxide (NaOH).

The available HCl reagent is 37 % in 2.5 L of container. From handbook, the molecular weight and the specific gravity of HCl is 36.46 g/mol and 1.19 kg respectively. The calculation of required amount of concentrated reagent for dilution is as follows:

$$\text{Molarity} = \frac{10 \times \text{SG} \times \%}{\text{MW}} = \frac{10 \times 1.19 \times 37\%}{36.45} = 12M$$

Adopting formula  $M_1V_1 = M_2V_2$  where

$$M_1 = \text{Concentration of available solution} = 12 M$$

$$V_1 = \text{Volume required for dilution} = x \text{ mL}$$

$$M_2 = \text{Concentration of desired solution} = 0.1 M$$

$$V_2 = \text{Volume of desired solution} = 500 \text{ mL}$$

Thus, the volume of 12 M HCl required is 4.116 mL.

For the required amount of NaOH, the molecular weight of NaOH is 40g/mol. The calculation is as follows:

$$\text{Molarity} = \frac{\text{moles}}{\text{volume}} = 0.1M$$

Moles of NaOH = 0.1 M X 1 L of deionized water

$$\text{Moles} = \frac{\text{mass}}{\text{MW}} = 0.1 \text{mole}$$

Moles of NaOH = 0.1 M X 1 L of deionized water = 0.1 mole of NaOH

Thus, the required weigh of NaOH pellets is 4 grams.

### 3.4 PROCEDURE IDENTIFICATION

#### 3.4.1 Preparation of Synthetic Wastewater

1. A 500 mL volumetric flask is filled with deionized water (twice distilled water).
2. Pure benzene (56.8  $\mu\text{L}$ ) is dosed into the synthetic water using a micropipette. The volumetric flask is immediately covered to avoid evaporation.
3. Crystallized phenol (0.1g) is dosed into the synthetic water. The volumetric flask is heated for 5 minutes to dissolve all crystallized phenols and shake to ensure homogeneity of synthetic wastewater containing pollutants.
4. The synthetic water is transferred into a 500 mL beaker.
5. Beaker is put into a water bath aquarium for constant temperature condition during photo-Fenton reaction.
6. 2 mL of the synthetic water is pipetted for COD test ( $t=0\text{min}$ ).
7. The pH of synthetic water is adjusted for acidic condition of 3 for optimum reaction condition using 0.1 M HCl.

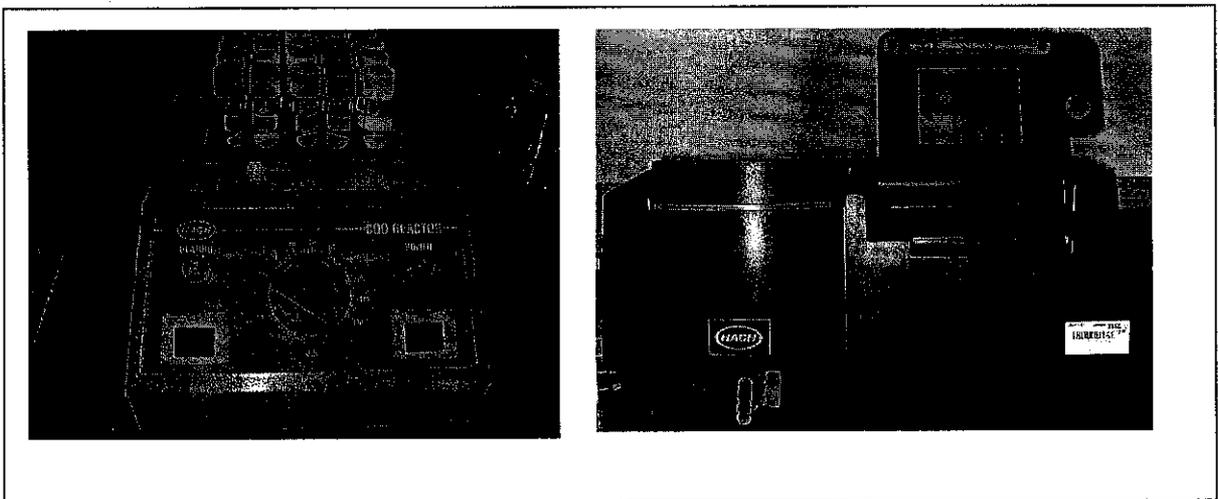
#### 3.4.3 Start-up of photo-Fenton Reaction

1. 6 mg of  $\text{FeSO}_4$  powder is dosed into the synthetic water.
2. The stirrer is on for 2-3 minutes to fully dissolve the  $\text{FeSO}_4$  powder.
3. Hydrogen peroxide is dosed into the synthetic water using micropipette to start the reaction. The required amount of  $\text{H}_2\text{O}_2$  is presented in Table 3.2.
4. The study lamp is on immediately upon the addition of  $\text{H}_2\text{O}_2$  to start the reaction.
5. Temperature and pH is monitored throughout the photo-Fenton reaction. These two parameters are strictly adjusted to ensure optimum condition for photo-Fenton experiment is achieved.
6. 2 ml of synthetic water is pipetted for COD test (at time =15, 30, 45, 60, 75, 90, 180).

### 3.5 CHEMICAL ANALYSIS

#### 3.5.1 Chemical Oxygen Demand (COD)

The COD is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. This analysis is carried out via a Hach-2000 spectrophotometer using dichromate solution as the oxidant in strong acid. Test solution (2 ml) is pipetted into the dichromate reagent and digested at 150°C for two hours. Color is developed during the oxidation and measured against water blank. Refer to Figure 3.2 for the equipment used in COD examination.



**Figure 3.2: Equipment Used for COD Analysis**

## CHAPTER 4

### RESULT AND DISCUSSION

This section presents the results obtained upon analysis of phenol and benzene degradation using photo-Fenton reagent. Important assumptions in interpretation of result obtained is that 1) the degradation of phenol and benzene is directly related to the level of COD reduction; 2) no quantitative method are available to determine the final concentration of both pollutants prior to treatment using photo-Fenton reagent due to technical problem of HPLC equipment; and 3) all conclusions are based only on the COD reduction level.

The experiment of photo-Fenton reaction with different concentration of hydrogen peroxide and catalyst ( $\text{Fe}^{2+}$ ) were conducted for the degradation of phenol and benzene. These contaminants were prepared so as to resemble the composition of effluent discharge from petroleum refinery industry. The retention time is set at 180 minutes. To ensure homogeneity of wastewater, the mixture is continuously stirred at constant temperature of 25, 40 and 70  $^{\circ}\text{C}$  and pH range within  $3.0 \pm 0.02$ .

