Degradation of Polycyclic Aromatic Hydrocarbon from hazardous waste landfill leachate using Photo-Fenton process

by

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CERTIFICATION OF APPROVAL

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Approved by,

____

Assoc. Prof. Dr. M. Hasnain Isa

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2017

CERTIFICATE OF ORIGINALITY

This is to certify that this submission is my own work and contains no material previously published or written by another person. I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

MUHAMAD AMIRUL HAFIZ BIN SALEH HODDIN

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ABSTRACT

Landfill leachate have been found that it is one of source of harmful organic matters called Polycyclic Aromatic Hydrocarbons (PAH). The releasing of leachate to the nearby rivers from the landfills without proper treatment are hazardous as PAH can contribute to various health problems to living things. Photo-Fenton process are known for its effectiveness in treating wastewater as it can remove organic matters and sometimes inorganic matters by oxidation process through hydroxyl radicals reaction. Wastewater that undergo Photo-Fenton shown significant COD removal.

In this research there are 2 phases. First is preliminary studies based on COD test, leachate samples are treated with Photo-Fenton process to investigate the removal of PAHs varying it reaction time, dosage and molar ratio to find the optimum condition and maximize the removal of PAHs. From the COD test conducted, the optimum molar ratio is at molar ratio 3, the optimum dosage is at 3 and the optimum time reaction is 90 minutes. Next is phase 2 where the condition obtained from COD test were inserted to software called Design expert 10 to define the optimum condition for the highest percentage of PAH removal. After conducted 20 runs of experiment and analyses the data using Response Surface Method (RSM), the highest percentage of PAH removal is 87.66% at molar ratio 3.25, reaction time at 98.2 minutes and dosage of hydrogen peroxide and ferrous sulphate at 0.08 and 0.025 mol/l respectively.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 Background

Polycyclic Aromatic Hydrocarbons (PAHs) are widely known unsafe chemical substances that exists. It is considered as pollutants because of its carcinogenic, mutagenic and deadly characteristics (Manoli & Samara,1999).PAHs can cause cancer, cardiovascular diseases and also disturb the fetal development of human. PAHs is an anthropogenic micro-pollutants produced from incomplete combustion of fossil fuels (Nielsen, 1996) and waste from petrochemical industry (Domeño & Nerín, 2003). There are many types of PAHs exists were recorded and each type have its own chemical arrangement. Although there are many types of PAHs exist but only 16 PAHs were prioritized by United States Environmental Protection Agency (USEPA). The 16 PAHs are Naphthalene, Acenaphthylene, Acenaphtene, Fluorene, Phenanthrene, Anthracene, Carbazole, Fluoranthene, Pyrene, Chrysene, Benz(a) anthracene, Benzo(b) fluoranthene, Benzo(K) fluoranthene, Indeno (1,2,3 – CD) pyrene, Dibenz (a,h) anthracene and Benzo (g,h,i) perylene.

PAHs cannot be removed by traditional method of physicochemical such as coagulation, flocculation, sedimentation, filtration or ozonation and it is also resistant from biological degradation. However, PAHs can be remove effectively by Advanced Oxidation Process (AOP). AOP is a method conducted to remove organic matter in wastewater by oxidation process by reaction with hydroxyl radicals (•OH). There are many type of AOP process were stated in previous research such as hydroxyl radical-based AOPs ranging from ozone-based AOPs, UV-based AOPs, Fenton-related AOPs and others (Deng & Zhao, 2015). In this study, it will focused on the Photo-Fenton process in treating leachate to remove PAHs. Based on previous research, Photo-Fenton process are the most efficient method in treating wastewater by showing significant COD removal in the wastewater compare to other method such as Fenton-like, Fenton and UV/H2O2 (Primo, Rivero, & Ortiz, 2008).

In this study, research are conducted to further the studies of previous works by Primo, Rivero et al. (2008). After the sample undergoes the Photo-Fenton process with different pH, reaction time and molar ratio, data were analyzed and optimum condition for the process are obtained. Optimum values were inserted into Design Expert 10 and 20 runs were designed to determine the highest percentage of PAH removal with optimum condition were conducted. The sample then will be tested by Gas chromatography–mass spectrometry (GC-MS) to determine the concentration of PAHs in the sample. The result later will be compared between before treatment and after treatment sample to find the condition for the highest percentage of PAHs removal by Photo-Fenton process.

1.2 Problem Statement

Every day in Malaysia, loads of waste were being dumped to an open dumpsites as it is a very common ways to dispose municipal solid waste. In year 1994, there were 3 million kg/day of waste were disposed in Kuala Lumpur and the number are increased as there were 7.9 million kg/day were generated on year 2000 and now more than 11 million kg of waste material were dumped every day in about 230 official dumpsites exists in Malaysia (Zakaria, Geik, Lee, & Hayet, 2005).The situation are getting serious day by day and in future it will cause great pollution if not be treated. All dumpsites in Malaysia receives dump from various origin such as agricultural, domestic, municipal, commercial, recreational and mixed industrial waste and mostly come from houses and industrial factory (Zakaria et al., 2005).

TABLE 1.1. Landfills in Malaysia (Fauziah & Agamuthu, 2010)

Status of disposal facilities	**Current Number**
Operating	155
Non-operating	136
Sanitary landfills	12
Total	303

Some dumpsite in Malaysia release their leachate directly to nearest river. The PAHs contained in the leachate exposed the environment may cause very dangerous pollution. Overly exposed to PAHs may cause cancer to skin, lung, bladder, liver and stomach as it is has been tested to mammals (Boström et al., 2002). Furthermore, it also can cause cardiovascular illness (Korashy & El-Kadi, 2006) and deprived fetal development to human (Šrám, Binková, Dejmek, & Bobak, 2005). The importance of this study is to determine efficiency of Photo-Fenton process in removing PAHs from leachate taken from Malaysia’s local dumpsite thus amount of PAHs in the leachate can be reduced with economical approach.

1.3 Objectives and Scope of Study

The objective of this study are:

I. To investigate the optimum reaction time, optimum dosage and optimum Molar ratio for maximum COD removal using Photo-Fenton process for preliminary studies.

