

**Degradation of Polycyclic Aromatic Hydrocarbons (PAHs)  
in Produced Water  
by Advanced Oxidation Process  
using Fenton's Reagent**

**ROSEDIANTY MARSILLA BINTI RASHID**

**CIVIL ENGINEERING  
UNIVERSITI TEKNOLOGI PETRONAS**

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by

**Rosedianty Marsilla binti Rashid**

Dissertation submitted in partial fulfillment  
of the requirement for the  
Bachelor of Engineering (Hons)  
Civil Engineering

SEPT 2013

Supervised by:

**Dr Mohamed Hasnain Isa**

**Universiti Teknologi PETRONAS  
Bandar Seri Iskandar  
31750 Tronoh  
Perak Darul Ridzuan**

**CERTIFICATION OF APPROVAL**

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Civil Engineering Programme  
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in partial fulfillment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
(CIVIL ENGINEERING)

Approved by,

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(Dr Mohamed Hasnain Isa)

UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK

September 2013

## **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.

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ROSEDIANTY MARSILLA BINTI RASHID

**Abstract:** - Produced water represents the largest volume of waste stream in oil and gas exploration and production operation. Presence of Polycyclic Aromatic Hydrocarbons (PAHs) in produced water has created tremendous effects on the environment and human health due to its toxicity, mutagenic and carcinogenic effects. In this study, the produced water sample was collected from a local petroleum refinery. This study determines the suitability of Advanced Oxidation Process using Fenton's reagent specifically for the treatment of PAHs-contaminated water. The samples were acidified to selected pH value, ranges from 2-5 and  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  were added following 1:4, 1:3, 1:2 and 1:1 ratio. The pH of reaction mixtures were raised to 10~12 to decompose  $\text{H}_2\text{O}_2$  and to stop oxidation of organic matter prior to COD and TOC measurement. Gas Chromatography-Mass Spectrometer (GC-MS) was used for determination of PAHs after an enrichment step of Liquid-Liquid Extraction (LLE) as re-concentration technique was implemented. The maximum COD and TOC removal achieved in the designed Fenton system was 77.0% and 83.9% respectively, under operating condition of pH 3, 1.5ml  $\text{H}_2\text{O}_2$ , 0.5g  $\text{Fe}^{2+}$  and 180 minutes reaction time. Total PAHs removal was 72.5%, using similar conditions established for COD and TOC removal.

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## **ABBREVIATIONS AND NOMENCLATURES**

AOP	Advanced Oxidation Process
bpd	barrels per day
BOD	Biochemical Oxygen Demand
BTEX	benzene, toluene, ethylbenzene, and xylene
CBM	Coal Bed Methane
COD	Chemical Oxygen Demand
EOP	Electrochemical Oxidation Potential
EU	European Union
GC-MS	Gas Chromatography- Mass Spectrometry
HMW	High Molecular Weight
IC	Inorganic Carbon
LLE	Liquid-Liquid Extraction
LMW	Low Molecular Weight
MW	Molecular Weight
NOM	Natural Organic Matter
NPOC	Non-Purgeable Organic Carbon
PAH	Polycyclic Aromatic Hydrocarbon
SBSE	Stir Bar Sorptive Extraction
SPE	Solid-Phase Extraction
SPME	Solid-Phase Microextraction
TOC	Total Organic Carbon
US-EPA	U.S Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile Organic Carbon
w/w	water to water

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Generally, produced water is a term used in the oil industry to describe water that is produced when oil and gas are extracted from the ground. Drewes et al. (2013) further explained produced water as byproduct of oil and gas exploration and production. It practically consists of a mixture of formation water contained naturally in reservoir; injected water used for the recovery of oil or treated chemicals added during production. In traditional oil and gas wells, produced water is brought to the surface along with oil or gas but this condition is contradicting in coal bed methane (CBM) production, where the wells are drilled into coal seams, and the water located there is pumped to the surface in order to allow gas to release from the seams. Thus, produced water is always found together with petroleum in reservoirs and lies below the hydrocarbons in porous reservoir media as illustrated in Figure 1.1 (Igunnu & Chen, 2012).

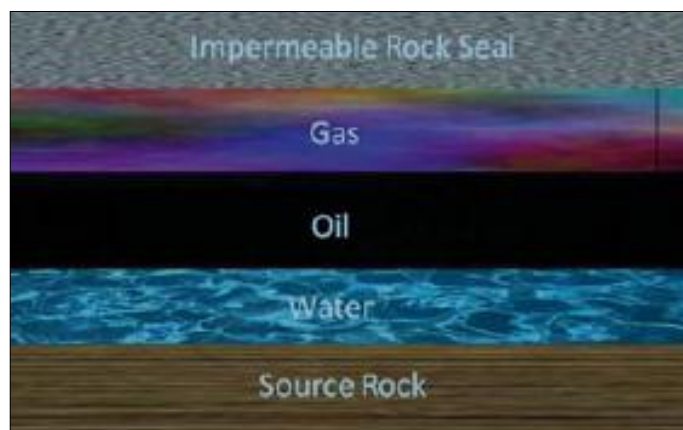


Figure 1.1: *Sketch of typical reservoir*

In that matter, oil reservoirs commonly contain larger volumes of water than gas reservoirs. This is due to the higher compressibility and sorption capacity of gas since gas is stored and produced from less porous reservoirs that contain source rock with a lower water capacity. Produced water generation commonly increases over

time in conventional reservoirs as the oil and gas is depleted during hydrocarbon production.

Produced water is the largest volume by-product or waste stream associated with oil and gas exploration and production. However, the volume of water differs dramatically depending on the type and location of the petroleum product. On average, about 7 to 10 barrels, or 280 to 400 gallons of water are produced for every barrel of crude oil (Guerra, Dahm, & Dundorf, 2011). Globally, 250 million barrels of water are produced daily from both oil and gas fields, and more than 40% of this is discharged into the environment. As of 2009, total oil production in Malaysia was 693,000 barrels per day (bpd) (A Barrel Full: A Barrel Full of Information for Oil Industry Professionals, 2013). This has made produced water generation in Malaysia scaling up to 4,851, 000 to 6,930,000 barrels per day.

Produced water has a complex composition, but its constituents can be broadly classified as organic and inorganic compounds, including oils, grease, heavy metals, radionuclide, treating chemicals, formation solids, salts, dissolved gases, scale products, waxes, microorganisms and dissolved oxygen (Hayes & Arthur, 2004). Narrow and typical classification in the oil and gas produced water composition reveals the non polar and polar hydrocarbons as well as dispersed and dissolved hydrocarbons as shown in Figure 2.

Compounds	ppm	Composition
Dispersed oil =	40 - 100	DA
Dispersed hydrocarbons =		
Dispersed Aliphatics = floating		
Dissolved hydrocarbons		B T E X PAHs A Ph
Toxic:	200 - 800	
- Benzene	Aromatics	
- Toluene		
- Ethyl benzene		
- Xylene		
- PAHs and NPDs	0.2 - 6	
- Alkyl Phenols	0.1 - 0.2	
Dissolved hydrocarbons		Polar
Readily Biodegradable	hundreds	
Polar:		
- Acids		
- Alcohols (Methanol)		

Figure 1.2: Typical classification in the oil and gas produced water composition

The non-polar aliphatic are mainly dispersed and have a tendency to float, while polar hydrocarbons are dissolved and are not floating. Within the dissolved hydrocarbons one can identify hydrocarbons with a clear toxic effect on the environment and hydrocarbons that are less or non toxic and more biodegradable. As indicated, the dispersed oil content can vary from 100 ppm down to 40 ppm or even 30 ppm or less depending on the flotation and coalescing techniques applied. More polar, less toxic and more readily biodegradable components like carboxylic acids and alcohols are generally present at hundreds of ppm. One of the causes of the harmful characteristics of produced water is the presence of toxic dissolved hydrocarbons like BTEX that vary between 100 and 800 ppm as well as Polycyclic Aromatic Hydrocarbons (PAHs), which are organic micro-pollutant compounds found at some hundreds of ppb.

Adham et al. (2012) mentioned that the most important factor that changed the way petroleum industry perceives produced water treatment is legislation. For a long time, only non-polar oil in water was regulated by government, while little attention was given to dissolved organics in produced water. Legislation related to produced water treatment and disposal has become increasingly stringent throughout years of oil and gas production and exploration. For instance, effluent water quality in Pul-A field located in offshore Terengganu, eastern Peninsular Malaysia is mandatory to be in compliance with regulatory effluent discharged water requirement of maximum oil content of 40 ppm (Hadi et al., 2011). In Canada on the other hand, the country sets the regulatory for Oil Sands operations using more than 500 000m<sup>3</sup> of water per year, to treat and recycle 75-90% of the produced water generated. (Produced Water Market- Opportunities in the Oil, Shale and Gas Sectors in North America, 2011).

## **1.2 Problem Statement**

As a pollutant, PAHs are of concern because most isomers of the compounds known to be toxic to living organisms. Their toxicity can also be associated with their photochemical conversion to more toxic photoproducts (Dabestani & Ivanov, 1999). PAHs are carcinogenic micro pollutants which are defiant to environmental degradation due to their highly hydrophobic nature. During their residence time in environment,

PAHs can undergo chemical and photochemical transformation to other products, which may or may not be biologically more inert than the parent compound. These organic contaminants that are resistant to degradation, can remain in the environment for long periods, and have the potential to cause adverse environmental effects. Lloyd (1971), Maclure, (1980), Mazumdar et al. (1975) and Dabestani & Ivanov (1999) stated that most of the experimental evidence for carcinogenicity of PAHs to humans is based on studies carried out on occupational workers exposed to these compounds during processing for coke production, roofing, and oil refining or coal gasification. These studies have associated lung and skin cancer observed in human subjects exposed to PAHs via inhalation or dermal contact. May et al. (1978) added that the extent and rate of dissolution of PAHs and their persistence in aquatic environment are governed by their aqueous solubility. Generally, PAHs solubility decreases and hydrophobicity increases with an increase in number of fused benzene rings. Heavier PAHs compounds are rapidly condensed or adsorbed onto particles when they are deposited directly onto the surface water while the dissolved hydrophilic fraction pollutes the water (Kanchanamayoon & Tatrahun, 2008). As a consequence of their hydrophobic nature, PAHs in aquatic environments rapidly tend to become associated to the particulate matter ending in sedimentation (Kafilzadeh et al., 2011). Thus, the level of PAHs in produced water has been increasing and consequently possesses dangerous threats to aquatic biota and humankind.

### **1.3 Significance of the Project**

Produced water originating PAHs have received greater attention due to alarming potential of PAH for causing long-term adverse effects on the marine environment (Durell et al., 1999). Only small fraction of the produced water is currently being treated to an extent that allows it to be recycled and reused. Hence, this study is significant to ensure that persistent and toxic PAHs are reduced to acceptable level before releasing it to the environment. This is due to fact that the occurrence and abundance of PAHs in aquatic environments represent a risk to aquatic organisms and ultimately to humans through fish and shellfish consumption. The constant need for PAHs determination and quantification to monitor presence of PAHs therefore can be performed through this work.

#### 1.4 Objective and Scopes of Study

- i. To assess the feasibility of Advanced Oxidation Processes (AOPs) using Fenton's reagent in degrading aromatic rings, specifically PAHs in produced water.
- ii. To optimize process conditions viz., Hydrogen Peroxide ( $H_2O_2$ ) and Ferrous Sulphate ( $FeSO_4$ ) dosages, pH and oxidation time for organics removal.
- iii. To implement gas chromatographic determination and quantification of various constituents PAHs

Scopes of study that should have been covered throughout the completion of this work are as follow;

- i. Literature Review

Literature reviews involved in this study are based on completed studies done by other researchers, in forms of journal, conference proceedings and documents from website. Information and reviews that are collected are compared to establish reliable laboratory-scale experiment. Deep background study is made on produced water, presence of PAH in produced water, application of AOPs in water treatment, efficiency of Fenton reaction in degrading aromatic compound, organic content analysis on account of COD and TOC as well as gas chromatographic determination of PAHs.

- ii. Laboratory set up and experiments

Laboratory set up and experiments involved in this study are on Fenton reaction, COD and TOC removal and gas chromatographic determination of PAHs. Selected variables on treatment of produced water through Fenton's reagent Advanced Oxidation Process such as  $H_2O_2$  and  $FeSO_4$  dosage, pH and oxidation time are optimized to determine the effects on degradation efficiency.

- iii. Analysis of result.



Result obtained at the end of each experiment is analyzed to determine whether or not the stated objectives are achieved. Conclusion is then can be established at the end of the study.