#### 4.1 DETERMINATION OF OPTIMUM FENTON'S REAGANT RATIO

The first objective of this project is to determine the optimum ratio of Fenton reagent ( $\text{H}_2\text{O}_2$ :  $\text{Fe}^{2+}$ ).

##### 4.1.1 Observations

Both phenol and benzene are observed to be completely dissolved in the deionized water. This is crucial to support preliminary assumption that homogeneous mixture of

synthetic wastewater is achievable for sampling of COD examination and possible HPLC analysis.

Upon addition of benzene and phenol into deionized water, no colour changes are observed. Addition of the iron salt ( $\text{FeSO}_4$ ) into synthetic wastewater resulted in no colour changes. At this stage, no reaction between pollutants and catalyst are triggered as long as no source of oxidants, i.e. hydroxyl radical is introduced into the solution. As hydrogen peroxide is dosed intermittently throughout the reaction and stirring are started, colour of solution darken to a brown clear solution. As the volume  $\text{H}_2\text{O}_2$  are increased gradually, turbidity in wastewater increases.

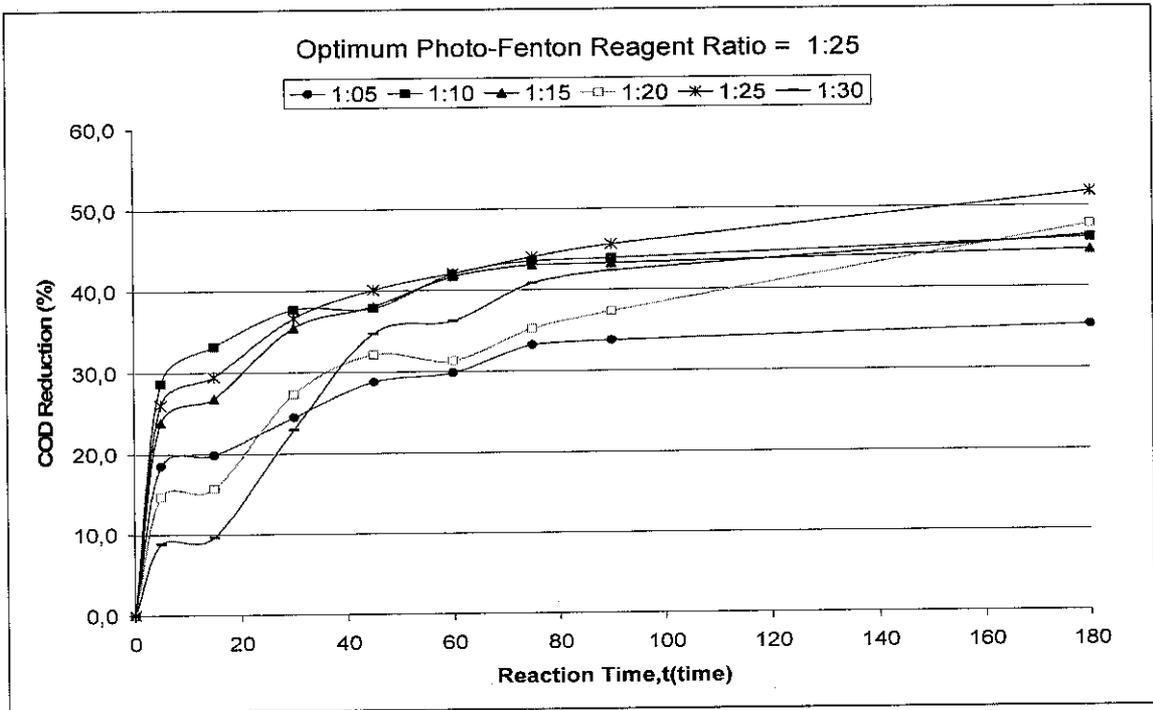
Initially, the pH of synthetic wastewater is slightly basic ( $\text{pH} = 7$  to  $8$ ). Upon start-up of photo-Fenton reaction, acidic condition is introduced to prepare optimum condition for reaction to take place. This pH is maintained throughout the reaction by addition of low concentration of acid and alkali. Very small drop of pH to acidic condition are observed during the reaction time of 180 minutes. At the end of the reaction, there is no observation of any iron precipitation.

#### 4.1.2 Interpretation of Result

The degradation of phenol and benzene were observed solely based on COD reduction percentage. The experimental result were analysed and depicted in Figure 4.1, 4.2 and 4.3, as a function of retention time. Three set of experiments were conducted, with the optimum ratio of Fenton reagent ( $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:25$ ) for two runs and ( $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:20$ ) for one run. The effects observed in the treatment of phenol and benzene is presented in Table 4.1 as a typical example for Set 1 of photo-Fenton reaction.

**Table 4.1: COD Analysis from Photo-Fenton Reaction for Set 1**

<i>Ratio of (<math>\text{Fe}^{2+}:\text{H}_2\text{O}_2</math>)</i>	<i>COD Initial (mg/L)</i>	<i>COD Final (mg/L)</i>	<i>COD Reduction (%)</i>
1:5	747	483	35.3
1:10	907	489	46.1
1:15	883	483	46.4
1:20	747	390	47.8
1:25	906	437	51.8
1:30	806	432	46.4



**Figure 4.1: COD Reduction of Photo-Fenton Process (Set 1)**

As can be seen from Figure 4.1 and Table 4.1, the increment of hydrogen peroxide concentration (volume of  $90\mu\text{L}$  to  $540\mu\text{L}$ ) with constant weight of  $\text{FeSO}_4$  powder (catalyst) clearly intensified the degradation of phenol and benzene in the synthetic wastewater.