II. To determine the optimum condition of Photo-Fenton method for removal of Polycyclic Aromatic Hydrocarbons (PAHs) present in landfill leachate using RSM.

All of above objective will be accomplished throughout the project. When determining the concentration of PAHs contained in the leachate sample, the procedure must be done precisely to ensure the results recorded from the procedure are valid and will be used for the next method in the research. If fail, the upcoming procedure cannot be conducted and must be repeated.

1.4 Scope of study

Meanwhile, the scope of study are limited to removing PAHs using Photo-Fenton process from leachate obtained from Kualiti Alam Sdn. Bhd. This can performed through suitable experiment design and analysis. Then from the experiment, the optimum reaction time, optimum molar ratio, and optimum pH for the Photo-Fenton process to remove its COD and PAHs were determined to maximize the removal of PAHs from the leachate sample. The project is feasible since, it will be carried out through two semesters of eight months in total.

CHAPTER 2

LITERATURE REVIEW

2.1 Leachate

Leachate is a waste product that we can found mostly in waste landfill. It formed when rainwater percolate through the waste landfill and the water becomes contaminated then the water that flows out called leachate. Mostly, landfill that not designed well produces more leachate because of the water that percolates into the waste were retained. The water that slip through the waste assist the decomposition of fungi and bacteria where it will create an environment called anoxic environment ant it will consume oxygen for the decomposition process. The process increase the volume of leachate produced and it produces many chemical substances that dissolves in it prior to the decomposition process such as methane, carbon dioxide, and complex mixture of organic acids, aldehydes, alcohols and simple sugars. The color of leachate that flowed out from a landfill is typically black, yellow or orange colored and it is have pungent smell.

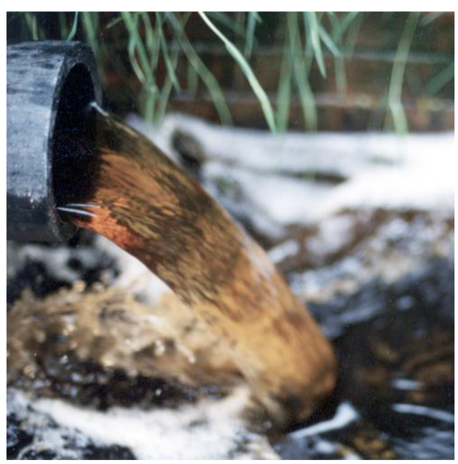

FIGURE 2.1. Typical color of landfill leachate

Because it is in liquid form, it can easily permeate to underground water and causes pollution to nearby water body. Underground water nearby dump site can easily contaminated especially if it is non-engineered solid waste landfill and the underground water contain significant amount of heavy metals which is not suitable as drinking water and other domestic consumption (Nagarajan, Thirumalaisamy, & Lakshumanan, 2012). Also, some landfill are not taking proper action in treating leachate and just channel it to nearby streams or rivers. Some researchers have conducted study and leachate can cause harm to living organism. It also contain Polycyclic Aromatic Hydrocarbon (PAH) also causes harm to human body if consumed. PAH can cause skin, lung, bladder, liver and stomach cancers to human if overexposed (Boström et al., 2002).

In dealing with its hazardous effect, most of engineered landfill treat their leachate before being channeled it to nearby rivers or drains. Collected leachate will be pumped to a special tanks and then were added with chemical substances to perform coagulation of suspended solid in the leachate thus lower harmful material before being discharged. However, mostly treated leachate still contain hazardous effect to be released to environment and it will be discharged to local sewerage systems for further treatment.

2.2 Polycyclic Aromatic Hydrocarbons, PAHs.

Polycyclic Aromatic Hydrocarbons or PAHs are chemical compound containing only hydrogen and carbon where it is are composed from multiple aromatic rings. There are 16 type of PAHs exists the each of them have a different chemical structure of the ring(Sparling, 2016). For example, naphthalene consist of two aromatic rings, meanwhile PAHs called phenanthrene were made up from three-ring compound. The most common PAHs are PAHs with six-membered rings where it is called alternant PAHs including benzenoid PAHs. All 16 type of PAHs are stated as below:

- Naphthalene
- Acenaphthalene
- Acenaphthene
- Fluorene
- Phenantren
- Antracene

- Fluoranten
- Pyrene
- Benzo(a)antracene
- Chrysene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(a)pyrene
- Indeno(1,2,3-cd) pyrene
- Dibenzo(a,h)antracene
- Benzo(g,h,i)perylene