### **1.5 The Relevancy of the Project**

This project is very relevant in relation to environmental concerns and prospect of beneficial uses in terms of industrial and knowledge application. PAHs are recalcitrant and not efficiently removed by conventional biological treatment. Based on detail and critical analysis of existing literature on degradation of PAHs in water by Fenton reaction, Fenton's reagent alone or in combination has proven to be an effective way to degrade organic pollutants. Hence, the success of this treatment will contribute to development of produced water treatment efficiency as the largest volume by-product or waste stream associated with oil and gas exploration and production. Risk of formation plugging in disposal wells associated with reinjection of pretreated produced water can be greatly reduced. Treatment of produced water also is imperative due to legislation and environmental concerns and this study can serve as a comparative literature for other people dealing with PAHs-contaminated water. Aside from that, the main theory behind Fenton reaction is advanced oxidation process and thus, theoretical and practical knowledge on Wastewater Engineering are very relevant in this project.

### **1.6 Feasibility of the Project within Scope and Time Frame**

Flotron, et al. (2005) pointed out that Fenton's reagent is the most suitable method of treatment due to its moderate cost, simplicity of operation and its advanced oxidative potential due to the formation of hydroxyl radical. Simplicity of operation ensures that laboratory experiments will not be time-consuming and feasible to be done within allocated time frame. The project's practicality is guaranteed as all the reagents, materials, tools and hardware are readily found in the laboratory.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Polycyclic Aromatic Hydrocarbons (PAHs)**




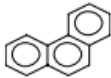
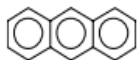
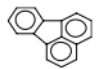

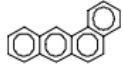
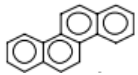
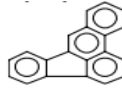
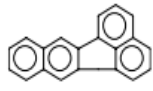
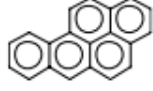
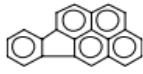
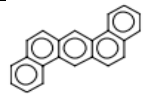

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of several hundred individual compounds made up of more than two fused aromatic rings in a linear or clustered arrangement, usually containing only carbon (C) and hydrogen (H) atoms, although nitrogen (N), sulphur (S) and oxygen (O) atoms may readily substitute in the benzene ring to form heterocyclic aromatic compounds (Yap et al., 2011). In organic chemistry, aromaticity is a chemical property describing the way in which a conjugated ring of unsaturated bonds, lone pairs or empty orbital exhibits stabilization stronger than would be expected by the stabilization of conjugation alone (Hofmann, 1856). Olfaction or olfactory perception on the other hand is the sense of smell. The first known use of the word aromatic as a chemical term occurs in an article by August Wilhelm Hofmann in 1855. However, Hoffman says nothing about why he introduced an adjective indicating olfactory character to apply to a group of chemical substances only some of which have notable aromas.

The widespread occurrence of PAHs is largely due to their formation and release in all processes of incomplete combustion of organic materials. As been stated by Rauscher et al. (2012), sources of PAHs are both natural and anthropogenic. PAHs are common constituent of petroleum-based products, and thus frequently concentrated in industrial sites associated with gas production, coke ovens and graphite electrode manufacturing, petroleum refining and wood preservation. Different types of combustion yield different distributions of PAHs in both relative amounts of individual PAHs and in which PAHs with the same formula and number of rings are produced. As for natural sources, PAHs are found in volcanic activity as well as forest fires. Hence, PAHs are becoming more and more prevalent in ecosystems as a result of growing industrial activities and expanding urbanization. Currently, there is a great concern regarding the occurrence and

handling of PAHs which is among the most frequently detected pollutants (Jonsson et al., 2007).

PAHs are classified as among the most persistent pollutants and are known to be toxic, mutagenic and carcinogenic. The toxicity of PAHs is structure-dependent where the isomers of PAHs can vary from being nontoxic to extremely toxic. As an example, one PAH compound, benzo[*a*]pyrene, is notable for being the first chemical carcinogen to be discovered and is one of many carcinogens found in cigarette smoke (Andreas, 2004). This statement is further elaborated by Pakpahan et al. (2012) that stated out of more than 10,000 known PAHs; about 200 compounds are possible carcinogens. Once absorbed in humans and animals, PAHs are distributed by blood route to several tissues, especially to lipophilic tissues, due to their non polar character. Owing to its adverse impacts on ecosystems and human health, PAHs are classified among the most persistent organic pollutants, some of which are listed in U.S Environmental Protection Agency (US-EPA) and European Union (EU) as priority pollutants in which even of these 16 PAHs are considered to be carcinogens (Zhang et al., 2013). 16 PAHs that are listed by US-EPA are tabulated in Table 2.1 as follows;

Table 2.1: Selected properties of 16 priority PAHs listed by US EPA and EU

Compound	Abbreviation and Structure	Formula/ MW	Melting Point (°C)	Boiling Point (°C)	No. of ring
Acenaphthylene	AC 	C <sub>10</sub> H <sub>8</sub> /128	81	218	2
Acenaphthene	CAN 	C <sub>10</sub> H <sub>8</sub> /152	95	270	3
Fluorene	FL 	C <sub>10</sub> H <sub>10</sub> /154	96.2	279	3
Phenanthrene	PHE 	C <sub>13</sub> H <sub>10</sub> /166	116	294	3
Anthracene	AN 	C <sub>13</sub> H <sub>10</sub> /178	101	338	3
Fluoranthene	FA 	C <sub>13</sub> H <sub>10</sub> /178	216	340	3
Pyrene	PY 	C <sub>16</sub> H <sub>10</sub> /202	109	383	4
Benzo [a] Anthracene <sup>a</sup>	B[a]A 	C <sub>16</sub> H <sub>10</sub> /202	150	393	4
Chrysene	CHR 	C <sub>18</sub> H <sub>12</sub> /228	161	425	4
Benzo [b] Fluoranthene <sup>b</sup>	B[b]F 	C <sub>18</sub> H <sub>12</sub> /228	254	431	4
Benzo [k] Fluoranthene <sup>b</sup>	B[k]F 	C <sub>20</sub> H <sub>12</sub> /252	168	481	5
Benzo [a] Pyrene <sup>a</sup>	B[a]P 	C <sub>20</sub> H <sub>12</sub> /252	271	481	5
Indeno[1,2,3-cd]Pyrene <sup>b</sup>	IP 	C <sub>20</sub> H <sub>12</sub> /252	178	496	6
Dibenzo[a,h] Anthracene <sup>b</sup>	D[ah]A 	C <sub>22</sub> H <sub>12</sub> /276	164	536	6
Benzo[g,h,i] Perylene	B[ghi]P 	C <sub>22</sub> H <sub>14</sub> /278	206	535	6

As each PAH has different physico-chemical properties, the level of difficulty in degrading the compounds varies. Molecular weights and boiling and melting point of PAHs are inversely proportional to its solubility and volatility. In that order, two to three fused aromatic rings correspond to low molecular weight (LMW) compound have high solubility, more volatile and more lipophilic; and are termed hydrophilic. In contrast, high molecular weight (HMW) PAHs with four to six fused aromatic rings are termed hydrophobic and are less volatile and less lipophilic. On the other hand, the biological activity and occurrence of the HMW PAHs do appear to be a continuation of LMW PAHs. They are found as combustion products, but at lower levels than the small PAHs due to the kinetic limitation of their production through addition of successive rings. However, hydrocarbons that are less or non toxic are more biodegradable (Meijer & Madin, 2010).

Degradation of PAHs by nonbiological ways occurs via oxidation reactions in the same way that the microbially mediated enzymatic reactions occur. In general, for a species to become oxidized, an electron from another species possessing a higher oxidation state needs to be transferred. Oxidation potentials for selected PAHs are tabulated in Table 2.2 as shown;

Table 2.2: *Oxidation potential of selected PAHs compounds\**

<b>PAHs Compounds</b>	<b>Oxidation Potential</b>
Acenaphthene	1.21
Acenaphthylene	1.21
Anthracene	1.09
Benz[a]anthracene	1.18
Benzo[a]pyrene	0.94
Benzo[ghi]perylene	1.01
Chrysene	1.35
Dibenz[ah]anthracene	1.26
Fluoranthene	1.45
Naphthalene	1.54
Phenanthrene	1.50
Pyrene	1.16

\*Dabestani & Ivanov (1999).

## 2.2 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) have not been widely applied yet because the chemical processes behind advanced oxidation are not completely understood (Bergendahl & O'Shaughnessy, 2004). However, the development and application of several AOPs to destroy toxic and biologically refractory organic contaminants in aqueous solution has caused significant research to be done in the field of environmental engineering during the last decades.

AOPs are used to oxidize complex organic constituents found in wastewater that are difficult to degrade biologically into simpler end products. AOPs typically involve the generation and use of the hydroxyl free radicals ( $\text{OH}\cdot$ ) as strong oxidant to destroy compounds that cannot be oxidized by conventional oxidants such as oxygen, ozone and chlorine. Generally, Chemistry in AOPs could be essentially divided into three parts;

- i. Formation of  $\cdot\text{OH}$ ;
- ii. Initial attacks on target molecules by  $\cdot\text{OH}$  and their breakdown to fragments;
- iii. Subsequent attacks by  $\cdot\text{OH}$  until ultimate mineralization.

Precise, pre-programmed dosages, sequences and combinations of these reagents are applied in wastewater treatment in order to obtain a maximum  $\cdot\text{OH}$  yield. Relative oxidizing powers of the hydroxyl radical, along with other common oxidants are summarized in Table 2.2 as shown;

Table 2.3: Comparison of oxidizing potential of various oxidizing agents<sup>a</sup>

Oxidizing Agent	Electrochemical Oxidation Potential (EOP), V	EOP relative to chlorine
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen Peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

<sup>a</sup>From Ozonia (1977)

Hydroxyl radicals are very reactive species that react unselectively with many organic and inorganic compounds and oxidation of chemical compounds with this reagent is a well-known process (Beltran et al., 1997). The OH<sup>•</sup> radical properties as the second most reactive chemical species known next to fluorine atom, allows the reactive species to serve as the primary radical to oxidize contaminants such as PAHs.

There are various means of chemical oxidation through AOPs and PAHs are removed from the environment by volatilization, photo and chemical oxidation, adsorption to soil particles, leaching, bioaccumulation and biodegradation (Nadarajah et al., 2002). Various reacting systems of AOPs have been developed to produce those hydroxyl radicals and among them are Peroxone (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), Ozone/Hydrogen Peroxide/Ultraviolet (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV), Ozone/Ultraviolet Radiation (O<sub>3</sub>/UV), Ultraviolet Radiation/Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>/UV), Titanium Dioxide/Ultraviolet Radiation (TiO<sub>2</sub>/UV) and Fenton reactions (Bergendahl & O'Shaughnessy, 2004).

AOPs differ from other treatment processes such as ion exchange or stripping because wastewater compounds are degraded rather than concentrated or transferred into a different phase. It could effectively eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phase. Due to remarkable reactivity of •OH, AOPs virtually react with almost every aqueous pollutants without much discrimination. AOPs could therefore be applicable in many, if not all, cases where many organic contaminants are expected to be removed at the same time. In some AOPs designs, disinfection could also be achieved, leading AOPs to an integrated solution to some of the water quality problems. Since the complete reduction product of •OH is H<sub>2</sub>O, AOPs theoretically do not introduce any new hazardous substances into the water. In short, when applied in properly tuned conditions, AOPs can reduce the concentration of contaminants from several-hundreds ppm to less than 5 ppb and therefore significantly bring TOC down, which earned it the credit of “water treatment processes of the 21st century” (Rein, 2001).

### 2.3 Fenton Reaction

Since the 1970s, research on the biological degradation of PAHs has demonstrated that bacteria, fungi and algae possess catabolic abilities for the remediation of PAH-contaminated soil and water. However, this bioremediation has been shown to be effective only in remediating soils and water contaminated with low molecular weight of PAHs and there was lack of microbial activity towards high molecular weight of PAHs (Juhasz & Naidu, 2000). In that matter, Fenton reaction is very relevant to degrade heavier PAHs due to its ability to generate strong oxidant to destroy high molecular weight organic compounds. The  $\bullet\text{OH}$  radical properties as the second most reactive chemical species known next to fluorine atom, allows the reactive species to serve as the primary radical to oxidize such contaminants. This statement is supported by (Flotron et al., 2004) that affirmed hydroxyl radicals are the most oxidative species that can be formed in aqueous solutions, and have been shown to degrade many organic compound including PAHs, using different AOPs.