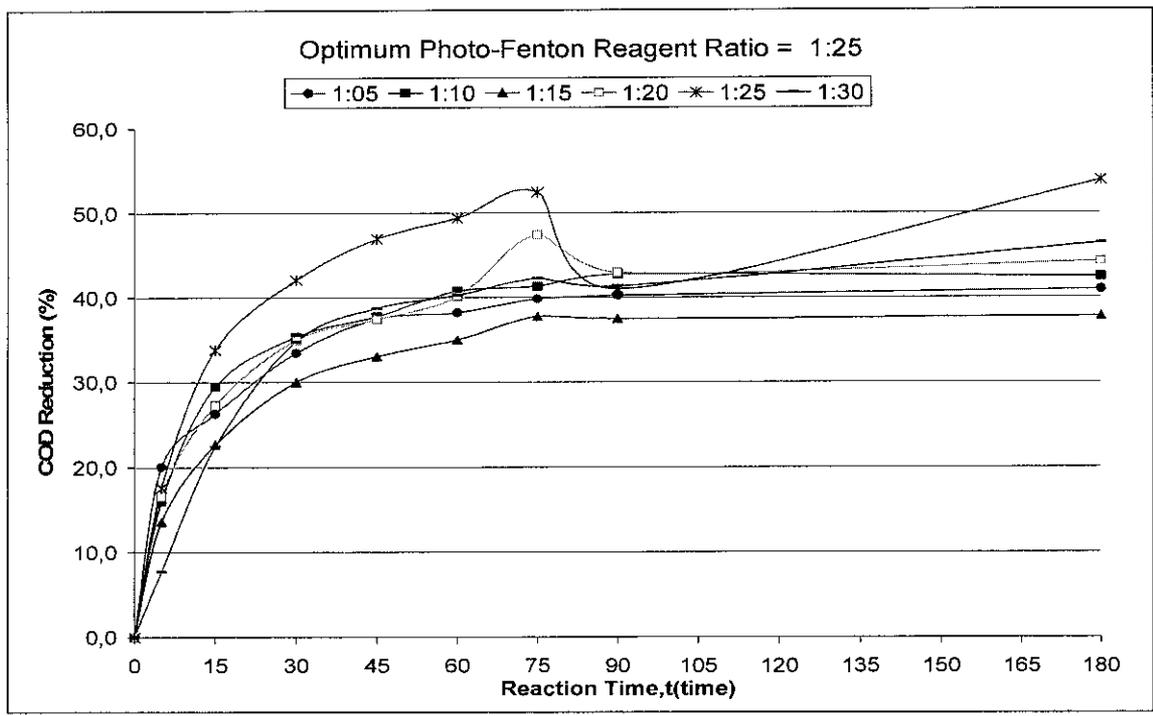
The COD reading was greatly reduced by the increment of  $\text{H}_2\text{O}_2$ , with significant reduction observed at the first 5 minutes, and further obvious reduction until time = 60 minutes of the total retention time. Subsequently, the reduction percentage levels off with very small decrement of COD level. Lunar (1999) also observed similar trend in which the degradation rate was high at the initial stage of the process, then the reaction was definitely retarded, and further degradation took place at a slow rate. This might be due to complete reaction of Fenton reagent with the pollutants, which neglects the effect of other driving force, i.e. UV light in the experiment. Note that this condition does not conclude that total degradation of phenol and benzene was achieved since the COD reading was still relatively high after the specified retention time.

This result coincide with the results reported by Goi (2001), Benitez et al. (1999) and Trapido et al. (1998), who observed positive effects of increasing hydrogen peroxide concentration in the photo-Fenton treatments of various pollutants. Extensive discussion on the effect of hydrogen peroxide concentration to the degradation of phenol and benzene upon treatment using photo-Fenton reagent is presented in Section 4.1.3.

To further investigate the extent of hydrogen peroxide concentration increment towards photo-Fenton reaction, a higher Fenton reagent ratio was adopted, i.e. ( $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:30$ ). The result portrays that further increasing the hydrogen peroxide concentration up to a certain ratio does not give positive effect as opposed to lower ratio. The typical range of  $\text{Fe}^{2+}:\text{H}_2\text{O}_2$  was adopted, as stated in [www.h2o2.com](http://www.h2o2.com) to be 1:5-25 parts respectively with the obtained experimental optimum ratio of ( $\text{Fe}^{2+}:\text{H}_2\text{O}_2=1:25$ ). This statement indicates that the maximum concentration of Fenton reagent to degrade phenol and benzene is ( $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:25$ ).

Typical  $\text{Fe}:\text{H}_2\text{O}_2$  ratios are 1:5-10wt/wt, though iron levels less than 25-50 mg/L can require excessive reaction times ([www.h2o2.com](http://www.h2o2.com)). In all photo-Fenton experiment, the amount of  $\text{Fe}^{2+}$  used is 6 mg as per calculation in Section 3.3.2. Variation of  $\text{Fe}^{2+}$  amount was experimented, with outcome depicts that relatively higher amount than 6 mg resulted in lower COD reduction percentage than the result presented in this report. Patricia (2001) state that iron amount should be as small s possible with the justification that 1) lowering the  $\text{Fe}^{2+}$  amount shall reduce the cost of photo-Fenton treatment and 2) large amount of  $\text{Fe}^{2+}$  shall indirectly increase the COD level as iron complex are generated by its reaction with  $\text{H}_2\text{O}_2$ .

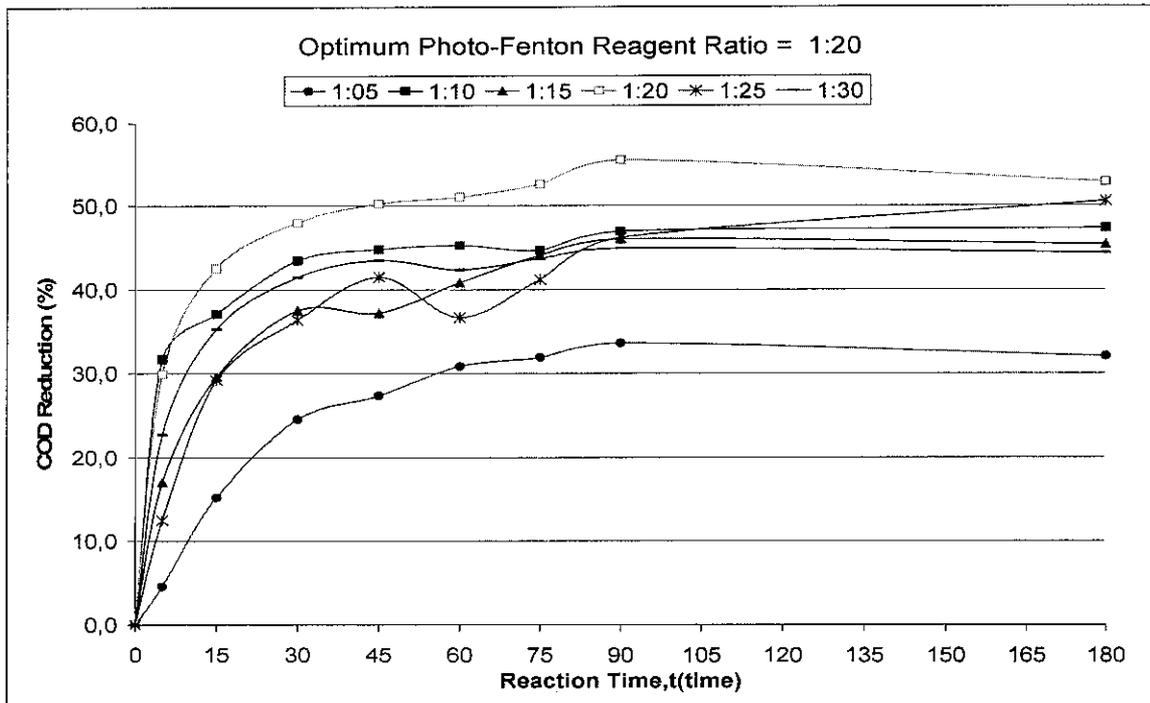
Thus, it is concluded that the optimum amount of  $\text{Fe}^{2+}$  for the degradation of phenol and benzene at the specified amount in Section 3.3.1 is 6 mg. Further discussion on the effect of iron amount to the degradation of phenol and benzene upon treatment using photo-Fenton reagent is presented in Section 4.1.4. Similar effects were observed for Set 2 of photo-Fenton reaction. The result for this Set 2 is depicted in Figure 4.2.