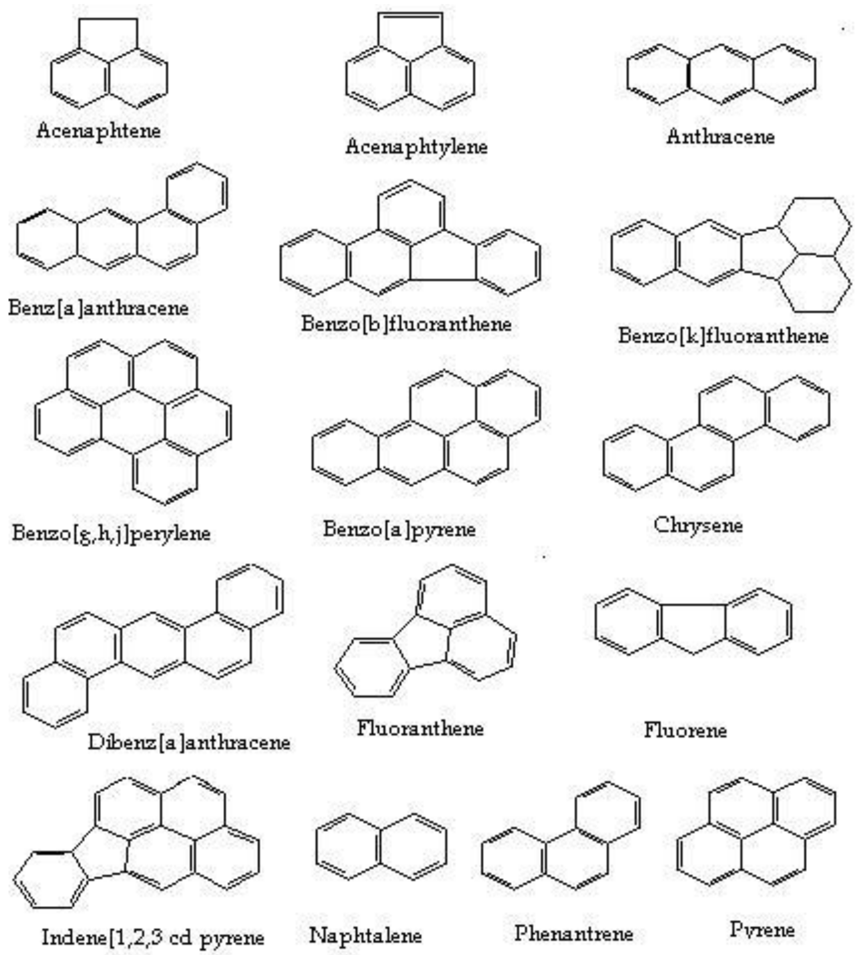

FIGURE 2.2. Priority listed PAHs (Keith, 2015)

Commonly, PAHs are colourless and sometimes white also exists in pale yellow solids (Abdel-Shafy & Mansour, 2016). Large PAHs are chemical compound that cannot be soluble in water because of its nonpolar and lipophilic characteristics. However, some PAHs are soluble in water and many cases about water contamination are because of PAHs. PAHs are very abundant chemical compound. They are basically were found in natural sources such as creosote (Sörensen & Wichert, 2000). PAHs are formed because of incomplete combustion of organic substances and produced when organic remains where chemically reacted to transformed in to fossil fuels such as gas and petroleum(Ravindra, Sokhi, & Van Grieken, 2008). Large amount of PAHs produced are because of humans daily activity such as wood-burning and fuel combustion. In India and China, the major contribution of PAHs synthesis are from usage of biofuels where it is stated to contribute half of annual global PAH emissions(Zhang & Tao, 2009).

Low molecular weight of PAHs are produced from lower-temperature combustion such as dead leaves or wood burning or also from smoking cigarettes. Meanwhile, large scale industrial process where uses high temperature process will produced PAHs with higher molecular weight. In aqueous condition, most PAHs are insoluble in water thus effect its mobility in the environment (Choi et al. 2010). The ability to dissolve in the water were determined by its ring. The lesser the ring, the higher the chance to dissolve in water. Two-ring and sometimes three-ring PAHs were most likely to dissolve in water thus making them available for degradation(Johnsen, Wick, & Harms, 2005).

PAHs are known for its hazardous, carcinogenic and mutagenic characteristics. All this characteristics will disrupt human health if were overexposed. One of the reason is PAHs can make human to suffer from skin, lung, bladder, liver and stomach cancers (Boström et al., 2002). This is cause by the carcinogenic characteristics of PAHs. This were recorded long ago back in 1775 when a surgeon at St. Bartolomew's Hospital in London where most of the chimney sweepers were diagnosed with scrotal cancer and he proposed that is because they were overly exposed with soot (Harvey, 1985). Next, over exposed to PAHs also can cause cardiovascular disease (Korashy & El-Kadi, 2006). This is shown where active cigarette smokers mostly diagnosed with cardiovascular diseases because of the PAHs contained together among other contaminant in the cigarette smoke.

Lastly, overexposed to PAHs can cause developmental impact. From studies conducted in Europe, United States and China to the people living there, person exposed to PAHs through air pollution or because of occupational contact where linked to deprived fetal development, diminished immune activity and insufficient neurological advancement including lower IQ.

2.3 Advanced Oxidation Process

Advanced Oxidation Process (AOPs) are a method of treatment techniques by oxidation using hydroxyl radicals (•OH) to eliminate organic matter in wastewater and it was proposed as efficient water treatment in the 1980s (Glaze, Kang, & Chapin, 1987). Later the oxidation process of AOPs has been extended with sulfate radicals ($SO_4^{\cdot-}$). The main purpose of AOPs are for the degeneration of organic and inorganic matter in water and wastewater different from other oxidation process which are chlorination and ozonation that are purposely for decontamination and disinfection. Radicals in the AOPs are powerful oxidizing agent that can possibly destroy water pollutant and convert them in to less toxic material, thus it is a supreme explication in treating wastewater (Huang, Dong, & Tang, 1993).

2.3.1 Hydroxyl Radical-Based AOPs

Performing water treatment by AOPs, hydroxyl radicals are the most powerful oxidizing agent with oxidation potential between 2.8 V (pH 0) and 1.95 V (pH 14) (Tchobanoglous & Burton, 1991). Hydroxyl radicals attack all kind of organic or inorganic substances rapidly in four basic ways which is radical addition, hydrogen abstraction, electron transfer, and radical combination. When it is reacted with organic compounds, it will eventually producing carbon-centered radicals (R· or R·–OH) and then if this radicals reacted with O_2, it will convert to organic peroxyl radicals (ROO·). Later, further reaction will occur with the assist from H_2O_2 and will degrade and mineralize the organic compounds. Hydroxyl radicals only have very limited lifetime since they are only produced during the utilization of different process such as fusion of oxidizing substances (H_2O_2 and O_3), radiation process (UV light) and catalyst (Fe^{2+}) (Huang et al., 1993).

2.3.2 Fenton-Related AOPs

Felton-related AOPs are basically a hydroxyl radical-based AOPs but with addition of metal ion to produce more hydroxyl radicals for water treatment process where the metals added is Fe^{2+}. The reaction produced more oxidizing agents and some part of the produced none other than hydroxyl radicals are ferryl ions that also contribute to the oxidizing process thus assist the oxidation process for the treatment. This process have been detailed on research carried out by Pignatello, Oliveros & MacKay (2006) . Chemical equation below showed the chemical reaction of Fenton process:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO\cdot 2 + H^+ \quad (2)$$