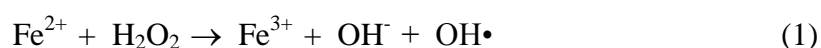
Following the fundamental research of Fenton reaction, remarkable developments have been made to advance its application in water treatment. The developments are focused on pH extension, in situ supply of  $\text{H}_2\text{O}_2$  via the cathodic reduction of oxygen, in situ supply of  $\text{Fe}^{2+}$  via the electrochemical anodic oxidation of elemental iron, and Fe (II) regeneration by illuminating the sludge iron sources (Chuan et al., 2012). Variety of Fenton reactions mentioned is as outlined in Table 2.3;

Table 2.4: *Various types of Fenton reactions*

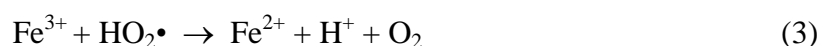
	Reagents	pH	Iron Loss	Light
Classic Fenton	$\text{H}_2\text{O}_2, \text{Fe}^{2+}$	2–4	Yes	No
Fenton-like	$\text{H}_2\text{O}_2, \text{Fe}^{3+}$	2–4	Yes	No
Photo-Fenton	$\text{H}_2\text{O}_2$ , iron complex, free iron ion	Acidic to neutral	Yes	Yes
Heterogeneous Fenton	$\text{H}_2\text{O}_2$ , solid iron oxide	Wide range	No	No
Electro-Fenton	Electrogenerated $\text{H}_2\text{O}_2$ , free iron ions; $\text{H}_2\text{O}_2$ , electrogenerated $\text{Fe}^{2+}$	2–4	Yes	
Heterogeneous photo-Fenton	$\text{H}_2\text{O}_2$ , solid iron oxide	Wide range	No	Yes
Heterogeneous photoelectro-Fenton	Electrogenerated $\text{H}_2\text{O}_2$ , solid iron oxide	Wide range	No	Yes



Historically, Fenton reaction has been applied to the destruction of toxic organics since last four decades (Englehardt & Deng, 2006). AOP through Fenton's reaction is based on the catalyzed decomposition of hydrogen peroxide by transition metal salts to produce very reactive hydroxyl radicals. Transition metal salts such as Ferrous Chloride and Ferrous Sulphate that act as catalyst in the process are contributing to the sources of iron in the reaction. This reaction is called Fenton reaction or classical Fenton reaction. It is a chain reaction with step (1) serving as chain initiation.



Cycle (1)-(2)-(3) form the chain for the site of O<sub>2</sub> evolution, while steps (4) and (5) act as termination reaction.



Among various AOPs, the Fenton's reagent is an interesting solution since it allows high depuration levels at room temperature and pressure conditions using harmless and easy to handle reactants (Benatti & Tavares, 2012). Fenton process is a relatively economical method since it requires no additional energy when compared to many other AOPs. Furthermore, both iron and hydrogen peroxide are relatively cheap and safe. Although many phases of reactions occur during the Fenton oxidation process, the overall reaction only producing water, oxygen, and carbon dioxide and thus by products from the reaction are non-toxic at the levels produced.

Cross referencing of literature studies generally highlighted that major parameters affecting Fenton process are solution's pH, amount of ferrous ions, concentration of H<sub>2</sub>O<sub>2</sub>, reaction time and H<sub>2</sub>O<sub>2</sub> to FeSO<sub>4</sub> ratio. The initial concentration of the contaminant and its character as well as temperature, may also have a substantial influence on the final efficiency. The optimum pH for Fenton's reagent processes ranges from 2 to 4 (Gogate & Pandit, 2008). Barbusiński (2004) supported the statement by reporting the pH value should be in the range of 2.5- 4.0 for maximum Fenton's reagent efficiency. At pH higher than 4, the Fe<sup>2+</sup> ions are unstable and they

are easily transformed to  $\text{Fe}^{3+}$  ions, forming complexes with hydroxyl. Under these alkaline conditions,  $\text{H}_2\text{O}_2$  will lose its oxidative power due to its breakdown to oxygen and water. Thus, Fenton reaction is limited by a narrow pH range and to overcome the limitation, wastewater pH adjustment is usually needed before treatment with Fenton processes.

For the  $\text{H}_2\text{O}_2$  and iron catalyst ratio, increase of ferrous ions and  $\text{H}_2\text{O}_2$  concentration results to an increase of degradation rate. However,  $\text{H}_2\text{O}_2$  possess toxicity effects to several microorganisms and thus the use of excess amounts of  $\text{H}_2\text{O}_2$  could possibly deteriorate overall degradation efficiency for cases that Fenton process is followed by biological oxidation (Gogate and Pandit, 2004). In presence of other ions, Fenton oxidation of organic compounds is inhibited by phosphate, sulfate, fluoride, bromide and chloride ions. Inhibition by these species may be due to precipitation of iron, scavenging of  $\bullet\text{OH}$  or coordination to dissolved  $\text{Fe(III)}$  to form a less reactive complex (Pignatello et al., 2006).

Recent applications of Fenton's reagent include The Pre-treatment of Olive Mill Wastewater (Lucas & Peres, 2009), The Treatment of Landfill Leachate (Deng & Englehardt, 2006; Zhang et al., 2005), Copper Mine Wastewater (Mahiroglu et al., 2009), Water-based Printing Ink Wastewater (Ma & Xia, 2009) and cellulose bleaching effluents (Torrades et al., 2003).

Table 2.5: Various application of Fenton reaction in PAHs degradation.

References	Wastewater treated	Summary of findings
<p>Benatti, C. T., &amp; Tavares, C. R. (2012). Fenton's Process for the Treatment of Mixed Waste Chemicals.</p>	<p>Chemical effluents generated during the laboratory operations</p>	<p>Hydrogen peroxide is most stable in the range of pH 3-4, but the decomposition rate is rapidly increased with an increasing pH above 5. Thus, the acidic pH level around 3 is usually optimum for Fenton oxidation. Regarding the Fenton's residues, they were classified as hazardous according to Brazilian waste regulations. The application of the sequential dissolution procedure indicated that the metals in the Fenton's residues are mainly constituted of amorphous material (over 80%). The reactive fractions of the residues that composed of exchangeable and amorphous iron oxide fractions retain most of remaining metals. Therefore, Fenton's residues present great potential for environmental contamination, and require an administration system and control of their final disposal.</p>
<p>Chu, L., Dong, J., Liu, H., Sun, X., &amp; Wang, J. (2012). Treatment of Coking Wstewater by an Advanced Fenton Oxidation Process Using Iron Powder and Hydrogen Peroxide. <i>Chemosphere</i>, Vol 86, 409-414.</p>	<p>Coking wastewater.</p>	<p>At an initial pH of less than 6.5 and H<sub>2</sub>O<sub>2</sub> amount of 0.3 M, COD removal reached 44–50% and approximately 95% of total phenol was removed at a reaction time of 1.0 h. After a reaction time of 1 h, the Specific Oxygen Uptake Rate (SOUR) increased by approximately 64.9% which contributed to further biological degradation</p>

Table 2.5(contd.): Various applications of Fenton reaction in PAHs degradation.

References	Wastewater treated	Summary of findings
Barbusiński, K. (2009). The Full Scale Treatment Plant for Decolourisation of Dye Wastewater. 1-6.	Dye wastewater from production of matches.	Fenton's reagent can achieve high removal efficiency for various parameters such as COD, colour and toxicity. Long term experiences on technical scale suggest that Fenton's reagent can also be applied successfully in other industries, which produced water resistant to biodegradation.
Lucas, M. S., & Peres, J. A. (2009). Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study. <i>Journal of Hazardous Materials</i> , 1253–1259.	Olive mill wastewater (OMW).	The effect of different operational conditions, namely, hydrogen peroxide and ferrous ion concentrations, temperature and initial pH were evaluated. Working with an initial pH equal to 3.5, a temperature of 30 °C, a molar ratio $H_2O_2/Fe^{2+} = 15$ and a weight ratio $R=H_2O_2/COD= 1.75$ makes possible a COD conversion of 70%.
Ma, X.-J., & Xia, H.-L. (2009). Treatment of Water-based Printing Ink Wastewater by Fenton Process Combined with Coagulation. <i>Journal of Hazardous Materials</i> , Vol 162, 386–390.	Water-based printing ink	Parameters affecting the Fenton process, such as pH, dosages of Fenton's reagent and the settling time, were determined by using jar test experiments. 86.4% of color and 92.4% of chemical oxygen demand (COD) could be removed at pH 4, 50 mg/l $H_2O_2$ , 25 mg/l $FeSO_4$ and 30 min settling time.
Englehardt, J. D., & Deng, Y. (2006). Treatment of Landfill Leachate by the Fenton Process. <i>ScienceDirect</i> , 3684.	Landfill leachate.	COD removal efficiency by coagulation peaked at pH 3.0–6.0. Ratio of Fenton's reagents greatly influences process efficiency because it determines the degree of scavenging of hydroxyl radicals.

Table 2.5(contd.): Various applications of Fenton reaction in PAHs degradation.

<p>Mahiroglu, A., Sevimli, F. M., &amp; Tarlan-Yel, E. (2009). Treatment of Combined Acid Mine Drainage (AMD)—Flotation Circuit Effluents from Copper Mine via Fenton's Process. <i>Journal of Hazardous Materials</i>, Vol 166, 782–787.</p>	<p>Copper mine wastewater, including heavy metals, AMD, as well as flotation chemicals.</p>	<p>Since original pH of AMD is already acidic, no additional pH adjustment at the beginning of the reaction is required. The utilization of existing <math>\text{Fe}^{2+}</math> and pH of the AMD will have considerable savings in the chemical costs for the oxidation. <math>\text{Fe}^{2+}/\text{H}_2\text{O}_2</math> molar ratio of 1.8 was enough to achieve the best treatment performance.</p>
<p>Barbusiński, K., &amp; Filipek, K. (2001). Use of Fenton's Reagent for Removal of Pesticides from Industrial Wastewater. <i>Polish Journal of Environmental Studies Vol. 10, No. 4</i>, 208.</p>	<p>Industrial wastewater contains pesticide (<math>\gamma</math>-HCH and inactive isomers <math>\alpha</math>- and <math>\beta</math>-HCH, DDT, DMDT, fenitrothion and chlorfenvinphos).</p>	<p>The optimum ratio of <math>[\text{Fe}^{2+}]</math> to <math>[\text{H}_2\text{O}_2]</math> was from 1:3 to 1:2 while the optimum pH was from 3.0 to 3.5. A test based upon a bioluminescent bacteria <i>Vibrio fischeri</i> NRRL B-11177, at optimized Fenton's reaction parameters, shows the reduction of toxicity to non-toxic levels.</p>
<p>Barbusinski, K. (2004). Toxicity of Industrial Wastewater Treated by Fenton's Reagent. <i>Polish Journal of Environmental Studies Vol. 14, No. 1 (2005), 11-16</i>, 1-6.</p>	<p>Wastewater from the production of maleic acid anhydride (MAA).</p>	<p>Optimized parameters of Fenton's reaction and changes of wastewater toxicity are <math>5.0\text{g}/\text{dm}^3</math> of <math>\text{H}_2\text{O}_2</math>, <math>\text{Fe}^{2+}/\text{H}_2\text{O}_2</math> ratio of 0.33, at pH of 3.0 and 1.5h reaction time. The final COD removal was 87.8%</p>
	<p>Wastewater from the production of 2-ethylhexyl alcohol (2-EHA).</p>	<p>Optimized parameters of Fenton's reaction and changes of wastewater toxicity are <math>5.0\text{g}/\text{dm}^3</math> of <math>\text{H}_2\text{O}_2</math>, <math>\text{Fe}^{2+}/\text{H}_2\text{O}_2</math> ratio of 0.5, at pH of 3.5 and 1.5h reaction time. The final COD removal was 86.3%</p>
	<p>Wastewater from the production of urea-formaldehyde resin adhesive (UFRA).</p>	<p>Optimized parameters of Fenton's reaction and changes of wastewater toxicity are <math>4.0\text{g}/\text{dm}^3</math> of <math>\text{H}_2\text{O}_2</math>, <math>\text{Fe}^{2+}/\text{H}_2\text{O}_2</math> ratio of 0.33, at pH of 3.5 and 1.5h reaction time. The final COD removal was 88.6%</p>

Since one of the objectives of this work is to adapt and implement relatively simple and rapid method for gas chromatographic determination and quantification of various constituent PAHs, Fenton reaction is definitely useful as Jonsson et al. (2006) used both Fenton's reagent and ozonation on nine samples from five different contaminated sites and found that Fenton's reagent was generally more efficient in degrading PAHs than ozone treatment. Fenton's reagent removed 40-86% of the initial PAHs, as opposed to 10-70% removal by ozone oxidation. Ozonation was more effective in degrading LMW PAHs than HMW PAHs, while Fenton's reagent removed PAHs of all weights. However, most researchers have found that the oxidation rate of LMW PAH compounds by Fenton's reagents is generally higher than that of HMW PAHs (Wilson and Jones, 1993).