**Figure 4.2: COD Reduction of Photo-Fenton Process (Set 2)**

Set 3 of photo-Fenton reaction however shows slightly different result in which the maximum reduction in COD level occurs at  $Fe^{2+}:H_2O_2 = 1:20$ . Possible explanation to justify on the inconsistency is incorrect dosage of either iron amount or hydrogen peroxide volume.

No unique comparison are available to other literature with respect to this project as there has not been any similar research conducted on the degradation rates of both refractory phenol and benzene using photo-Fenton treatment.



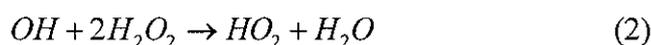
**Figure 4.3: COD Reduction of Photo-Fenton Process (Set 3)**

### 4.1.3 Effect of Hydrogen Peroxide Concentration

Hydrogen peroxide ( $H_2O_2$ ) is one of the most powerful oxidizers known; stronger than chlorine, chlorine dioxide, and potassium permanganate (Table 2.1). In a photo-Fenton reaction, hydrogen peroxide is the major source for the generation of highly reactive hydroxyl radical ( $\cdot OH$ ), with reactivity second only to fluorine. The detailed chemistry of this reaction is in Section 2.2.1. The reason why  $H_2O_2$  can be used for this applications is the different ways in which its power can be directed, termed selectivity. By simply adjusting the conditions of reaction,  $H_2O_2$  can often be made to oxidize one pollutant over another, or to favour different oxidation products from the same pollutant.

Two sets of experiments are conducted to explain on the effect of hydrogen peroxide addition to the wastewater containing phenol and benzene. For controlled case, no addition of  $H_2O_2$  is performed and it was observed that there is no COD reduction. Upon addition of  $H_2O_2$ , the degradation rates of organic substance increase as depicted by the COD reduction. From Figure 4.1, 4.2 and 4.3, it is analysed that 90% of pollutant degradation took place during the first 15 minutes of reaction time. The reaction is rapid by the effect of additionally produced  $\cdot OH$  radicals in the equation (1) and (3).

However, above a certain  $H_2O_2$  concentration, the reaction rate levels off and sometimes is negatively affected, by the progressive increase of  $H_2O_2$  (Patricia, 2001). This may be due to auto-decomposition of  $H_2O_2$  to oxygen and water and recombination of  $\cdot OH$  radicals as follows:



Excess of  $H_2O_2$  will react with  $\cdot OH$  competing with organic pollutants and consequently reducing the efficiency of the treatment. Therefore,  $H_2O_2$  should be added at an optimal concentration to achieve the best degradation, which depends on the nature and concentration of the compound to treat and on the iron concentration (Patricia, 2001).

#### 4.1.4 Effect of Iron Amount

The more difficult-to-oxidize pollutants may require the  $\text{H}_2\text{O}_2$  to be activated with catalysts such as iron, copper, manganese, or other transition metal compounds. These catalysts may also be used to speed up  $\text{H}_2\text{O}_2$  reactions that may otherwise take hours or days to complete. In this photo-Fenton reaction, the catalyst used is iron (II) salt in the form of ferrum (II) sulphate.

As in the case of  $\text{H}_2\text{O}_2$ , degradation rates increase with iron salt amount, but after a determined iron concentration the efficiency decreases. This may be due to the increase of a brown turbidity that hinders the absorption of the light required for the photo-Fenton process (Patricia, 2001). Thus, it is desirable for the ratio of  $\text{H}_2\text{O}_2$  to iron salts to be as small as possible, so recombination of  $\text{Fe}^{2+}$  and  $\cdot\text{OH}$  can be avoided and iron complex production is minimized.

## 4.2 DETERMINATION OF OPTIMUM TEMPERATURE

The second objective of this project is to determine the optimum temperature of Fenton reagent. Three operating temperature of 25, 40 and 70 °C was adopted to study the effect of different temperature on the COD reduction level.

### 4.2.1 Observation

Throughout the reaction, very small temperature increment was observed in the synthetic wastewater. However, this increment was inhibited by the usage of water bath to maintain the operating temperature at its desired level.

### 4.2.2 Interpretation of Result

The degradation of phenol and benzene were observed solely based on the COD reduction percentage. The experimental result were analysed and depicted in Figure 4.4 and 4.5 as a function of retention time. Two set of experiments were conducted, both resulted the optimum temperature of 40°C. The significant effect of increasing the operating temperature of the photo-Fenton reaction can be observed in Table 4.4.

**Table 4.2: COD Level from Photo-Fenton Reaction as a Function of Temp. (Set 1)**

Sample	Time (min)	H <sub>2</sub> O <sub>2</sub> Dosage (μL)	Temperature(°C)		
			20°C	40°C	70°C
			COD (mg/L)	COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0	0
1	0	250	654	689	751
2	5	50	539	337	423
3	30	50	379	353	412
4	60	50	331	337	373
5	90	50	311	273	340

It is clearly observed in Figure 4.4 and 4.5 that increasing the temperature does give significant effect to the COD reduction percentage for both trial set. The COD reduction percentage was observed to be positively affected by 20% upon operating at higher temperature of 40°C. However, there is an extent of increasing the temperature; in which

very high temperature resulted in lower COD reduction as compared to operating at intermediate temperature of 40°C.