$$OH\cdot + H_2O_2 \rightarrow HO\cdot 2 + H_2O \quad (3)$$

$$OH\cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (4)$$

$$Fe^{3+} + HO\cdot 2 \rightarrow Fe^{2+} + O2H^+ \quad (5)$$

$$Fe^{2+} + HO\cdot 2 + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$

$$2HO\cdot 2 \rightarrow H_2O_2 + O_2 \quad (7)$$

From equation 1, when ferum ion react with hydrogen peroxide, it will produced hydroxyl radicals by transferring the electron from hydrogen peroxide to ferum ion and it can effectively done in low pH condition. However, each of the produced ions and hydroxyl radicals can also react each other and causing the hydroxyl radicals and to decreased as shown in equation 2 and 3. Because of this effect, researchers have to find the optimum molar ratio of both reagents in order to maximize the reaction process by reducing the scavenging effect. In equation 2, the reaction of Fe^{3+} and H_2O_2 produced Fe^{2+} which are used to activate the H_2O_2 as shown on equation 1, however it cannot act as catalyst as the rate is fixed. This process produces big amount of sludge and it does decrease the efficiency of the process at its need to be removed. There are several Fenton process that have been altered to increase its efficiency such as Photo-Fenton process, E-Fenton process and Fenton-like process. Each of them have significant difference in their efficiency in oxidizing matters.

2.3.2.1 Photo-Fenton process

Photo-Fenton process is basically a Fenton process but with the presence of UV radiation from UV light. UV radiation reduced Fe^{3+} to Fe^{2+} during the process thus decrease the production of sludge and enhance the oxidation process. It is more effective compared to the basic Fenton process and show significant removal for wastewater treatment (Primo et al., 2008). Below shows basic equation for Photo-Fenton process:

$$Fe^{2+} + H_2O_2 \rightarrow Fe\,(OH)^{2+} + \bullet OH \quad (1)$$

$$Fe\,(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH \quad (2)$$

From equation 1, Fe^{2+} reacts with H_2O_2 and generate hydroxyl radicals for the oxidizing process and it is also produced Fe $(OH)^{2+}$. Later, UV radiation that exposed to the process takes its place in breaking Fe $(OH)^{2+}$ to Fe^{2+} and hydroxyl radicals, meaning that more hydroxyl radicals were generated to assist the oxidization process thus increase its efficiency.

CHAPTER 3

METHODOLOGY

3.1 Flow of research

In the beginning of this research, students were given topic to choose from according to their interest and start to make contact with supervisor to get some insight and information about the project before the commencement of the project. Preliminary studies were conducted to give some acumen on the research in order to scrutinize the topic on bigger extension. Background study, problem statement and objectives of this research have already been decided and concluded in the written report during the phase. Literature review related to this research also have been identified to the understanding about this research are sufficient before it started.

Later, the variables of this research were identified to separate this research from the earlier study that have been conducted. In the beginning of the experiment, sample were collected and preliminary studies have been conducted to determine the optimum condition for the Photo-Fenton process in degrading PAH from hazardous waste landfill leachate. Later, the optimum values obtained were added to response surface method software to design several experiment in order to get the optimum condition by combining three different condition for the degradation process. All the results obtained were analyzed and discussed before it is concluded and suggested some recommendation for further studies.

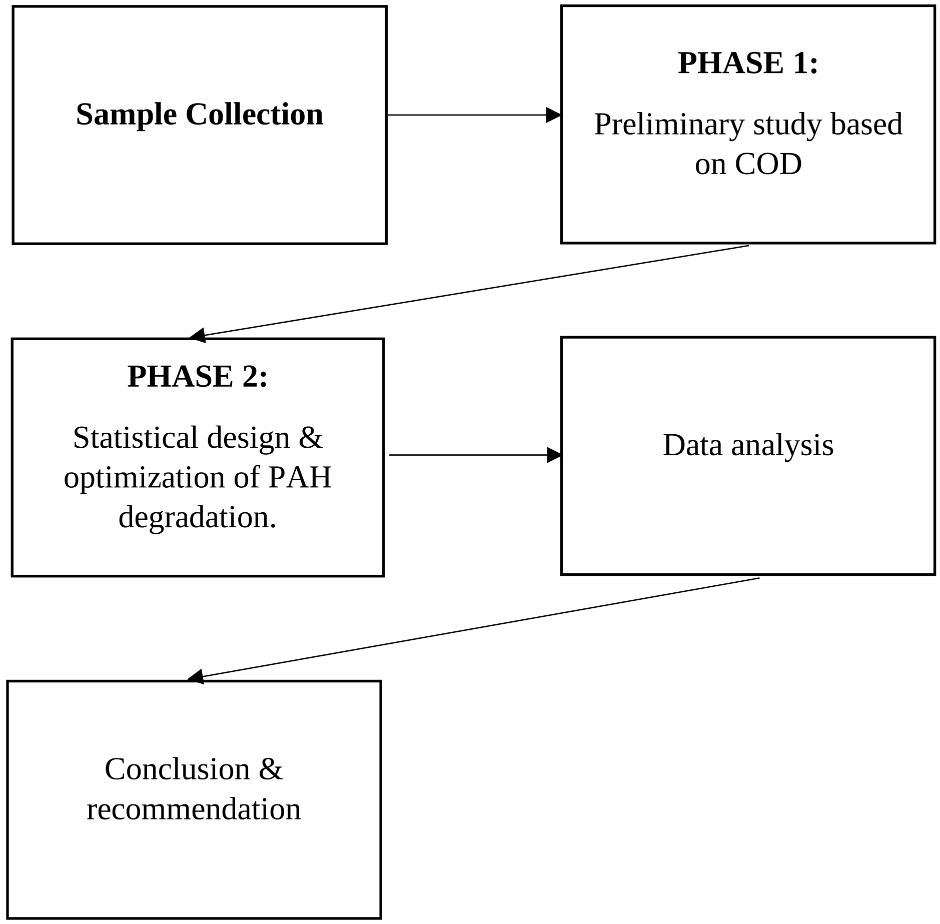

FIGURE 3.1. Flow of Research Project.