#### **2.4 Liquid-Liquid Extraction (LLE)**

In general, Wells M. J., (2003) stated that three widely used techniques for extraction of semi-volatile organics from liquids are liquid-liquid extraction (LLE), solid-phase extraction (SPE), and solid-phase micro-extraction (SPME). Sometimes, stir bar sorptive extraction (SBSE), is also discussed. Extraction or separation of dissolved chemical component X from liquid phase A is accomplished by bringing the liquid solution of X into contact with a second phase, B, given that phases A and B are immiscible. Phase B may be a solid, liquid, gas, or supercritical fluid. A distribution of the component between the immiscible phases occurs. After the analyte is distributed between the two phases, the extracted analyte is released or recovered from phase B for subsequent extraction procedures or for instrumental analysis (Wells M. J., 2003)

In LLE, phases A and B are both liquids. The two liquid phases must be immiscible. For that reason, LLE has also been referred to as immiscible solvent extraction or partitioning. In practice, one phase is usually aqueous while the other phase is an organic solvent. It is a method where separation of compounds is based on their relative solubility in two different immiscible liquids, usually water and an organic solvent. An extraction can be accomplished if the analyte has favorable solubility in the organic solvent. Solvents that have a density smaller than that of water, that is

<1.00, will separate as the top layer, and solvents that have a greater density than water will separate into the lower layer. Following are the densities of some common extraction solvents;

Table 2.6: *Common types of extraction solvent*

<b>Solvent</b>	<b>Density (g/mL)</b>
Ligroin (mixture of low boiling hydrocarbons)	0.67-0.69
Diethyl ether (ether)	0.71
Toluene	0.87
Water	1.00
Methylene chloride (dichloromethane)	1.33

The organic solvents used for extraction should readily dissolve substance to be extracted, should not react with the substance to be extracted, should not react with or be miscible with water as water is the usual second solvent and should have a low boiling point so it can be easily removed from the product. In LLE, no solvent is completely insoluble in another solvent. In practice, one additional step is usually carried out before evaporating the organic solvent which is to dry the solvent over drying agent. Common drying agents used are tabulated as below;

Table 2.7: *Common types of drying agents*

<b>Drying Agent</b>	<b>Formula</b>	<b>Speed</b>	<b>Capacity†</b>	<b>Hydration††</b>
Sodium Sulfate	Na <sub>2</sub> SO <sub>4</sub>	Medium	High	7-10
Magnesium Sulfate	MgSO <sub>4</sub>	Fast	High	7
Calcium Chloride	CaCl <sub>2</sub>	Fast	Low	2
Calcium Sulfate (Drierite)	Ca SO <sub>4</sub>	Fast	Low	½-2

† Capacity refers to the amount of water removed per given weight of drying agent.

†† Hydration is the number of water molecules removed per molecule of drying agent.

Extraction processes are well suited to the petroleum industry because of the need to separate heat-sensitive liquid feeds according to chemical type that includes aliphatic, aromatic, and naphthenic rather than by molecular weight or vapour pressure. Hence, PAHs in produced water is extracted using Liquid-liquid extraction (LLE) followed by an analysis by means of gas chromatography–mass spectrometry (GC-MS) to provide a detailed chemical characterization of PAHs.

## 2.5 Gas Chromatography–Mass Spectrometry (GC-MS)

The use of a mass spectrometer as the detector in gas chromatography was developed during the 1950s after being originated by James and Martin in 1952. Generally, Gas Chromatography–Mass Spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. In early years of invention, these sensitive devices were limited to laboratory settings. However, applications of GC-MS has widened over the years that nowadays the application includes drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. Detection of PAHs in materials is often done using GC-MS.

GC-MS device generally consists of an injection port at one end of a metal column packed with substrate material and a detector at the other end of the column. A carrier gas propels the sample down the column and flow meters and pressure gauges are used to maintain a constant gas flow. (Hites, 2000) mentioned that a gas that does not react with the sample or column is essential for reliable results. In that matter, typical carrier gases used are argon, helium, hydrogen, nitrogen, or hydrogen. However, helium is the most common used carrier gases among many analysts because of its inert property. Hydrogen usually is a good carrier gas but it may react and convert the sample into another substance and sometimes, the ultimate choice for a carrier gas may depend on the type of detector used.

Kraleva, Karamfilov, & Hibaum (2012) stated that determination of PAHs using GC-MS in produced water has to be carried out with great care to avoid serious losses occurring during the sampling and storage stage. This is due to the hydrophobic nature of these compounds, and their tendency to be adsorbed to surfaces they are in contact with, including suspended particulate matter. Hence, the best technique to separate PAHs is through GC-MS. Good separation in the shortest period of time is the ideal condition for good GC analysis. This condition is related to the liquid phase of columns, film thickness, length, internal diameter, and temperature.



## 2.6 Total Organic Carbon (TOC)

Total organic carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality or cleanliness of pharmaceutical manufacturing equipment. TOC may also refer to the amount of organic carbon in a geological formation, particularly the source rock for a petroleum reservoir (Clescerl et al., 1999). TOC test on produced water measure water pollutional characteristics by assessing the amount of organic matter in the sample. In some cases, it has been possible to relate TOC to Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). Due to the deep confined nature of produced water, reservoirs systems are anoxic, although oxidation may occur during pumping and transport if the water comes in contact with the atmosphere. COD is a reflection of this anoxic system, but it also indicates the high carbon content (Guerra et al., 2011).

TOC in water comes from decaying natural organic matter (NOM) and from synthetic sources. Humic acid, fulvic acid, amines, and urea are among types of NOM. As for synthetic sources, TOC comes from detergents, pesticides, fertilizers, herbicides, industrial chemical and chlorinated organic (Hendricks, 2007). Clescerl et al. (1999) mentioned that a typical analysis for TOC measures both the total carbon present and inorganic carbon (IC) where the latter representing the content of dissolved carbon dioxide and carbonic acid salts. TOC is yielded by subtracting the inorganic carbon from the total carbon. Another common variant of TOC analysis involves removing the IC portion first and then measuring the leftover carbon. This method involves purging an acidified sample with carbon-free air or nitrogen prior to measurement, and thus more accurately called non-purgeable organic carbon (NPOC).

In produced water, typically the TOC value ranges from non-detect concentrations to almost 2,000 mg/L that includes suspended carbon or carbon that is not dissolved. Suspended carbon could include oils or high carbon mass particles that can be removed by filtration. Table 2.7 lists the concentration ranges of organic material commonly found in produced water from oil operations.

Table 2.8: *Organic material in produced water from oil operations*

Constituents	Units	Concentration range			Technique (Method)
		Low	High	Median	
TOC	mg/L	ND	1700	NA	UV Oxidation/ IR (USEPA 415.1)
COD	mg/L	1220	1220	NA	Redox Titration (USEPA 410.3)
TSS	mg/L	1.2	1000	NA	Gravimetric (USEPA 160.2)
Total Oil	mg/L	2	565	NA	Gravimetric (USEPA 413.1)
Volatiles	mg/L	0.39	35	NA	GC-MS (USEPA 1624 Rev B and USEPA 24 & CLP)
Total Polars	mg/L	9.7	600	NA	Florisil column/IR
Phenols	mg/L	0.009	23	NA	Silylation GLC/MS
Volatile Fatty Acids	mg/L	2	4900	NA	Direct GLC/FID of water

\* ND = below detection limit; NA = not available.

TOC test is preferred as it only takes 5-10 minutes to complete. The test methods for TOC utilize heat and oxygen, ultraviolet radiation, chemical oxidants or some of these methods are combined to convert organic carbon to carbon dioxide which is measured with an infrared analyzer or by other means. (Tchobanoglous et al., 2004). Cross referencing with existing literature seldomly focusing on TOC as toxicity analysis. Instead, BOD and COD values are set as measuring parameters in determining the practicability of Fenton process (Barbusiński & Filipek, 2001; Englehardt & Deng, 2006).

## CHAPTER 3

### METHODOLOGY

#### 3.1 Sampling

The produced water sample was collected from a local refinery's crude oil terminal. The sample collected is then stored in a cold room at 4°C.

#### 3.2 Tools

##### 3.2.1 Chemicals and Reagents

- 50% w/w NaOH solution
- 98% Pure H<sub>2</sub>SO<sub>4</sub> solution
- 30% H<sub>2</sub>O<sub>2</sub> w/w solution
- FeSO<sub>4</sub>.xH<sub>2</sub>O powder
- Methylene Chloride, CH<sub>2</sub>Cl<sub>2</sub>  
(Dichloromethane)
- Solid Anhydrous Sodium Sulfate
- Hydrochloric Acid, HCl
- Buffer pH solution

##### 3.2.2 Materials and Hardware

- Shimadzu TOC-VCSH- TOC analyzer
- Clarus 600 S Mass Spectrometer
- Model 722 Orbital Shaker
- Thermolyne Maxi Mix II Type 37600 Mixer
- HACH model 51910 pH meter
- Whatman No. 1 47mm diameter filter paper
- Kimtech Science Kimwipes
- Mass electronic balance
- 250-ml conical flask
- 50-ml flat-bottomed flask
- 500-ml separatory funnel
- 500-ml measuring cylinder
- 5000-ml beaker
- Micropipette
- 40-ml TOC vials
- 1.5-ml GC-MS vial
- Teflon-coated magnetic bar

### **3.3 Analytical Method**

For characterization of produced water parameters, the initial pH, COD and TOC of the sample were determined. Gas Chromatographic determination of PAHs was carried out after an enrichment step of Liquid-Liquid Extraction.

#### **3.3.1 Measurement of pH**

pH of the sample was determined using HACH model 51910 pH meter and the pH meter is calibrated using pH buffer solution to ensure the accuracy.

#### **3.3.2 Measurement of Chemical Oxygen Demand, COD**

The COD concentration of water sample was determined by using HACH DR 2800 spectrophotometer under Program 430. The blank was prepared first by using distilled water for the purpose of calibration of the spectrophotometer to zero reading. The sample was diluted with 1:50 dilution ratio and 2ml of diluted sample was then pipetted into a vial containing potassium dichromate. The vial was shaken with Thermolyne Maxi Mix II Type 37600 Mixer for few second before inserting into the digester for heating at 150°C for 2 hours. It was later cooled down to room temperature. The vial was wiped clean using Kimtech Science Kimwipes and put into the cell holder in spectrophotometer. “Read” button was pressed to determine the COD concentration.

#### **3.3.3 Total Organic Carbon (TOC) Analysis**

Virtually all TOC analyzers measure the CO<sub>2</sub> formed when organic carbon is oxidized or when inorganic carbon is acidified or both occasions occur simultaneously. Evaluation using this method is prescribed in the European Standard, Determination of samples containing particles (EN1484 Annex C).

Test solution : TOC 100 mgC/l suspension of 20 to 100+µm cellulose (Ultrasonic treatment should not be used.)

Measurement method: 3 repeated measurements during stir with a magnetic stirrer.

Evaluation criteria: Mean measured value between 90 and 110 mgC/l. Coefficient of variation (CV) should be < 10%

Shimadzu TOC-VCSH Instrument operating conditions for the analysis are as shown in Table 3.1.

\*Table 3.1: *Shimadzu TOC-VCSH Instrument Operating Parameters*

Compressed Air Pressure:	
• Supply pressure @ tank regulator	550 kPa
• Carrier Gas Pressure	200 kPa
Carrier Gas Flow Rate	150 ml/min
Sample Volume	500 $\mu$ L
Acid Addition	1.5 % v/v 2N HC
Analysis	NPOC
Calibration Method	Linear Regression
Catalyst	High Sensitivity
Spurge Time	4 minutes
Washes	2
Combustion Temperature	680°C

\* Standard Operating Procedure for the Analysis of Dissolved and Total Organic Carbon CCAL 20A.0

A carbon analyzer using an infrared detection system was used to measure total organic carbon where it was oxidized to carbon dioxide. The CO<sub>2</sub> produced was carried by a carrier gas into an infrared analyzer that measures the absorption wavelength of CO<sub>2</sub>. The instrument utilizes a microprocessor that will calculate the concentration of carbon based on the absorption of light in the CO<sub>2</sub> and the amount of carbon will be expressed in mg/L. The system was stabilized with pH 2 using HCl with sets of 10 repeated measurements and peak profile was monitored for consistency. Shimadzu TOC-VCSH Instrument Operating Parameters instructions were followed for calibration, analysis and data processing. Sample vials and septum were rinse well with distilled water and soaked overnight in 0.5 N HCl after used. The vials were later soaked overnight in deionized water and air dried. The vials were baked at 550°C for at least one hour, let it cool, and finally stored in a seal container until further use.

### **3.3.4 Liquid-Liquid Extraction (LLE)**

Water samples were extracted according SW-846 Method 3510 C (Separatory Funnel Liquid-Liquid Extraction). 250-ml water sample aliquot was transferred into a 500-ml separatory funnel and 15 ml Methylene Chloride was then added. The separatory funnel was stoppered and shaken gently. The stem was pointed up and the stopcock was slowly opened to release excess pressure and was closed shortly. The step was repeated until only a small amount of pressure was released when it was vented. The funnel was shaken vigorously for a few seconds to release the pressure and then again was shaken vigorously. About 30 seconds total vigorous shaking was usually sufficient to allow solutes to come to equilibrium between the two solvents. The funnel was vented frequently to prevent pressure buildup, which can cause the stopcock and perhaps hazardous chemicals from blowing out. The funnel was allowed to rest undisturbed until the layers are clearly separated. When the layers are clearly separated, the stopper was removed and a 50-ml flat-bottomed flask containing 2 g of Anhydrous Sodium Sulfate was placed under the separatory funnel. The stopcock was carefully opened and the lower layer was allowed to drain into the flask. Drain just to the point that the upper liquid barely reaches the stopcock. The remaining organic layer out was poured of the top of the funnel into a beaker and the extraction step was repeated twice if necessary, and the resulting extracts are combined. The samples must be analyzed by GC-MS within 40 days after re-concentration (EPA, OSWER, & Engineering Response Team, 2004).