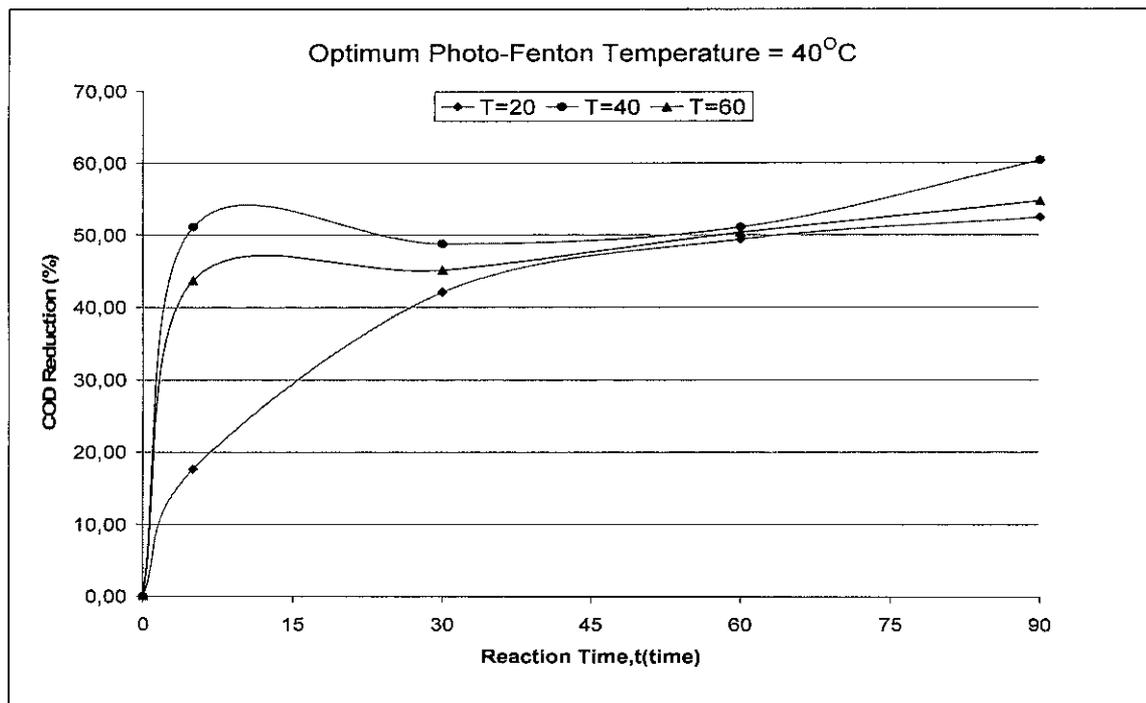


Figure 4.4: COD Reduction of Photo-Fenton Process as a Function of Temp. (Set 1)

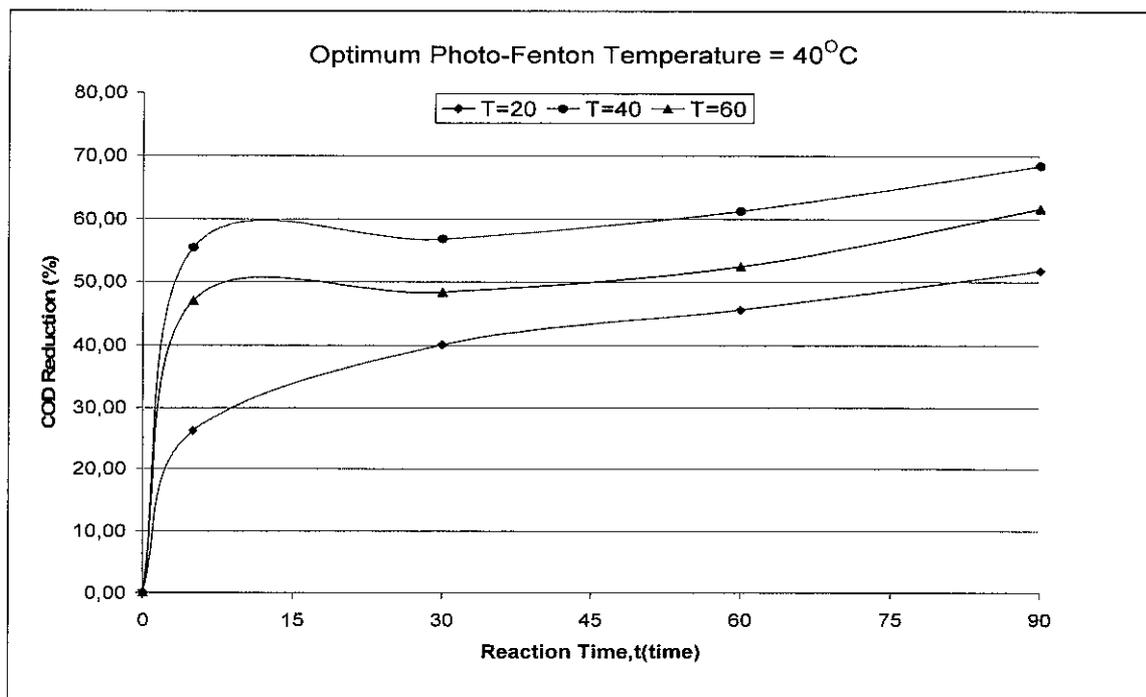


Figure 4.5: COD Reduction of Photo-Fenton Process as a Function of Temp. (Set 2)

### 4.2.3 Effect of Temperature

To explain on the observed temperature increment throughout the reaction, two possible reasons are justified. First is due to the fact that the degradation reaction of phenol and benzene with the hydroxyl radical towards mineralization is exothermic in nature. Nevertheless, this effect is not significant as the rate of degradation reaction is very small. The main source to temperature increment is due to the usage of UV light to enhance the decomposition of pollutants.

The result obtained is consistent with Lunar (1999); in which increasing the temperature increases the rate of reaction. However, there is conflict in explaining the positive effect on the degradation of the pollutants. [www.h2o2.com](http://www.h2o2.com) stated that as temperatures increase above 40-50°C, the efficiency of H<sub>2</sub>O<sub>2</sub> utilization declines. This is due to the accelerated decomposition of H<sub>2</sub>O<sub>2</sub> into oxygen and water, which inhibited the desired reaction of  $\cdot OH$  with both phenol and benzene.