3.1.1 Project Key Milestones

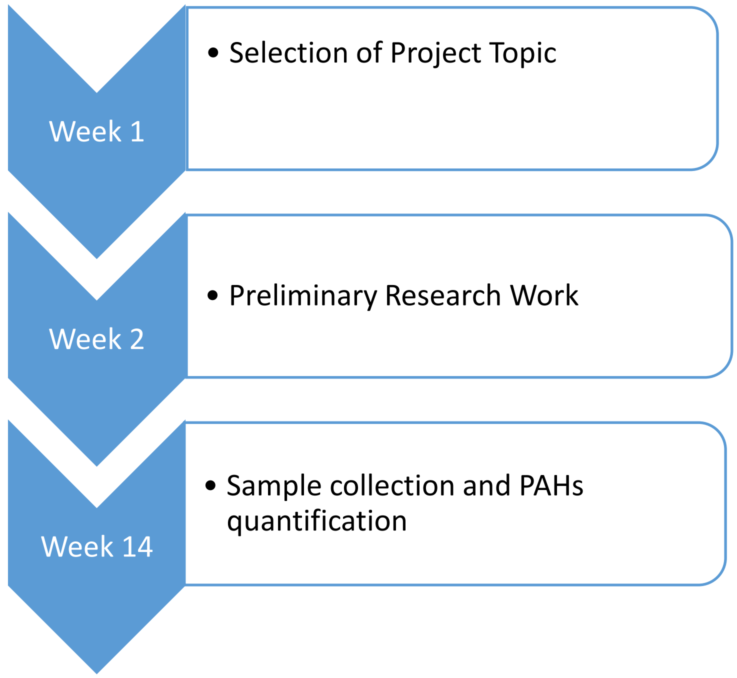

FIGURE 3.2. FYP I Key Milestone

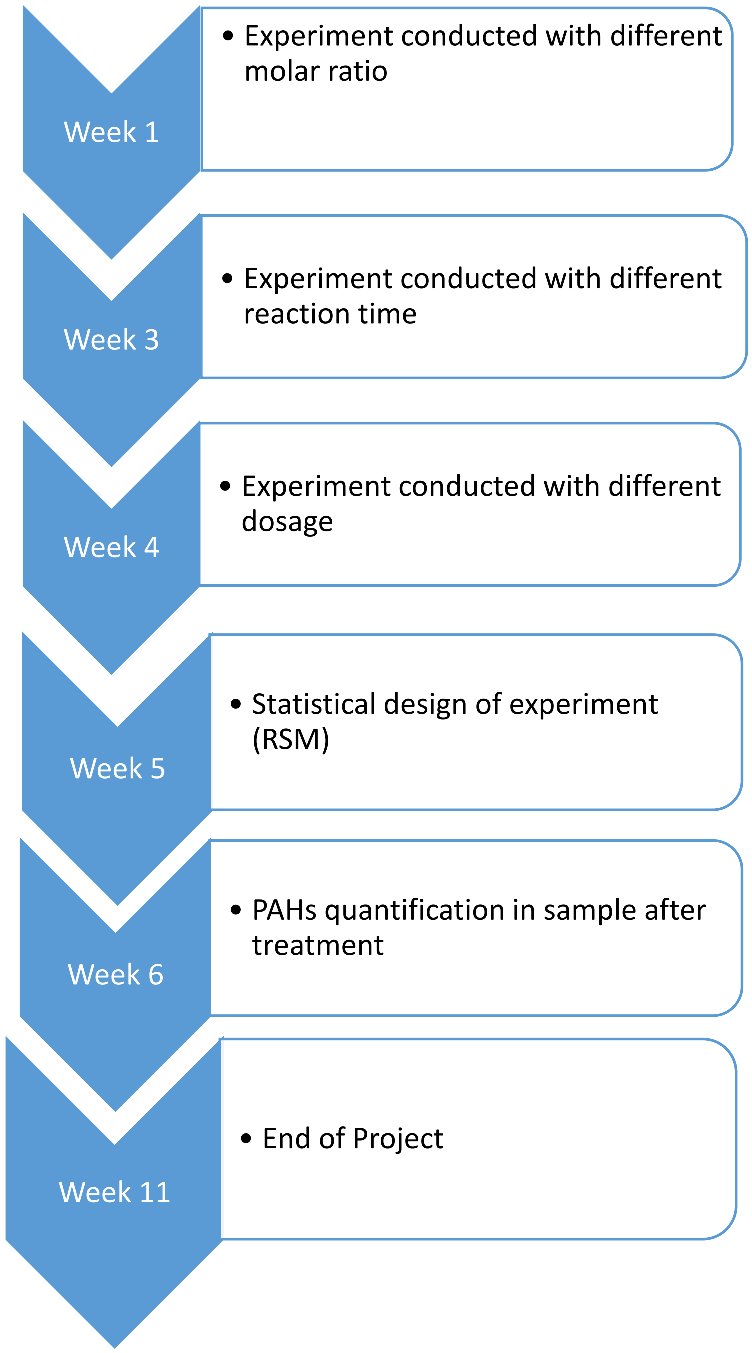

FIGURE 3.2. FYP II Key Milestone

3.1.2 Gantt Chart

TABLE 3.1. FYP I Gantt Chart

No.	Details	FYP 1													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic														
2	Preliminary Research Work														
3	Sample collection and PAHs quantification														

TABLE 3.2. FYP II Gantt chart

No.	Details	FYP 2													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
4	Experiment conducted with different molar ratio		●												
5	Experiment conducted with different reaction time				●										
6	Experiment conducted with different dosage					●									
7	Statistical design of experiment (RSM)									●					
8	PAHs quantification in sample after treatment									●					
9	Result Review														
10	End of Project														

● Key Milestones

3.2 Determining PAH in leachate

Initial sample were taken to determine its PAHs content using GC-MS. The PAHs in the sample are extracted by shaking it with dichloromethane in a separating funnel. After extraction, PAHs were determined with gas chromatography/mass spectrometry (GC/MS) with helium as a carrier gas and a flow rate of 30 cm s^{-1}. Sample are also tested to determine its COD and done in triplicate. PAHs determined by comparing the retention time and MS spectrum with those of standard reagents.

3.3 Preliminary studies based on COD test

Leachate sample will undergo Photo-Fenton process in a beaker with 500 ml. Sodium Hydroxide and Sulphuric Acid used for pH adjustment. Sample were added with certain amount of Hydogen Peroxide and Ferrous Sulfate Heptahydrate. Sample then stirred with magnetic stirrer and immersed with Quartz sleeved UV lamp and it will run in certain amount of time. After that, the pH of the sample increased to 10 to stop the oxidation process and sample are allowed to settle for 30 minutes. Test for COD of the sample. Run the same procedure with different molar ratio to determine the optimum molar ratio for Photo-Fenton process. The suggested molar ratio to be used is 0.5, 1, 2, 3, 4 and 5.