### **3.3.5 Gas Chromatography–Mass Spectrometry (GC-MS)**

Quantitative analysis of individual PAHs in samples was carried out by comparing with corrected peak areas of PAHs in standard mixture with internal standards. Generally, GC analysis separates all of the components in a sample and provides a representative spectral output. After injecting sample into port of the GC device, the GC instrument vaporizes the sample and then separates and analyzes the various components. (Douglas, n.d.) described that each component ideally produces a specific spectral peak that may be recorded on a paper chart or electronically. The time elapsed between injection and elution is called the retention time and it helps to differentiate between different compounds. The size of the peaks is proportional to

the quantity of the corresponding substances in the specimen analyzed. The peak is measured from the baseline to the tip of the peak. In this study, GC–MS analysis was performed on PAHs using the Perkin Elmer® Clarus® 600 Mass Spectrometry (MS). It is a detector that is interfaced with Clarus 600 Gas Chromatograph (GC). The entire system is controlled through the PerkinElmer TurboMass™ GC-MS software. It is equipped with Elite Column 5MS with 30m long, 0.25mm internal dimension, 0.25µm thickness and a quadrupole with prefilter analyzer. The injector was operated at 250°C in the splitless mode with a 3 minute splitless period. With injection volume of 10µL, Helium was used as the carrier gas with 1 ml/min constant flow rate and the initial column temperature was set to be 50°C for 1 min, increased to 250°C at a rate of 25°C/min and then kept constant at 30 minutes. The total run for each sample was set to 54 minutes.

### **3.4 Experimental Procedure**

#### **3.4.1 Preliminary Experiments**

Preliminary experiments were carried out to determine the optimum range for the experimental condition of Fenton system in degrading PAHs contaminated water. The analysis was divided into two sets of experiments to determine the most favorable reaction time and Fe<sup>2+</sup> dosages. For determination of reaction time, the experiments were performed by dosing 1.5ml of H<sub>2</sub>O<sub>2</sub> and 0.5g of FeSO<sub>4</sub> and pH of the sample was kept unadjusted at pH 7.92. Reaction times from 0 to 240 minutes were tried at this time and three COD readings were taken for every 30 minutes interval.

For determination of Fe<sup>2+</sup> dosages, the experiments were conducted based on optimum reaction time obtained. The experiments were performed by dosing FeSO<sub>4</sub> in the range of 0.2g, 0.5g, 1.0g, 1.5g and 2.0g. The pH of the sample and H<sub>2</sub>O<sub>2</sub> dosage were kept unadjusted at 7.92 and 1.5ml respectively. COD readings were taken for every different dosage of Fe<sup>2+</sup> and required dosage was determined based on the highest COD removal. All experiments were performed in triplicate.

### 3.4.2 Fenton System

To investigate the efficiency of Fenton's reagent in degrading PAHs, several parameters need to be manipulated to obtain optimum condition of degradation. To find the optimum pH and H<sub>2</sub>O<sub>2</sub> concentration for maximum degradation of PAH in produced water, reactions are to be carried out in different pH values in the range of 2–5 with four different reagent concentrations, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> ratios of 1:4, 1:3, 1:2 and 1:1.













1.0 liter of produced water was measured and poured into a beaker, and the pH was adjusted to pH 2 using 98% Pure H<sub>2</sub>SO<sub>4</sub> solution. 100 ml was measured from the beaker and poured into a 125 ml conical flask. The sample was continuously mixed at 250 rpm at room temperature for 5 minutes. The required amount of reagents was determined according to COD<sub>i</sub> value. For COD < 2000mg O<sub>2</sub>/L, amount of 0.4-0.6g/L of H<sub>2</sub>O<sub>2</sub> was sufficient. For COD > 2000mg O<sub>2</sub>/L, higher H<sub>2</sub>O<sub>2</sub> was necessary, approximately 1.5-2.0g/L (Barbusiński, 2004). Following that, 0.5g FeSO<sub>4</sub> was added to the reaction mixture. The Fenton reaction was initiated by sequential addition of the required amount of 30% w/w H<sub>2</sub>O<sub>2</sub> solution following 1:4 ratio. Initiation of Fenton reaction time was by the addition of the first required amount of H<sub>2</sub>O<sub>2</sub> to the reaction mixture. The mixture was continuously shaken using an orbital shaker. On completion of the reaction time, pH of reaction mixtures was raised to 10 using 50% w/w NaOH solution to decompose H<sub>2</sub>O<sub>2</sub> and to stop oxidation of organic matter. The final samples supernatant was taken for determination of COD and TOC and all experiments were performed in triplicate. The steps were repeated for ratios of 1:3, 1:2 and 1:1 with pH 3, 4 and 5. The sample was then extracted using Dichloromethane as solvent and dehydrated using anhydrous Sodium Sulphate for determination of PAHs concentration by GC-MS. Chemical properties of Fenton's reagent used are as tabulated in Appendix A.



### 3.5 Gantt Chart

#### 3.5.1 FYP 1

Table 3.2 shows Gantt chart and key milestones of the project for the first semester.

No	Detail/Week	1	2	3	4	5	6	7	MID SEMESTER BREAK	8	9	10	11	12	13	14	
1	Selection of Project Topic																
2	Finalization on Project Topic with Assigned Supervisor																
3.	Literature Review																
4.	Submission of Draft Extended Proposal																
5.	Submission of Extended Proposal																
6.	Preparation on Proposal Defense																
7.	Proposal Defense																
8.	Continuation of Project Works																
9.	Submission of Interim Draft Report																
10.	Submission on Interim Report																

 Progress

 Key Milestone

Table 3.2: Gantt chart for FYP 1.

### 3.5.2 FYP 2

Table 3.3 shows Gantt chart and key milestones of the project for the second semester.

No.	Detail/Week	1	2	3	4	5	6	7	MID SEMESTER BREAK						
		8	9	10	11	12	13	14	15						
1	<b>Laboratory Preparation</b>														
	• Laboratory safety briefing	■													
2	<b>Laboratory Tests</b>														
	• Fenton reaction		■												
	• Total Organic Carbon						■								
	• GC-MS Determination														
3	<b>Progress Report Preparation</b>														
	• Data Collection & Result Compilation		■							■					
	• Submission of Draft Progress Report							■							
	• Submission of Progress Report										●				
4	Pre-SEDEX														
5	Submission of Draft Dissertation														
6	Submission of Project Dissertation (Soft bound)														
7	Submission of Technical Paper														
8	Oral Presentation														
9	Submission of Final Dissertation (Hard Bound)														

■ Progress

● Key Milestone

Table 3.3 Gantt chart for FYP 2

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Data Collection and Analysis

##### 4.1.1 Sample Characteristics

The characteristics of produced water used are as summarized in Table 4.1 as shown;

Table 4.1: *Sample characteristics*

Parameters	Unit	Value
pH	-	7.92
COD	mg/L	1866.67
TOC	mg/L	242.17

The total concentration of PAHs detected in the sample was 124.2 ppb and the concentration of each PAH was analyzed and summarized in Table 4.2:

Table 4.2: *Concentration of 12 PAH found in the sample*

Compound Name	No. of Rings	Concentrations (ppb)
Acenaphthene*	3	13.610
Carbazole*	3	9.070
Fluoranthene*	3	9.150
Pyrene	4	10.830
Benzo (a) Anthracene	4	11.750
Chrysene	4	7.210
Benzo (b) Fluoranthene	4	11.860
Benzo (k) Fluoranthene	5	12.060
Benzo (a) Pyrene	5	7.310
Indeno (1,2,3-cd) Pyrene	6	8.910
Dibenzo (a,h) Anthracene	6	12.250
Benzo (g,h,i) Perylene	6	10.140
LMW-PAHs*		31.830
HMW-PAHs		92.320
TPAHs		124.150

Two to three fused aromatic rings correspond to low molecular weight compounds, whilst high molecular weight PAHs are the ones with four to six fused aromatic

rings. Based on the data obtained, a graph is plotted with corresponding retention time of each compounds as shown in Figure 4.1.

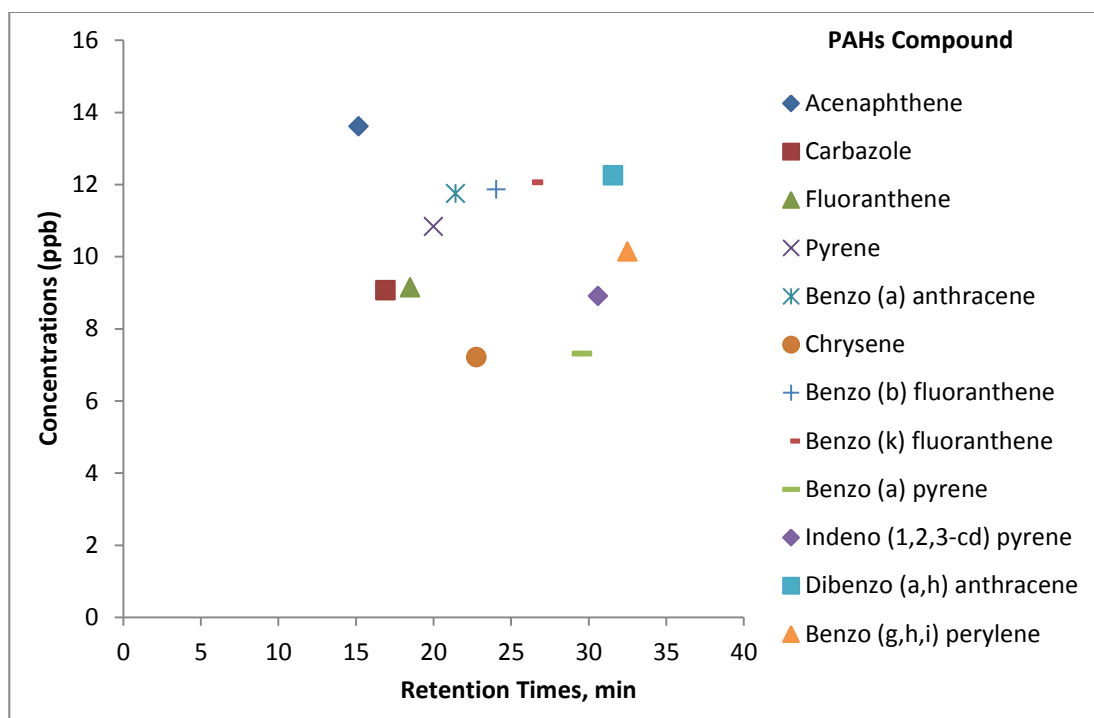


Figure 4.1: Concentration of PAHs compound found in produced water with respect to retention times.

Based on Table 4.2 and Figure 4.1, all 12 PAHs compounds detected are among those 16 that are listed by US-EPA and EU as priority pollutants. The remaining four which were not present in the sample were Acenaphthylene, Fluorene, Phenanthrene and Anthracene. Acenaphthene was found with the highest concentration of 13.61 ppb and the lowest compound concentration detected was Chrysene with 7.21 ppb.

Cross referencing with existing literature reveals that PAHs concentrations in water are usually quite low relative to the concentrations in the bottom sediments. This happens due to the hydrophobic nature of PAHs that exhibit a high affinity for suspended particulates once they enter the aquatic environment. As PAHs tend to sorb to these particles, they are eventually settled out of the water course onto the bottom sediments. Conditions of sorptive characteristics of PAHs have normally been exploited in waste treatment processes by means of coagulation, flocculation, sedimentation, and filtration with sand or activated carbon (PAHs: Occurrence in the Environment, 2013)

## 4.2 Preliminary Experiments

In the first stage, some preliminary experiments were carried out to determine the optimum range of the operational variable which is reaction time for the degradation of PAHs. The experiments were performed by dosing 1.5ml of  $H_2O_2$  and 0.5g of  $FeSO_4$ . Reaction times from 0 to 240 minutes were tried at this time. The pH of the sample was kept unadjusted and the results are graphically shown in Figure 4.1.