The best justification to clarify on this phenomenon is that the best temperature to operate a photo-Fenton reaction is in the range of 35-45 °C. Overlooking at exothermic reaction for other significant chemical reaction, the temperature should be set as high as possible to take advantage of increasing the degradation rate of phenol and benzene (Smith, 2000). This widely accepted rule of thumb is applicable to the photo-Fenton reaction to further enhance the mineralization of contaminants in the wastewater.

On the other hand, there is practical limit in setting the temperature too high. First is to agree with the fact that very high temperature will accelerate the decomposition of H<sub>2</sub>O<sub>2</sub> into oxygen and water, limiting the source of oxidant in the reaction. This shall further reduce efficiency of photo-Fenton treatment in degrading the pollutants. Though no available quantitative method is present to determine the exact concentration of pollutant upon treatment, the COD level serves well as the indicator towards the amount of phenol and benzene. Second is to consider safety factor upon operating the reaction at very high temperature. Thus, trade off between the positive effects on the rate of reaction and safety limit is crucial to be analyzed upon determining the optimum temperature for photo-Fenton reaction.

## 4.3 OTHER PARAMETERS AFFECTING PHOTO-FENTON REACTION

### 4.3.1 Effect of pH

From literature ([www.h2o2.com](http://www.h2o2.com)), optimal pH for photo-Fenton reaction occurs between pH 3 and pH 6. The pH value influences the generation of  $\cdot OH$  radicals and thus the oxidation efficiency. Due to fluctuating pH as the reaction proceeds, constant monitoring of pH is crucial to ensure suitable acidic condition is available to promote the degradation of phenol and benzene in the wastewater. Throughout the reaction, slight pH decrement was observed as the reaction progressively takes place. This is due to the fact that decomposition of phenol and benzene demineralized into compound that exhibit acidic condition.

For basic pH values, degradation strongly decrease since iron precipitates as hydroxide derivate, reducing the  $Fe^{2+}$  availability. In the case, iron catalytically decomposes the  $H_2O_2$  into oxygen and water, without forming hydroxyl radicals. In the practical application, introducing basic condition into the wastewater solution is applicable to recycle the iron. This can be done by raising the pH to basic condition, separating the iron floc, and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

### 4.3.2 Effect of UV Lamp Intensity

Major limitation of the experiment was that the UV source used is not adequate as per recommended by US EPA (1998). However, based on the observation conducted on the Dark Fenton that was commissioned in parallel with this study, there is significant reduction in COD level upon treatment of phenol and benzene using the available UV source. Thus it is assumed that light does serve as a driving force to further degrade the pollutant, although not achieving the desired requirement as per standard for wastewater degradation of pollutants.

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 CONCLUSION

From the study, the efficiency of photo-Fenton process in the degradation of phenol and benzene were investigated. From literature, various study on photo-Fenton process resulted in a very high removal of organic pollutant in wastewater. However, the reaction are crucially dependent upon other parameters such as Fenton reagent concentration ratio, temperature, pH and light intensity to the extent that optimising these condition is vital to achieve desirable reaction.

One important assumption in result analysis is the degradation rate of phenol and benzene was based solely upon the COD reduction level. Experiments shows that the pollutant degradation was significantly increased upon the increment of photo-Fenton reagent; with the optimum ratio of  $\text{Fe}:\text{H}_2\text{O}_2=1:25$ . The effect of increasing the hydrogen peroxide amount is more pronounced compared to the iron amount towards the level of COD reduction. The optimum temperature for operating photo-Fenton reaction was at  $40^\circ\text{C}$ . Trade-off between increasing the reaction rate by operating at higher temperature and safety limit is crucial in setting the temperature for practical application.

However, one specific objectives of this project have not yet achieved at this point, which is to determine the extent of phenol and benzene degradability upon treatment with photo-Fenton reaction. The result obtained by far is not conclusive to evaluate the overall efficiency of photo-Fenton process since there are no available means to conduct quantitative analysis on the final concentration of respective pollutants. Future research to address this issue is essential to provide in depth knowledge on photo-Fenton reaction and appreciate its effectiveness to achieve ultimate degradation of refractory pollutants.

Likewise, future recommendations on current studies are encouraged so as to improvise and trigger diverse view of photo-Fenton reaction parameters and application. Several items are proposed in the next section to package the comprehension of this advance oxidation process towards the objective of finding noble and cost-effective ways in wastewater treatment system.

Conventional technologies that currently faced several limitations, especially in petroleum refinery industry is hoped to benefit as further investigation is conducted with the reference to this project.

## **5.2 RECOMMENDATIONS**

This section will discuss the recommendation of future project work with regard to this study.

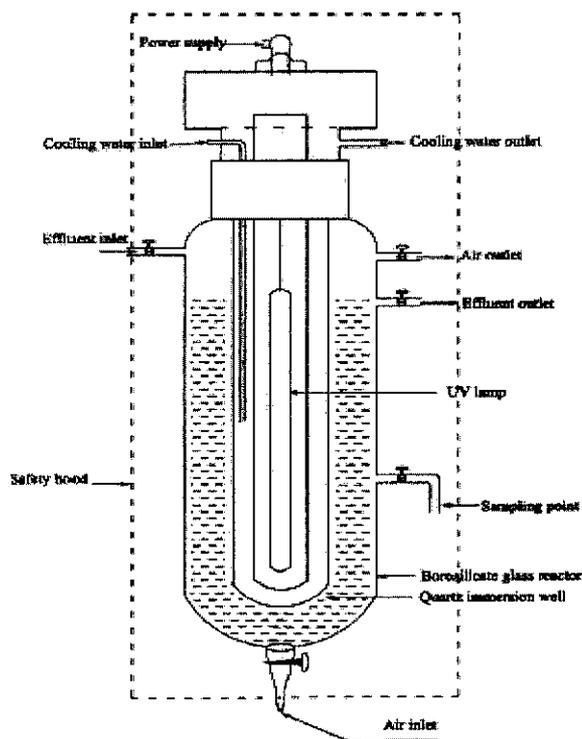
### **5.2.1 Quantitative Analysis on Pollutant Level upon Treatment**

Although the specific objectives of this study are achievable, future investigation should be conducted regarding the final concentration of phenol and benzene after the photo-Fenton reaction. In the initial proposal, Total Organic Carbon (TOC) and HPLC are included for examination to predict the efficiency and overall performance of photo-Fenton process. The limitation imposed on the current study have created boundary for data analysis in which the compliance limit of phenol and benzene are not comparable with the experimental analysis. It is crucial to ensure that the HPLC equipment is ready to be used in future studies to enable accurate interpretation of result.