Run the same procedure with different dosage to determine the optimum dosage for Photo-Fenton process. The suggested dosage combination used is as in table below:

TABLE 3.3. Hydrogen peroxide and ferrous sulphate dosage combination

Combination	**H_2O_2 / Fe^{2+} (mol)**
1	0.03/0.01
2	0.06/0.02
3	0.09/0.03
4	0.12/0.04
5	0.15/0.05

Run the same procedure with different time reaction to determine the optimum time reaction for Photo-Fenton process. The suggested time reaction to be used is 60 minutes, 90 minutes, 120 minutes, 150 minutes and 180 minutes. Test COD for each sample after undergo Photo-Fenton process and compare the initial and residual COD after treatment. Equation below are used to determine the removal percentage:

$$R = \frac{(C_0 - C_1)100}{C_0}$$

3.4 Statistical design and optimization of PAH degradation

The values for optimum condition of the Photo-Fenton process were inserted into response surface method software and 20 runs of experiment were designed to find the optimum condition for three different independent variable which is molar ratio, dosage and time reaction. The 20 runs of experiment that already been given by the software are as follows:

TABLE 3.4. 20 different runs designed by RSM

Run	**Molar Ratio**	**H_2O_2 Dosage (mol/L)**	**Reaction Time (min)**
1	5	0.06	60
2	5	0.12	120
3	5	0.12	60
4	1	0.09	90
5	5	0.06	120
6	3	0.09	90
7	1	0.06	120
8	3	0.09	90
9	3	0.09	140.45
10	3	0.09	90
11	3	0.09	90
12	1	0.12	60
13	3	0.09	90
14	3	0.04	90
15	3	0.14	90
16	3	0.09	90
17	3	0.09	39.55
18	1	0.12	120
19	1	0.06	60
20	6.36	0.09	90

Sample of each runs were extract by shaking it with dichloromethane in a separating funnel. After extraction, PAHs were determined with gas chromatography/mass spectrometry (GC/MS) with helium as a carrier gas and a flow rate of 30 cm s^{-1}.

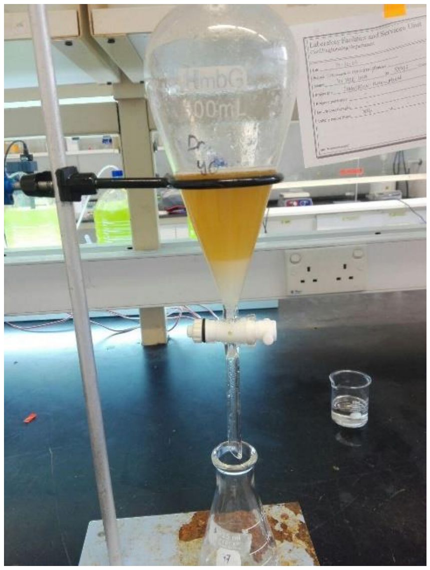

FIGURE 3.4. PAH liquid-liquid extraction from leachate.

CHAPTER 4
RESULTS AND DISCUSSION

Leachate sample collected have been tested with GC-MS to determine its PAHs content. The PAHs content for untreated must be determine to compare it with the leachate treated with Photo-Fenton later. Table shown below are the result of PAHs content in leachate sample expressed in parts per billion (ppb).

TABLE 4.1. Quantification of PAHs in Hazardous Waste Landfill Leachate

No.	PAH	ppb
1	Naphthalene	1073.24
2	Acenaphthylene	1364.62
3	Acenapthene	110.23
4	Fluorene	1313.83
5	Phenanthrene	1603.10
6	Anthracene	1326.40
7	Carbazole	1396.78
8	Fluoranthene	526.13
9	Pyrene	42.99
10	Chrysene	59.80
11	Benz(a) anthracene	171.76
12	Benzo(b) fluoranthene	430.20
13	Benzo(K) fluoranthene	343.20
14	Indeno (1,2,3,-CD) pyrene	1495.24
15	Dibenz (a,h) anthracene	2686.45
16	Benzo (g,h,i) perylene	685.32

From the quantification conducted with GC-MS, the highest PAH in the leachate sample is Benzo (b) fluoranthene meanwhile, Pyrene does not shown any existence in the leachate sample. From COD test that already conducted, the initial COD of the leachate is 4123 mg/L.

4.1 Optimum Molar Ratio

The most crucial chemical to be used in Photo-Fenton process is hydrogen peroxide and iron the one that responsible for the elimination of organic substances in leachate by producing hydroxyl radicals that will act as oxidizing agent. Hydroxyl radicals will oxidizes organic substances in the leachate as for the subject in this experiment is PAH. However, if the hydroxyl radicals is excessive, the oxidization process cannot occur completely thus PAH in the leachate cannot be eliminated because hydroxyl radicals have scavenging effect. COD test were conducted in order to find the optimum molar ratio of H_2O_2 and Fe^{2+} for the Photo-Fenton reaction process. The dosage of Fe2+ are constant at 1388 mg/500ml and the time reaction also constant at 60 minutes. The molar ratio is varied at 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0.

TABLE 4.2. Effect of molar ratio on COD removal efficiencies.

Molar ratio	**COD reading 1 (mg/L)**	**COD reading 2 (mg/L)**	**COD reading 3 (mg/L)**	**Average COD (mg/L)**	**% Removal**
0.5	3240	3410	3310	3320	19
1	2730	2650	2580	2653	36
2	2100	2250	2180	2177	47
3	**1980**	**1890**	**1850**	**1907**	**54**
4	1990	2220	2000	2070	50
5	2250	2390	2310	2317	44

Based on figure 3 below, the highest percentage removal of COD is at 54% where the molar ratio is at 3. This show that the ratio of H_2O_2 and Fe^{2+} at 3 is the best as there is no excessive hydrogen peroxide that could scavenge the hydroxyl radicals thus decrease the percentage of COD removal.