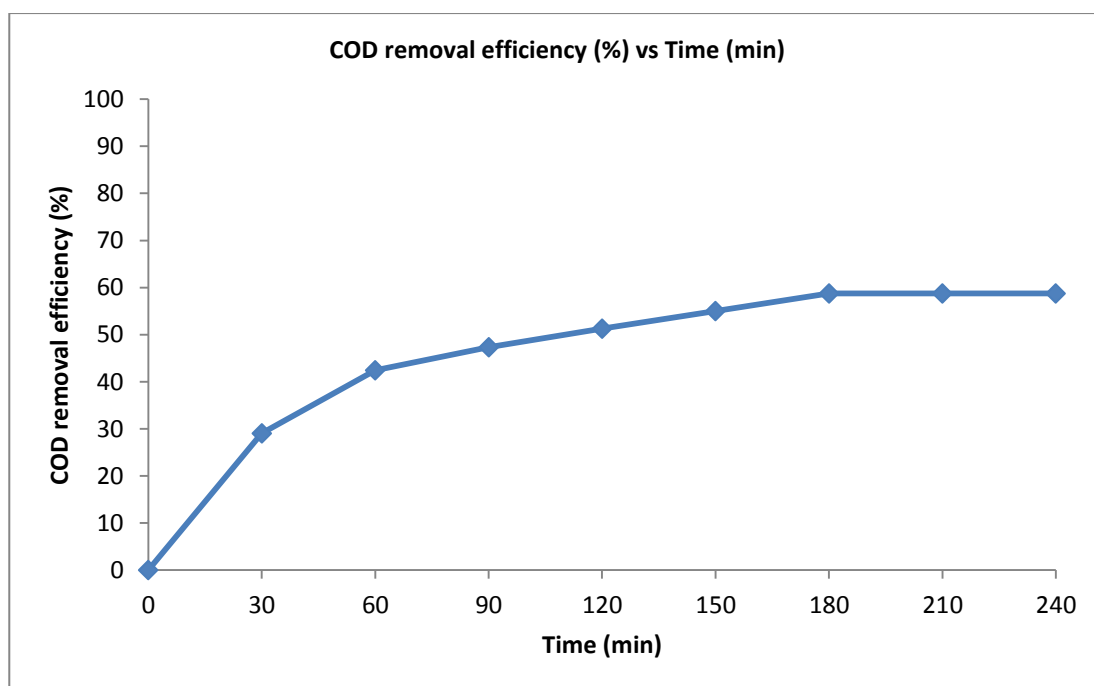


Figure 4.2: *Effect of Fenton's reaction time on COD removal efficiency ( $H_2O_2=1.5ml$ ,  $Fe^{2+}=0.5g$ ) at  $T=298K$ ,  $pH_o=7.92$*

As shown in Figure 4.1, at reaction time of 30, 60, 90, 120 and 150, the COD removal efficiency was 29.0%, 42.4%, 47.3%, 51.3% and 55.0% respectively. The COD removal efficiency achieved equilibrium after 180 minutes reaction time. From 180 minutes onwards, the removal efficiency remains 58.8%. This indicates that no substantial decrease in organic matter was observed and further increase in reaction time will not affect the COD removal efficiency of the sample.

Following determination of reaction time, preliminary experiment on  $Fe^{2+}$  dosage was carried out to determine the optimum dosage needed for the degradation of organic matter. For most applications, it does not matter whether ferrous ions, Fe (II) or ferric ions, Fe(III) are used to catalyze the reaction as the catalytic cycle indicated

in Eq 1-5 in Section 2.3 begins quickly if  $\text{H}_2\text{O}_2$  and organic pollutants are abundant. However, if low doses of Fenton's reagent are used, some research suggest that  $\text{Fe}^{2+}$  ions may be preferred (Walling, 1975). Hence, the experiments were performed by dosing  $\text{FeSO}_4$  in the range of 0.2g, 0.5g, 1.0g, 1.5g and 2.0g. The pH of the sample and  $\text{H}_2\text{O}_2$  dosage were kept unadjusted at 7.92 and 1.5ml respectively, and the results are graphically shown in Figure 4.3.

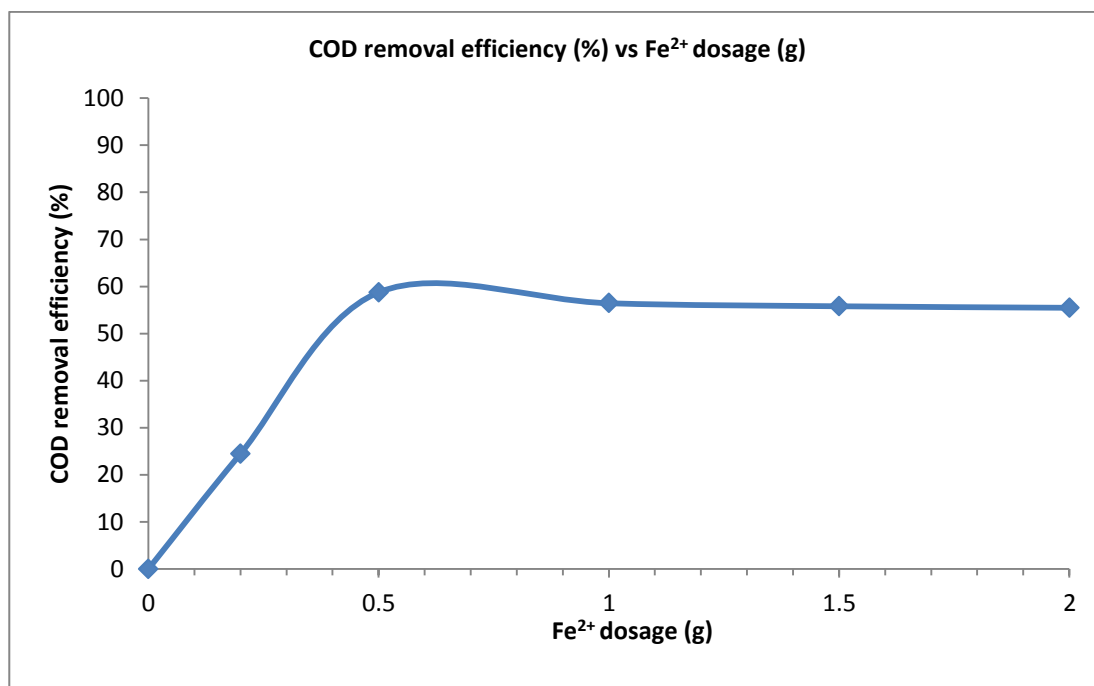


Figure 4.3: Effect of  $\text{Fe}^{2+}$  dosage on COD removal efficiency ( $\text{H}_2\text{O}_2=1.5\text{ml}$ ) at  $T=298\text{K}$ ,  $\text{pH}_0=7.92$ , reaction time = 180 minutes

In the absence of iron, there is no evidence of hydroxyl radical formation. When  $\text{H}_2\text{O}_2$  is alone added to the samples, no reduction in COD occurred. At  $\text{H}_2\text{O}_2$  dose of 1.5ml and  $\text{Fe}^{2+}$  dosage of 0.2, 0.5, 1, 1.5 and 2g, the COD removal efficiency was found to be 24.5%, 58.5%, 56.5%, 55.0% and 55.5% respectively. The COD removal efficiency increased abruptly with  $\text{Fe}^{2+}$  dosage from 0.2 to 0.5g and decreased with further increment of  $\text{Fe}^{2+}$  dosage. As the concentration of  $\text{Fe}^{2+}$  is increased, COD removal accelerates until a point is reached where further addition of iron becomes inefficient. From the result obtained,  $\text{FeSO}_4$  dose is set to be 0.5g for the subsequent tests.

Changes in color were observed immediately following addition of Fenton's reagent. Initially, the water was mildly cloudy and the reaction mixture turned the color into

light brown. When the pH of the samples was raised to 10 to stop the reaction, change of color was again observed; to dark reddish brown. This may be associated with the formation of ferric sludge as the by-products of the reaction. Bubbles were also seen to have formed at the surface of the mixture and began to disappear with time. Sediments were seen to have settled at the bottom of the conical flasks at the end of each experiment.

### **4.3 Fenton Reaction's Optimization**

#### **4.3.1 Effects of pH**

Following preliminary experimentation that concludes reaction time of 180 minutes and  $\text{Fe}^{2+}$  dosage of 0.5g, experiments were conducted to determine the optimum dosage of  $\text{H}_2\text{O}_2$  and pH needed for the degradation of organic matter. The experiments were performed by dosing 30% w/w  $\text{H}_2\text{O}_2$  solution in the range of 0.5ml, 1.0ml, 1.5ml and 2.0ml while the  $\text{FeSO}_4$  dosage was kept constant. The pH of the sample was reduced to 2, 3 4 and 5 respectively. Each sample tested was performed in triplicate to ensure consistency and accuracy. After 180 minutes, COD readings were taken and the reaction was stopped by increasing the pH to 10 by using 50% w/w NaOH solution. In Fenton oxidation process, organic substances react with  $\text{H}_2\text{O}_2$  in the presence of inexpensive  $\text{FeSO}_4$  to reduce toxicity and organic load. Figure 4.4 presents the COD removal efficiency of  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  oxidation at pH between 2 and 5.

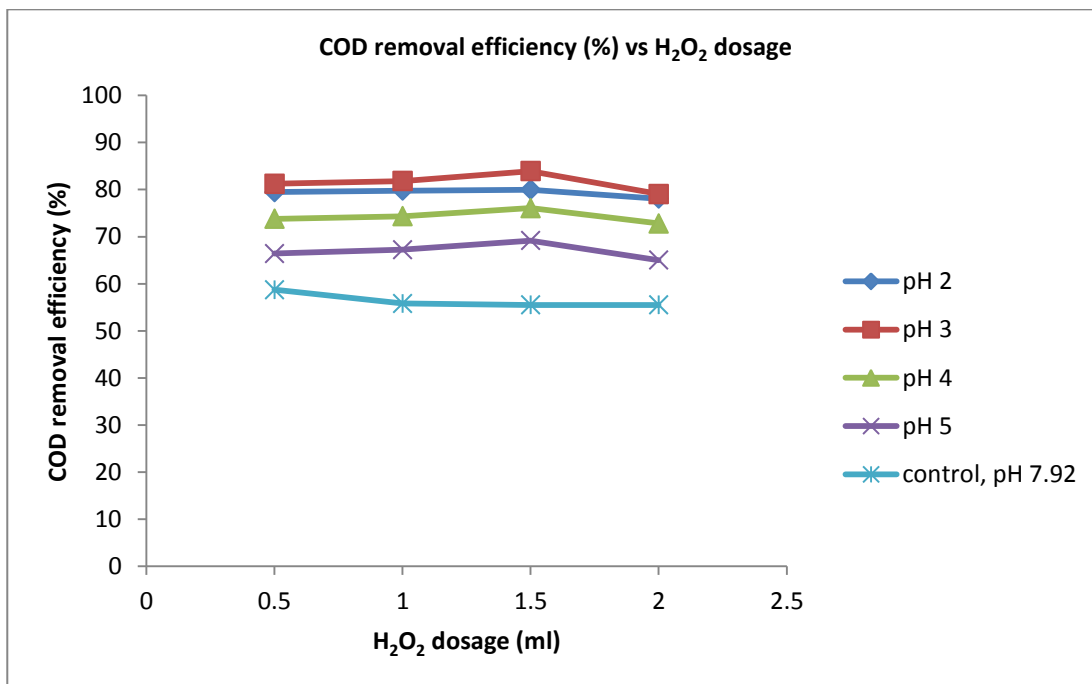


Figure 4.4: Effect of pH and H<sub>2</sub>O<sub>2</sub> dosage on COD removal efficiency ( $Fe^{2+} = 0.5g$ ) at  $T = 298K$ , reaction time = 180 minutes

As can be seen in Figure 4.4, pH significantly influences the decomposition of organics in the sample which progressed at highest rates at pH 3 with COD removal efficiency of 83.9%. This is consistent with the optimum pH range of 2-4 reported in literature (Gogate & Pandit, 2008; Barbusiński, 2004). The COD removal efficiency with H<sub>2</sub>O<sub>2</sub> of 1.5ml, at pH 4 and 5 was obtained as 76.4% and 69.5% respectively. As stated by Groher (2001), it is the nature of Fenton's system that consists of ferrous salts combined with H<sub>2</sub>O<sub>2</sub> to function at optimum performance under acidic conditions. Hence, the capability of H<sub>2</sub>O<sub>2</sub> to act as both an oxidizing and reducing agent allows it to readily oxidize Fe(II) to Fe(III) at low pH.

The decomposition significantly decreases as the pH increases from 3-5 probably because the dissolved fraction of iron species decreases, as colloidal ferric species appear. If the pH is too high, the iron might precipitate as Fe(OH)<sub>3</sub> and catalytically decomposes the H<sub>2</sub>O<sub>2</sub> to O<sub>2</sub>. Besides the insolubility nature of Fe(OH)<sub>3</sub>, precipitation of Fe(III) will inhibit or prevent the Fenton reactions. However, the low activity is not only due to decomposition of H<sub>2</sub>O<sub>2</sub>, but also deactivation of ferrous catalyst by formation of ferric hydroxo complexes in the chain reaction. This statement is supported by Watts et al. (2011) that stated pH has a strong effect on hydrogen peroxide chemistry and effectiveness. pH impacts catalyst solubility and reactivity



towards hydrogen peroxide, as well as the radicals formed and the degradation of target contaminants. It generally has been determined that the best breakpoint between the highest level of hydroxyl radical activity while still keeping iron in solution lies around pH 3. Since the oxidation mechanism by Fenton's reagent is due to the reactive  $\text{OH}\cdot$  generated in an acidic solution by the catalytic decomposition of hydrogen peroxide, the effect of pH is related to the oxidation state of iron, which influences the production of hydroxyl radicals. At pH values lower than 3, the reduced  $\text{OH}\cdot$  production is attributed to formation of the complex species  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , which reacts more slowly with  $\text{H}_2\text{O}_2$  than  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^+$ , thus producing a smaller amount of  $\text{OH}\cdot$  radicals. This is shown in COD removal efficiency at pH 2 which is lower than pH 3.