### **5.2.2 Comprehensive Equipment Set-up**

Temperature and pH are two major parameters that require attentive control to provide optimum condition for the degradation of pollutant in photo-Fenton reaction. One major flaw of current set-up was that the control of these parameters was done manually; knowing that fluctuations are expected throughout the reaction. In addition, source of UV for photo degradation was not adequate as per standard recommended in literature.

Celin (2003) conducted a photo-degradation of toluene in an annular type photo-reactor, with an immersed double-walled 125 W medium pressure mercury lamp at the centre. The detailed illustration of the reactor is shown in Figure 5.1. A simple apparatus can be constructed to resemble this reactor to take the advantage of constant irradiation source and temperature control.



**Figure 5.1: Annular Type Reactor**

### **5.2.3 Conduct Comparative Analysis with Other AOP Technologies**

One obvious comparative study to be conducted is on the efficiency of Fenton and photo-Fenton oxidation process in degrading refractory component; i.e. phenol and benzene. Goi (2002) conducted similar study on the degradation of seven nitrophenols (NPs) in terms of its degradation rates and cost-effectiveness.

The results of the study demonstrated that UV-radiation improved the action of the Fenton system and at the same concentrations of hydrogen peroxide, photo-Fenton reaction led to a more rapid decomposition of all NPs than the Fenton treatment. Due to the regeneration of the consumed  $\text{Fe}^{2+}$  through the irradiation, the amount of catalyst

can be reduced in photo-Fenton treatment. However, the application of the more complicated and costly method is not reasonable, as more than 90% degradation of NPs in the Fenton reagent treatment was achieved in time that is quite acceptable for practical application. The experimental observations and cost analysis strongly suggest that the Fenton treatment is most effective for NPs degradation among all treatments studied. Refer to Table 5.1 for detailed analysis of operating cost for several AOP.

**Table 5.1: Operating Cost for NPs treatment for 90% Reduction of Initial Concentration =0.4mM**

Treatment process	Compound	$[H_2O_2]_0$ (mM)	$[Fe^{2+}]_0$ (mM)	Energy required (Kwh $m^{-3}$ )	Energy cost (\$ $m^{-3}$ )	$H_2O_2$ cost (\$ $m^{-3}$ )	$FeSO_4 \cdot 7H_2O$ cost (\$ $m^{-3}$ )	Total cost ( $m^{-3}$ )
UV	4,6-DN-o-CR	0	0	901	63.1	0	0	63.1
	2,6-DNP	0	0	658	46.1	0	0	46.1
	4-NP	0	0	872	61.1	0	0	61.1
UV/ $H_2O_2$	4,6-DN-o-CR	4	0	60.4	4.22	0.12	0	4.34
		10	0	21.9	1.53	0.29	0	1.82
	2,6-DNP	4	0	55.5	3.88	0.12	0	4.00
		10	0	16.3	1.14	0.29	0	1.43
	4-NP	4	0	15.7	1.10	0.12	0	1.22
		10	0	5.15	0.36	0.29	0	0.65
Fenton	4,6-DN-o-CR	4	0.4	0	0	0.12	0.013	0.13
	2,6-DNP	4	0.4	0	0	0.12	0.013	0.13
	4-NP	2	0.1	0	0	0.06	0.003	0.06
Photo-Fenton	4,6-DN-o-CR	4	0.4	2.39	0.17	0.12	0.013	0.30
	2,6-DNP	4	0.1	2.06	0.14	0.12	0.003	0.26
	4-NP	2	0.1	2.00	0.14	0.06	0.003	0.20

#### 5.2.4 Specific Case Study on Related Industry

All of the above recommendations are the fundamental research towards developing strong understanding and experience on photo-Fenton process.

To appreciate more of its application, specific case study on industry is strongly suggested. Wide industries are available in Malaysia such as petroleum refining, textile industry, petrochemicals processes, etc. that discharges refractory pollutants currently treated by conventional method. With more stringent regulations on their waste effluent quality, integration between university students and industries can be very beneficial towards improving the current wastewater treatment.

## REFERENCES

- Agency for Toxic Substances and Disease Registry (ATSDR), December 1998, "*Toxicological Profile for Phenol and Benzene*", U.S. Department Of Health And Human Services
- Airgas™ Material Safety Data Sheet, January 1998, Airgas Incorporation, Document Number: 1062
- Benitez F.J., Beltran-Heredia J., Acero J.L., Rubio F.J., 1999. "*Chemical decomposition of 2,4,6-trichlorophenol by ozone, Fenton's reagent, and UV radiation*", Ind. Eng. Chem. Res., pg 1341–1349
- Bull A.R and Zeff D.J, "*Hydrogen Peroxide in Advanced Oxidation Processes Treatment of Industrial Processes and Contaminated Groundwater*" in Chemical Oxidation: Technologies for the Nineties
- Canadian Center for Occupational Health and Safety (CCOHS), February 1995, *CHEMINFO database*, Record Number: 179
- Celin S.M., M. Pandit, J.C. Kapoor, R.K. Sharma, April 2003, "*Studies on Photo-Degradation of 2,4-Dinitro Toluene in Aqueous Phase*" Elsevier Science, pg 63-69
- Eckenfelder Jr., W.Wesley, 1993, "*The Role of Chemical Oxidation in Wastewater Treatment Processes*" in Chemical Oxidation: Technologies for the Nineties
- Energy Information Administration (EIA), November 2003, *Malaysia Country Analysis Briefs* home page <<http://www.eia.doe.gov>>
- Glaze W. H., Kang, J.W., Ziegler S., March 1991, "*Treatment of Hazardous Waste Chemicals Using AOPs*". In Proc. 10th Ozone World Congress, Monaco, pg 261–279