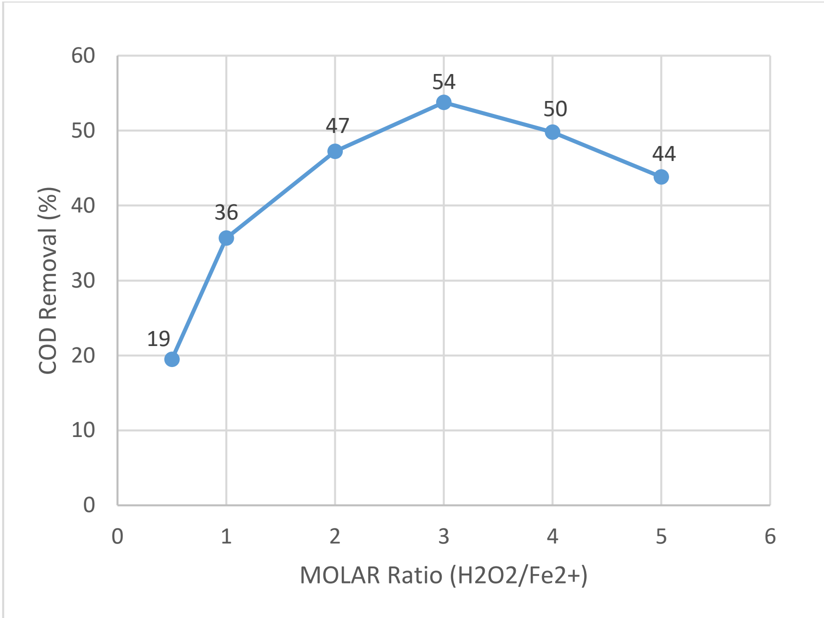

FIGURE 4.1. Effect of molar ratio on COD removal efficiencies.
(Fe^{2+} = 0.01 mol L^{-1}, pH= 3, RT = 60)

The molar ratio that exceed 3 showing that the excessive hydroxyl radicals are not increasing the COD removal but it will decrease it. For molar ratio below 3, the condition are different compared to molar ratio above 3. From figure 3, the removal of COD for molar ratio below 3 also decreasing as the molar ratio decrease. This shows that high amount of Fe^{2+} also results in diminished of hydroxyl radicals thus reduce the efficiency of COD removal.

4.2 Optimum Dosage

The optimum dosage also must be determined to find the highest COD removal as the concentration of the reagents used in the experiment will determine the effectiveness of the oxidization process as it is not sufficient if only find its optimum molar ratio. This study is conducted by varying the dosage of hydrogen peroxide and Fe^{2+} while maintaining the molar ratio. In this test, the molar ratio to be used is fixed at 3 which is the optimum molar ratio and the time for reaction also constant at 60 minutes. 5 different combination of H_2O_2 and Fe^{2+} dosages are used in this experiment are shown as the following:

TABLE 4.3. Different combination of H_2O_2 and Fe^{2+} dosages

Combination	**H_2O_2 / Fe^{2+} (mol)**
1	0.03/0.01
2	0.06/0.02
3	0.09/0.03
4	0.12/0.04
5	0.15/0.05

From figure 4, the highest COD removal from leachate is combination 3 where the mole of the H_2O_2 and Fe^{2+} are 0.09 and 0.03 respectively. The removal of COD kept increasing as the dosages is increase until it reach the point where it is the maximum hydroxyl radicals are present. After reaching 63% of removal, the efficiency of COD removal are decreasing as the dosage of the H2O2 and Fe2+ exceeded. This cause the scavenging of hydroxyl radicals results in low hydroxyl radicals exists during the experiment thus the removal of COD efficiency is not efficient. The highest COD removal are at 10.2 ml/L H_2O_2 and 8340 mg/L Fe^{2+}.

TABLE 4.4. Effect of dosages on COD removal efficiencies.

Combination	H2O2/Fe2+ (mol)	COD reading 1 (mg/L)	COD reading 2 (mg/L)	COD reading 3 (mg/L)	Average COD (mg/L)	% Removal
1	0.03/0.01	1980	1890	1850	1907	54
2	0.06/0.02	1780	1890	1530	1733	58
3	**0.09/0.03**	**1580**	**1550**	**1480**	**1537**	**63**
4	0.12/0.04	1690	1660	1710	1687	59
5	0.15/0.05	1800	1850	1790	1813	56