#### 4.3.2 Effects of Hydrogen Peroxide, $\text{H}_2\text{O}_2$

As seen in Figure 4.3 before, as concentration of  $\text{H}_2\text{O}_2$  increases, the degradation of organics also increases, because the amount of oxidant present in the reaction system is higher for the same initial concentration of organics and catalytic ferrous ions. COD removal is the most effective at  $\text{H}_2\text{O}_2$  dosage of 1.5ml and further addition of  $\text{H}_2\text{O}_2$  has caused the opposite outcomes. The increase of  $\text{H}_2\text{O}_2$  concentration will generate more hydroxyl radical for the oxidation process to degrade the organic pollutants, thus contribute to the increment of COD removal efficiency. However, considerable excess of  $\text{H}_2\text{O}_2$  or  $\text{Fe}^{2+}$  might be detrimental, since these species can react with some of the intermediates such as  $\text{OH}\cdot$ , responsible for the direct oxidation of the organic load, precluding by mineralization (Schrank et.al., 2005). When hydrogen peroxide is in excess, the hydroxyl radicals tend to undergo scavenging of  $\text{OH}\cdot$  by  $\text{H}_2\text{O}_2$  and formation of hydroperoxyl radical which will lead to the decrease in COD removal efficiency. This is portrayed in COD removal efficiency of 2.0ml  $\text{H}_2\text{O}_2$  that is lower compared to 1.5ml of  $\text{H}_2\text{O}_2$ .

To determine the effect of the  $\text{H}_2\text{O}_2$  concentration on the Fenton process, the concentration of  $\text{FeSO}_4$  was kept constant, while the amount of  $\text{H}_2\text{O}_2$  was varied ranging from 0.5ml to 2.0 ml with 0.5ml increment. COD removal was the most effective with 1.5ml of  $\text{H}_2\text{O}_2$  dosage at every pH tested as shown in Figure 4.4.

### 4.3.3 Effects of Ferrous ion Concentration, $\text{Fe}^{2+}$

The  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  dose show a great influence in the evolution of the process and there is a relationship between both. Like all dissolved metals, iron complexes with water and hydroxide species. As discussed, after several minutes of reaction the bulk of iron is anticipated to be in the  $\text{Fe}^{3+}$  form in the system. Ferric hydroxide  $[\text{Fe(III)(OH)}_3]$  forms a solid precipitate at neutral pH, and dissolved  $\text{Fe}^{3+}$  concentrations will be extremely low. However, at acidic pH,  $\text{Fe}^{3+}$  is much more soluble and available for reaction. In addition, other  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  hydroxyl-complexes affect the catalytic activity of iron species with hydrogen peroxide.

Since the COD test measures the oxygen demand of organic compounds in a sample of water, it is important that no outside organic material be accidentally added to the sample to be measured, as it may give falsely high results. Hence, it is best to minimize the levels in the dilution water, as they may release organics and in this experiment, the dilution factor used is 1:50. On the other hand, oxidizable inorganic materials may also interfere with the determination of COD. They may be oxidized by dichromate and give erroneously high COD results.

## 4.4 Total Organic Carbon (TOC) Analysis

Although COD measurement has been carried out to determine the efficiency of the Fenton system in degrading organic matter, TOC analysis was performed to support the conditions established. It is due to the fact that TOC content tends to show less variation over large periods of sample collection, which is suitable for this experiment. TOC has the advantage of advising directly on the degree of mineralization, namely, complete oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . pH of the reaction mixture was raised to 10~12 to stop the reaction prior to filtration, followed by TOC analysis. High pH creates alkaline environment and alkalinity measures the amount of alkaline compounds in water, such as carbonates ( $\text{CO}_3^{2-}$ ), bicarbonates ( $\text{HCO}_3^-$ ), and hydroxides ( $\text{OH}^-$ ). These compounds are natural buffers that can remove excess hydrogen ions that have been added from Fenton's reagent, hence stop the reaction completely (Skipor, 2012). It is a great concern to know whether or not an increase in

pH will affect the TOC readings. From the result obtained, effects of pH on TOC or vice versa depends upon what the carbon-containing chemical compound is added. If it was acetic acid, it may lower the pH, if it was an amine it may increase the pH and if it was a neutral compound such as ethanol, it will have virtually no effect on the pH. In all three conditions mentioned above, none of the chemical added affect the TOC . Thus, it is safe to say that TOC and pH are not directly related.

TOC-VCSH, in combination with Auto sampler ASI-V was used for the TOC analysis. Combining the ASI-V automatic sample injector with a TOC-V Series-V analyzer creates a fully automatic analysis system that allows user to leave the system. The print outs of the results were later transformed into a graph as shown in Figure 4.5.

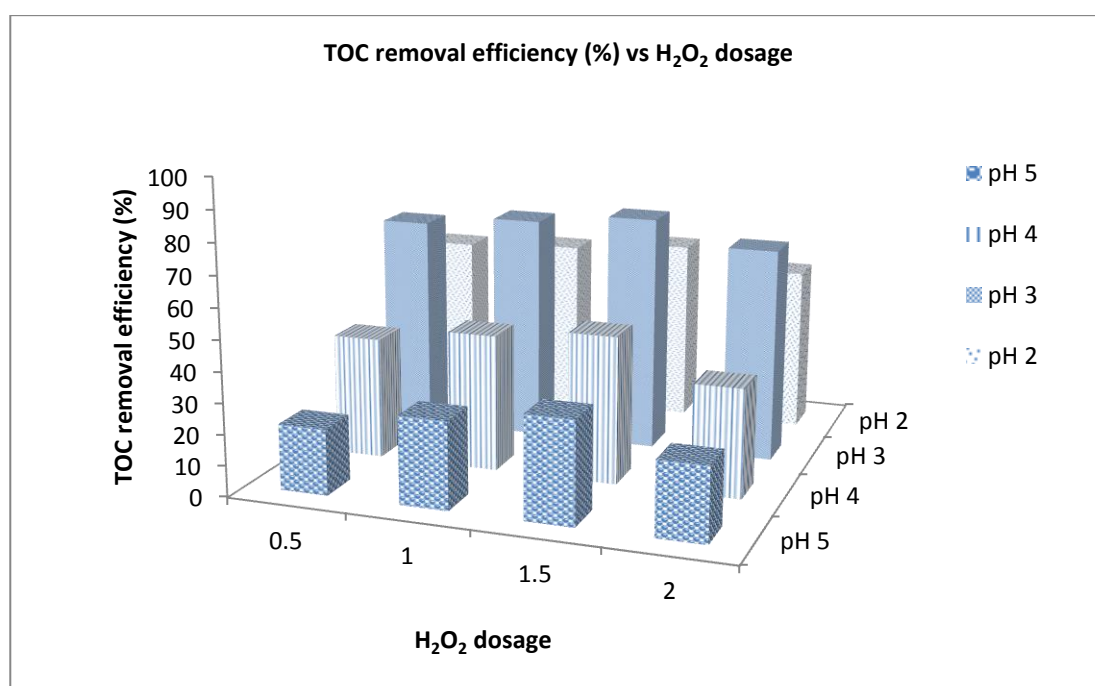


Figure 4.5: Effect of pH and H<sub>2</sub>O<sub>2</sub> dosage on TOC removal efficiency ( $Fe^{2+} = 0.5g$ ) at  $T=298K$ , reaction time = 180 minutes

Theoretically based on O<sub>2</sub>/ C-relation, COD/TOC-relation is 2.67 (Shimadzu: Information on Relationships between Common Parameters, 2006). In certain cases, the ratio could be as high as 3.5 for inlet water and as low as 2.5 for outlet treated water . The low value indicates the decrement of the dichromate oxidizability of the organic residues after the biological oxidation. The overall TOC removal of the sample was 77.0% which is lower than overall COD removal of 83.9%. This may

happen due to oxidation of organic compounds that is not followed by mineralization, resulting in a COD decrease while TOC remained constant.

From Figure 4.5, TOC conversion by Fenton reaction after 180 minutes' oxidation ranges from 21.6% to 77.0% depending on the operating conditions. This TOC data was directly related to organic matter content in samples. When the pH increased from 2 to 3, the TOC removal efficiency is increased. However, it decreased drastically when pH was raised from 3 to 5. Performance significantly decreased at pH above 3, mainly because the dissolved fraction of iron species also decreased (Pera-Titus et al., 2004). Fe (III) precipitates at high pH values thereby decreasing the concentration of dissolved Fe (III). Consequently, Fe (II) species' concentration also decreased because Fe (III) hydroxides are much less reactive towards H<sub>2</sub>O<sub>2</sub> than dissolved Fe (III) species.

The effects of H<sub>2</sub>O<sub>2</sub> on TOC conversion can be observed in the figure. It is clearly shown that TOC removal efficiency was the greatest with 1.5ml of H<sub>2</sub>O<sub>2</sub>. The degradation rate increased for increasing H<sub>2</sub>O<sub>2</sub> dose, from 0.5ml to 1.5ml and decreased when the dose was changed to 2.0ml. The fact that high H<sub>2</sub>O<sub>2</sub> dose led to a decrease in TOC conversion in those condition is possibly due to the competition between species of hydroxyl radicals. Indeed, OH• radicals are quite non-selective, reacting with the organic matter present but also with other species (Martinez et al., 2013).

#### **4.5 Gas Chromatography- Mass Spectrometry (GC-MS) Analysis.**

The final concentrations of PAHs in the treated sample under optimized conditions of pH 3 with 1.5ml of H<sub>2</sub>O<sub>2</sub> and 0.5g of FeSO<sub>4</sub> after 180 minutes reaction time are shown in Appendix D with their respective removal efficiencies. The data was analyzed and Figure 4.6 shows the initial and final concentration of each PAH detected in the sample as well as removal efficiencies in graphical form. The EPA has classified seven PAH compounds as probable human carcinogens, and they are Benz[a]anthracene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene,

Chrysene, Dibenz(a,h)anthracene, and Indeno(1,2,3-cd)pyrene. All these seven carcinogenic PAHs are found in this sample.

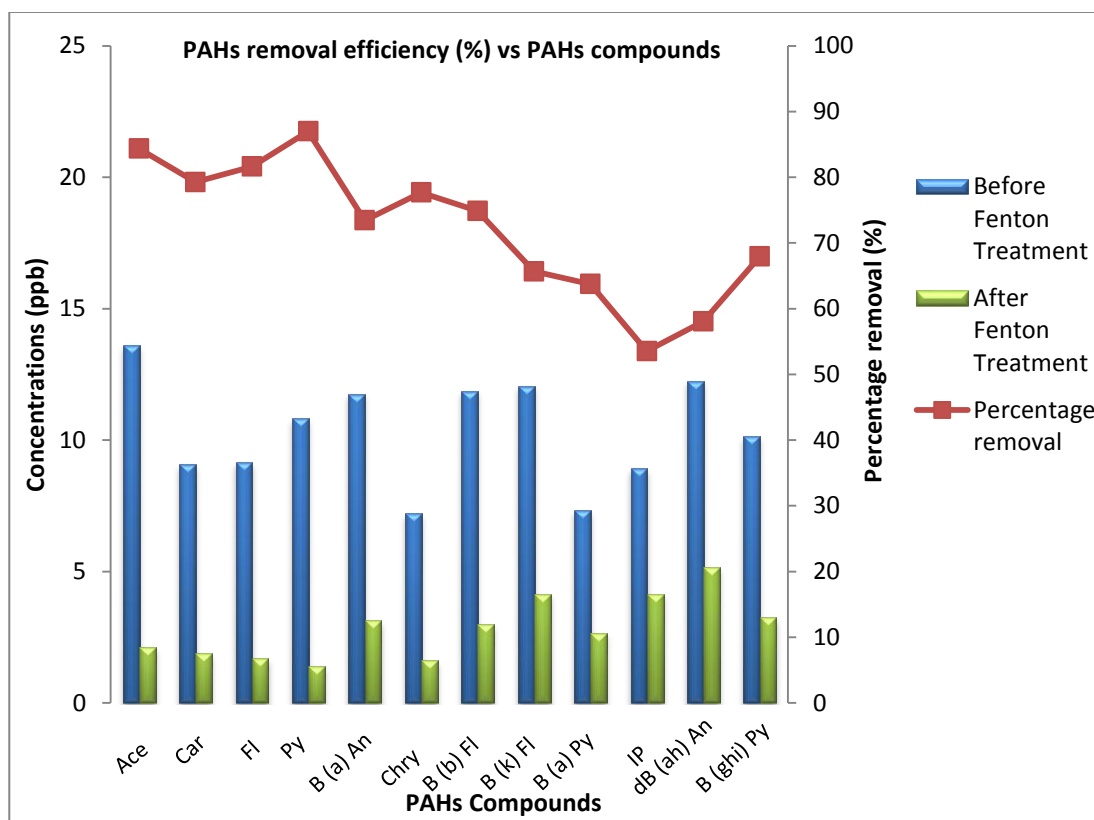


Figure 4.6: Initial and final concentration of PAHs compound in association with Fenton reaction ( $H_2O_2=1.5ml$ ,  $Fe^{2+}=0.5g$ ) at  $T=298K$ , reaction time = 180 minutes

The final concentration of PAHs obtained was originated from sample with maximum TOC and COD removal of 77.0% and 83.9% respectively. From the results obtained, total PAHs removal efficiency was 72.5%. The persistence of PAHs in the environment depends on the physical and chemical characteristics. LMW-PAHs achieved higher removal efficiency of average 81.75% compared to HMW-PAHs which only achieved average removal efficiency of 69.1%. Owing to different physico-chemical properties of each compound, the level of difficulty in degrading the compounds varies. In general, PAH solubility in water decreases as the molecular weight increases. In other words, molecular weights of PAHs compounds are inversely proportional to its solubility (Pampanin & Sydnes, 2013). Hence, as can be seen in the figure, the last nine compounds detected that correspond to high molecular weighted PAHs have lower removal efficiency compared to the first three. Exception to this is Benzo[a]pyrene, possibly due to its high reactivity towards hydroxyl radicals. This is shown in the experiments whereby among nine HMW-

PAHs detected, Benzo[a]pyrene has the highest concentration removal due to its lower oxidation potential of 0.94, which is actually lower than most of the lighter compounds. This efficient oxidation of Benzo[a]pyrene using the Fenton's reagent is of great interest due to its recalcitrance to microbial degradation. Hence, quantitative analyses by GC-MS showed that 12 compounds present in the sample were dramatically reduced in concentration by Fenton oxidation.