- Goi A., Trapido M., August 2001, "*Hydrogen Peroxide Photolysis, Fenton Reagent and Photo-Fenton for the Degradation of Nitrophenols: A Comparative Study*", Elsevier Science, pg 913-922
- Lunar L., Sicilia D., Rubio S., Perez-Bendito D., Nickel U., July 1999, "*Degradation of Photographic Developers by Fenton's Reagent: Condition Optimization and Kinetics For Metal Oxidation*" Elsevier Science, pg 1791-1802
- Mallinckrodt Chemicals Incorporation, *Material Safety Data Sheet, Liquefied Phenol*, MSDS Number: P1952
- Mutter Rein, February 2001, "*Advanced Oxidation Processes – Current Status and Prospects*", Department of Chemical Engineering, Tallinn Technical University
- Ohio Environmental Protection Agency (EPA), September 2002, *Pollution Prevention Fact Sheet*, <<http://www.epa.state.oh.us/opp>>
- OSHA Technical Manual, "*Petroleum Refining Processes*" United States Department of Labor Occupational Safety & Health Administration, <<http://www.osha.gov>>, Section IV: Chapter 2
- Patricia Sandra, "*Coupling Of Photocatalytic and Biological Processes as a Contribution to the Detoxification of Water: Catalytic and Technological Aspects*", 2001, Institute of Environmental Engineering, Department of Rural Engineering, EPFL
- Persatuan Alumni AOTS Malaysia, *The Principle of Water Treatment*, <<http://www.aots.org/>>
- Smith Robin, 2000, *Chemical Process Design*, Chemical Engineering Series, The McGraw-Hill Companies, Inc., pg 39-40

Tang, W.Z. and C.P. Huang, “*2,4-Dichlorophenol Oxidation Kinetics by Fenton's Reagent*” *Environmental Technologies*, 1996. 17: p. 1371-1378

Trapido M., Kallas J., 2000, “*Advanced Oxidation Processes for the Degradation and Detoxification Of 4-Nitrophenol*”, *Environmental Technology*, pg 799–808

United States Environmental Protection Agency, December 1998, “*Handbook on Advanced Photochemical Oxidation Processes*” National Risk Management Research Laboratory (NRMRL), section 2-1

World Bank Group, July 1998, “*Petroleum Refining*” *Pollution Prevention and Abatement Handbook - Project Guidelines: Industry Sector*, pg 377-381>

Reference Library Peroxide Applications,

<<http://www.h2o2.com/application/industrialwastewater/fentonsreagent.html>>

*APPENDIX*  
*A1- EXPERIMENTAL RESULT*

Table 4.1: COD Reduction for Fenton's Reagent Concentration ( $Fe:H_2O_2 = 1:5$ )

Sample	Time (min)	$H_2O_2$ Dosage ( $\mu L$ )	Set 1	Set 2	Set 3
			COD (mg/L)	COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0	0
1	0	50	747	804	571
2	5	-	609	643	545
3	15	10	599	593	484
4	30	10	564	535	431
5	45	10	532	503	415
6	60	10	524	497	395
7	75	-	499	484	389
8	90	-	495	481	379
9	180	-	483	475	388

Table 4.2: COD Reduction for Fenton's Reagent Concentration ( $Fe:H_2O_2 = 1:10$ )

Sample	Time (min)	$H_2O_2$ Dosage ( $\mu L$ )	Set 1	Set 2	Set 3
			COD (mg/L)	COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0	0
1	0	100	907	707	833
2	5	-	647	594	569
3	15	20	606	499	524
4	30	20	565	457	471
5	45	20	564	440	460
6	60	20	526	419	456
7	75	-	512	415	461
8	90	-	509	405	442
9	180	-	489	407	439

Table 4.3: COD Reduction for Fenton's Reagent Concentration ( $Fe:H_2O_2 = 1:15$ )

Sample	Time (min)	$H_2O_2$ Dosage ( $\mu L$ )	Set 1	Set 2	Set 3
			COD (mg/L)	COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0	0
1	0	150	883	654	615
2	5	-	672	565	510
3	15	30	646	506	433
4	30	30	570	458	384
5	45	30	547	438	386
6	60	30	515	425	364
7	75	-	503	407	344
8	90	-	501	409	332
9	180	-	489	407	336

Table 4.4: COD Reduction for Fenton's Reagent Concentration ( $Fe:H_2O_2 = 1:20$ )

Sample	Time (min)	$H_2O_2$ Dosage ( $\mu L$ )	Set 1	Set 2	Set 3
			COD (mg/L)	COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0	0
1	0	200	747	778	719
2	5	-	638	649	504
3	15	40	630	566	413
4	30	40	543	506	374
5	45	40	507	487	358
6	60	40	513	466	352
7	75	-	484	409	341
8	90	-	468	444	320
9	180	-	390	434	339

Table 4.5: COD Reduction for Fenton's Reagent Concentration ( $Fe:H_2O_2 = 1:25$ )

Sample	Time (min)	$H_2O_2$ Dosage ( $\mu L$ )	Set 1	Set 2	Set 3
			COD (mg/L)	COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0	0
1	0	250	906	654	665
2	5	-	670	539	582
3	15	50	639	433	471
4	30	50	574	379	423
5	45	50	543	347	389
6	60	50	525	331	421
7	75	-	507	311	391
8	90	-	493	386	358
9	180	-	437	302	329

Table 4.6: COD Reduction for Fenton's Reagent Concentration ( $Fe:H_2O_2 = 1:30$ )

Sample	Time (min)	$H_2O_2$ Dosage ( $\mu L$ )	Set 1	Set 2	Set 3
			COD (mg/L)	COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0	0
1	0	300	806	741	810
2	5	-	735	684	626
3	15	60	728	575	524
4	30	60	621	483	474
5	45	60	526	454	458
6	60	60	514	443	467
7	75	-	477	428	456
8	90	-	465	435	446
9	180	-	432	397	451

Table 4.7: COD Reduction for Photo-Fenton Temperature =20°C

Sample	Time (min)	H <sub>2</sub> O <sub>2</sub> Dosage (μL)	Set 1	Set 2
			COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0
1	0	250	654	906
2	5	50	539	670
3	30	50	379	543
4	60	50	331	493
5	90	50	311	437

Table 4.8: COD Reduction for Photo-Fenton Temperature =40°C

Sample	Time (min)	H <sub>2</sub> O <sub>2</sub> Dosage (μL)	Set 1	Set 2
			COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0
1	0	250	689	785
2	5	50	337	350
3	30	50	353	339
4	60	50	337	304
5	90	50	273	248

Table 4.9: COD Reduction for Photo-Fenton Temperature =70°C

Sample	Time (min)	H <sub>2</sub> O <sub>2</sub> Dosage (μL)	Set 1	Set 2
			COD (mg/L)	COD (mg/L)
0(Blank)	-	-	0	0
1	0	250	751	751
2	5	50	423	398
3	30	50	412	388
4	60	50	373	357
5	90	50	340	288