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

Advanced oxidation process through Fenton's reagent, is proven to be effective for degradation of aromatic compound. The main factors affecting the performance of the  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  process were found to be  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  dosage, pH and reaction time. In the obtained optimum  $\text{H}_2\text{O}_2$  dosage of 1.5ml and 0.5g of  $\text{Fe}^{2+}$ , pH significantly influenced the decomposition of organics which progressed at highest rates at pH 3, with COD removal efficiency of 83.9%. Ample reaction time should be provided to ensure complete decomposition of the organics, and in this case the reaction time needed was 180 minutes.

TOC analysis on the other hand provides a speedy and convenient way of determining the degree of organic contamination. By using TOC measurements, the number of carbon-containing compounds in a source can be determined. From the results obtained, it is clearly shown that TOC removal efficiency of 77.0% was the greatest at pH 3 with 1.5ml of  $\text{H}_2\text{O}_2$  and 0.5g of  $\text{Fe}^{2+}$ , similar to conditions established for maximum COD removal.

GC-MS is successfully used to determine concentrations of aromatic compounds present in the sample and the results obtained have shown total PAHs removal efficiency to be 72.5%. LMW-PAHs achieved higher removal efficiency of average 81.8% compared to HMW-PAHs which only achieved average removal efficiency of 69.1%.

Application of Advanced Oxidation Process through Fenton's reagent has thus proven to be a good method for PAHs degradation. Through this method, PAHs compounds in produced water were degraded rather than concentrated or transferred into a different phase. In other words, it can effectively eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phase.

Due to the remarkable reactivity of  $\bullet\text{OH}$ , AOPs virtually react with almost all aqueous pollutants without much discrimination. AOPs could therefore be applicable in many, if not all, cases where many organic contaminants are expected to be removed at the same time. In environmental aspects, although many phases of reactions occur during the Fenton oxidation process, the overall reaction only produces water, oxygen, and carbon dioxide and thus by products from the reaction are harmless as it does not introduce any new hazardous substances into the water at the levels produced. Fenton's reagent is an interesting solution since it allows high depuration levels at room temperature and pressure conditions using harmless and easy to handle reactants. Fenton process is a relatively economical method since it requires no additional energy when compared to many other AOPs aside from both iron and hydrogen peroxide are relatively cheap and safe.

In short, when applied in properly tuned conditions, AOP using Fenton's reagent earned it the credit of water treatment processes of the 21st century.



## 5.2 RECOMMENDATIONS

As far as this project is concerned, there is great scope for future work expansion. Possible future enhancements to the project are as follow;

- i. In situ supply of  $\text{H}_2\text{O}_2$  via the cathodic reduction of oxygen and in situ supply of  $\text{Fe}^{2+}$  via the electrochemical anodic oxidation of elemental iron.
- ii. Replacing  $\text{FeSO}_4$  as source of transition metal salt with treated iron sludge, or in other words Fe (II) regeneration by illuminating the sludge iron sources by raising the pH, separating the iron flocs, and re-acidifying the iron sludge.
- iii. Compare the classical Fenton reaction on PAHs degradation efficiency with Modified Fenton with additional of catalysts or chelating agents such as Catechol and Gallic acid.
- iv. Compare the result of re-concentration techniques of LLE with SPE before implementing gas chromatographic determination of individual PAHs.

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**Appendix A: Chemical properties of Fenton's reagent used**

Compound	Formula	Molecular weight (g/mol)	Density (g/cm <sup>3</sup> )	Physical state	Solubility limit in water
Hydrogen peroxide, H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	34.01	1.135 (30% solution)	Liquid	Miscible
Ferrous sulfate	FeSO <sub>4</sub>	151.91	2.97	Solid	30 wt.%

**Appendix B: Preliminary Experiments**

Table B.1: COD value of raw sample

COD value (mg/L)			
i	ii	iii	Average
2000	1600	2000	1866.67

Table B.2: TOC value of raw sample

TOC value (mg/L)			
i	ii	iii	Average
236.4	244.9	245.2	242.167

Table B.3: Effect of Fenton's reaction time on COD removal efficiency  
(H<sub>2</sub>O<sub>2</sub>=1.5ml, Fe<sup>2+</sup>=0.5g) at T=298K, pH<sub>0</sub>=7.92

Reaction Time (min)	COD value (mg/L)				Removal Efficiency (%)
	i	ii	iii	Average	
30	1300	1400	1350	1325	29.02
60	1050	1075	1100	1075	42.41
90	980	975	995	983.33	47.32
120	400	907	913	910	51.25
150	550	835	845	840	55.0
180	767	776	768	770.33	58.75
210	769	300	771	770	58.75
240	768	773	768	770	58.75

Table B.4: Effect of Fe<sup>2+</sup> dosage on COD removal efficiency  
(H<sub>2</sub>O<sub>2</sub>=1.5ml) at T=298K, pH<sub>0</sub>=7.92

Fe <sup>2+</sup> dosage(g)	COD value (mg/L)				Removal Efficiency (%)
	i	ii	iii	Average	
0.2	1400	1420	770	1410	24.46
0.5	767	776	768	770.33	58.75
1.0	813	810	816	813	56.45
1.5	822	828	600	770	55.8
2.0	510	833	828	723.67	55.48



## Appendix C: Fenton Reaction's Optimization on COD and TOC removal

Table C.1: Effect of pH and H<sub>2</sub>O<sub>2</sub> dosage on COD removal efficiency (Fe<sup>2+</sup> =0.5g) at T=298K

pH	H <sub>2</sub> O <sub>2</sub> dosage (mL)	COD value (mg/L)				Removal Efficiency (%)
		i	ii	iii	Average	
2	0.5	480	378	388	383.	79.5
	1.0	379	375	378	377.33	79.8
	1.5	508	374	373	373.5	80.0
	2.0	418	413	406	409.5	78.1
3	0.5	350	350	450	350	81.3
	1.0	338	163	341	339.5	81.8
	1.5	300	305	295	300	83.9
	2.0	396	387	390	391	79.1
4	0.5	485	490	493	489.33	73.8
	1.0	478	610	480	479	74.3
	1.5	622	445	448	446.5	76.1
	2.0	511	509	503	507.67	72.8
5	0.5	622	631	628	627	66.4
	1.0	610	220	613	611.5	67.2
	1.5	581	573	572	575.33	69.2
	2.0	650	330	656	653	65.0

Table C.2: Effect of pH and H<sub>2</sub>O<sub>2</sub> dosage on TOC removal efficiency (Fe<sup>2+</sup> =0.5g) at T=298K

pH	H <sub>2</sub> O <sub>2</sub> dosage (mL)	COD value (mg/L)				TOC remaining (%)	Removal Efficiency (%)
		i	ii	iii	Average		
Raw sample	-					-	-
2	0.5	107.1	108.6	111.9	109.2	45.09	55.00
	1.0	102.20	105.80	106.90	104.97	43.34	56.66
	1.5	99.70	97.30	95.10	97.37	40.21	59.79
	2.0	111.10	109.50	116.50	112.37	46.40	53.60
3	0.5	69.00	71.30	75.00	71.77	29.64	70.36
	1.0	63.10	67.00	61.00	63.70	26.30	73.70
	1.5	56.70	54.50	55.7	55.60	22.96	77.04
	2.0	73.30	75.70	71.60	73.53	30.36	69.64
4	0.5	147.90	149.00	141.20	146.03	60.30	39.70
	1.0	133.20	133.90	135.80	134.30	55.46	44.54
	1.5	124.10	126.50	127.10	125.90	51.99	48.01
	2.0	153.50	158.70	156.10	156.10	64.46	35.54
5	0.5	191.80	188.60	189.20	189.87	78.40	21.60
	1.0	175.30	171.40	171.60	172.77	71.34	28.66
	1.5	161.70	157.60	163.20	160.83	66.41	33.59
	2.0	183.00	178.00	189.70	183.57	75.80	24.20



Figure C.1: COD measurement

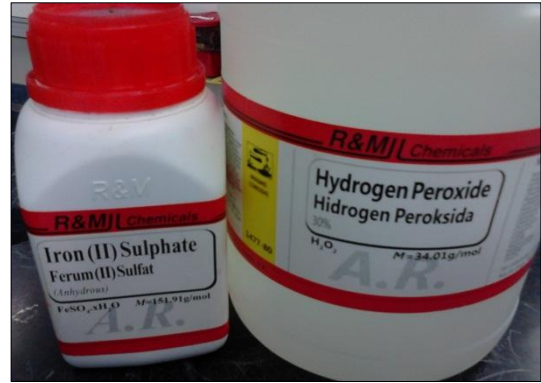


Figure C.2: Fenton's reagent



Figure C.3: 180 minutes reaction time on orbital shaker



Figure C.4: Addition of Fenton's reagent into the sample

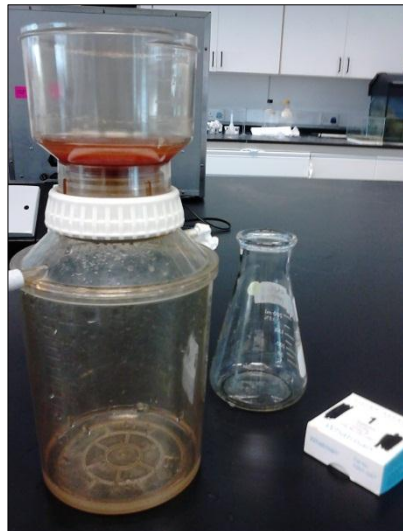


Figure C.5: Filtration

Figure C.6: Changes of color before (left) and after (right) filtration





Figure C.7: *TOC-VCSH, in combined with Auto sampler ASI-V*

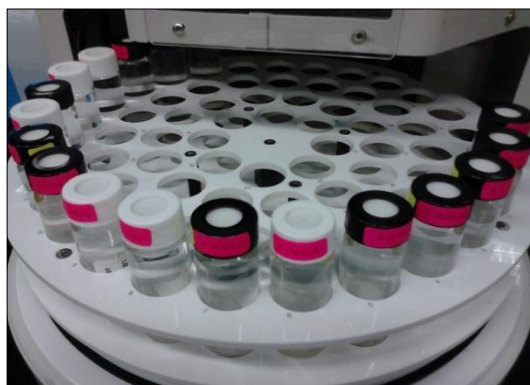


Figure C.8: *Preparation for TOC analysis*

## Appendix D: LLE and GC-MS Analysis

Table D.1 Initial and final concentration of PAHs compound in association with Fenton reaction

Compounds	Before Treatment, (ppb)	After Treatment, (ppb)	Percentage Removal (%)
Acenaphthene	13.610	2.130	84.34974
Carbazole	9.070	1.880	79.27233
Fluoranthene	9.150	1.680	81.63934
Pyrene	10.830	1.410	86.98061
Benzo (a) Anthracene	11.750	3.120	73.44681
Chrysene	7.210	1.610	77.6699
Benzo (b) Fluoranthene	11.860	2.980	74.87352
Benzo (k) Fluoranthene	12.060	4.140	65.67164
Benzo (a) Pyrene	7.310	2.650	63.74829
Indeno (1,2,3-cd) Pyrene	8.910	4.140	53.53535
Dibenzo (a,h) Anthracene	12.250	5.140	58.04082
Benzo (g,h,i) Perylene	10.140	3.250	67.94872



Figure D.1: *Extraction using separatory funnel*



Figure D.2: *GC-MS Clarus 600 S*