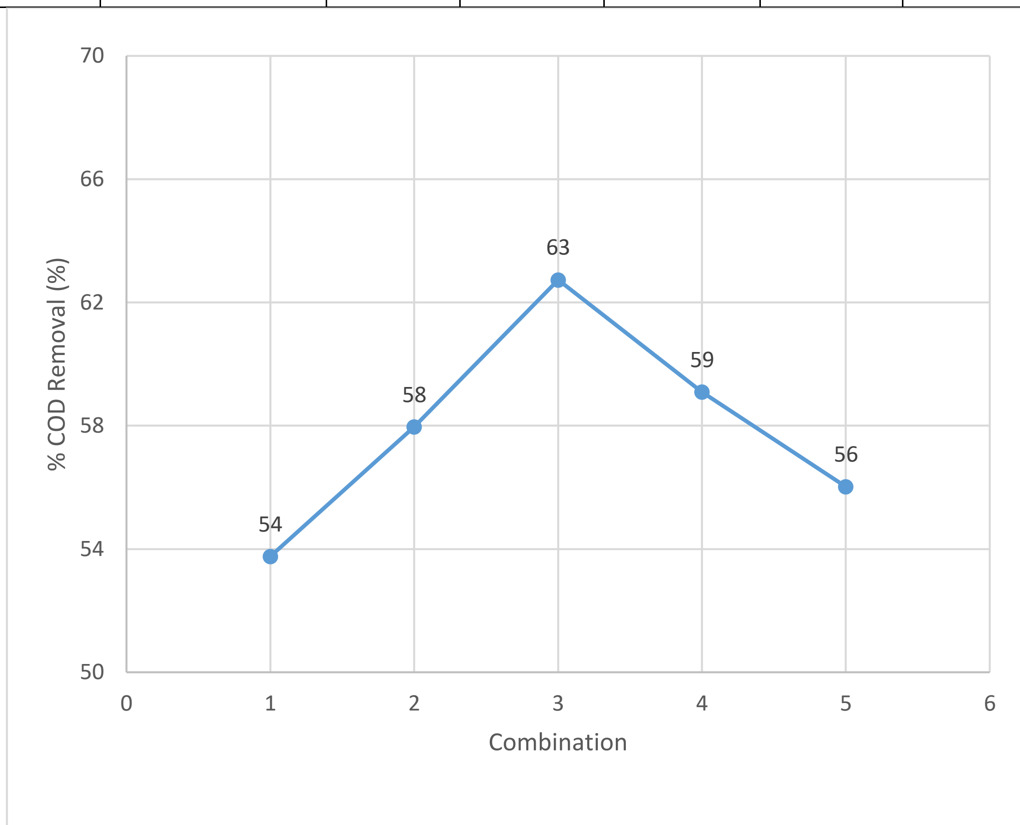

FIGURE 4.2. Effect of dosages on COD removal efficiencies.
(H_2O_2/Fe^{2+} = 3, pH= 3, RT = 60)

4.3 Optimum Reaction Time

Experiment setup also was conducted to find the optimum reaction for the Photo-Fenton process. Time for reaction are varied 60 minutes, 90 minutes, 120 minutes, 150 minutes and 180 minutes. In the experiment, molar ratio of H_2O_2 and Fe^{2+} are fixed at 3 and the dosage of both reagents are also fixed at 0.09 mol and 0.03 mol of H_2O_2 and Fe^{2+} respectively. Based on figure 5 below, the reaction time at 90 minutes are the optimum time reaction for the process. Reaction time after 90 minutes shows no significant differences thus it shows that at 90 minutes, the reaction process are almost complete.

TABLE 4.5. Effect of time reaction on COD removal efficiencies.

Reaction Time (min)	COD reading 1 (mg/L	COD reading 1 (mg/L	COD reading 1 (mg/L	Average COD (mg/L)	% Removal
60	1580	1550	1480	1537	63
90	**1300**	**1290**	**1350**	**1313**	**68**
120	1400	1420	1160	1327	68
150	1350	1310	1250	1303	68
180	1320	1340	1260	1307	68

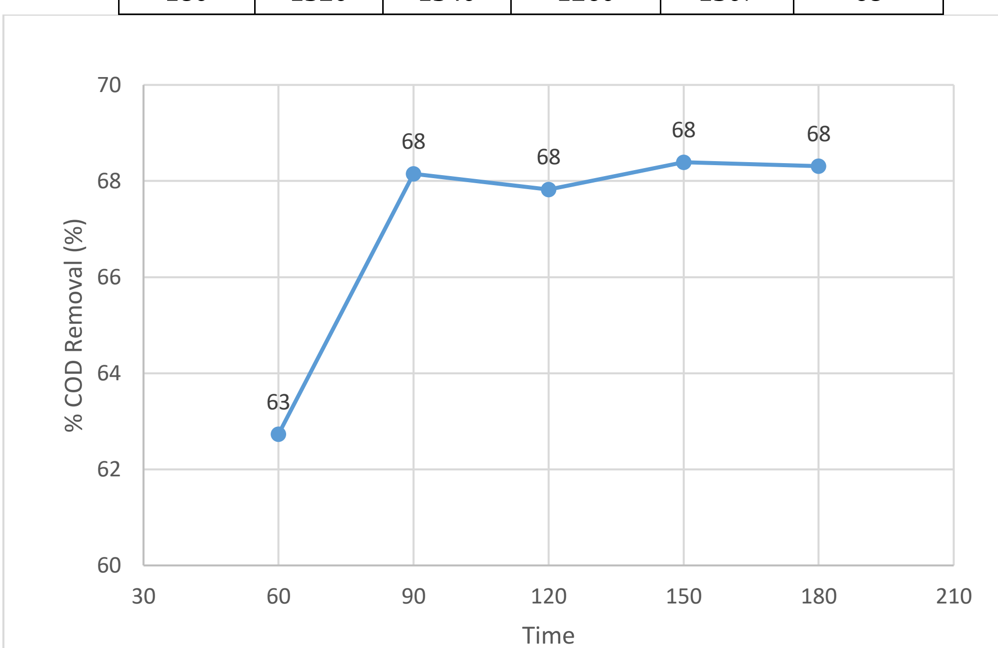

FIGURE 4.3. Effect of reaction time on COD removal efficiencies.
(H_2O_2/Fe^{2+} = 3, pH= 3, H_2O_2 = 0.09 mol/L, Fe^{2+}= 0.03 mol/L)

4.3 Satistical design and optimization of experiment

After obtaining of the optimum condition for Photo-Fenton process to degrade PAH in leachate, all the values were added in to Design Expert 10 software and 20 runs were design by response surface method. 20 runs of experiment were conducted according to the given molar ratio, time reaction also hydrogen peroxide and ferrous sulphate dosage. Percentage of PAH removal for each run were determined using GC-MS and presented as in table below:

TABLE 4.6. % of PAH removal obtained from different condition generated by RSM

Run	Molar Ratio	H_2O_2 Dosage (mol/L)	Reaction Time (min)	% PAH Removal
1	5	0.06	60	71.24
2	5	0.12	120	68.39
3	5	0.12	60	61.21
4	1	0.09	90	53.19
5	5	0.06	120	73.65
6	3	0.09	90	86.38
7	1	0.06	120	55.6
8	3	0.09	90	83.76
9	3	0.09	140.45	85.32
10	3	0.09	90	88.18
11	3	0.09	90	83.43
12	1	0.12	60	49.76
13	3	0.09	90	87.54
14	3	0.04	90	82.13
15	3	0.14	90	79.23
16	3	0.09	90	86.67
17	3	0.09	39.55	68.5
18	1	0.12	120	51.74
19	1	0.06	60	48.9
20	6.36	0.09	90	63.4

After added all the percentage of PAH removal in to the software according to its condition, it immediately interpolate the data into 3D graph with different combination of variables (molar ratio and reaction time, reaction time and dosage & dosage and molar ratio) against percentage of PAH removal. Data and results are presented as below:

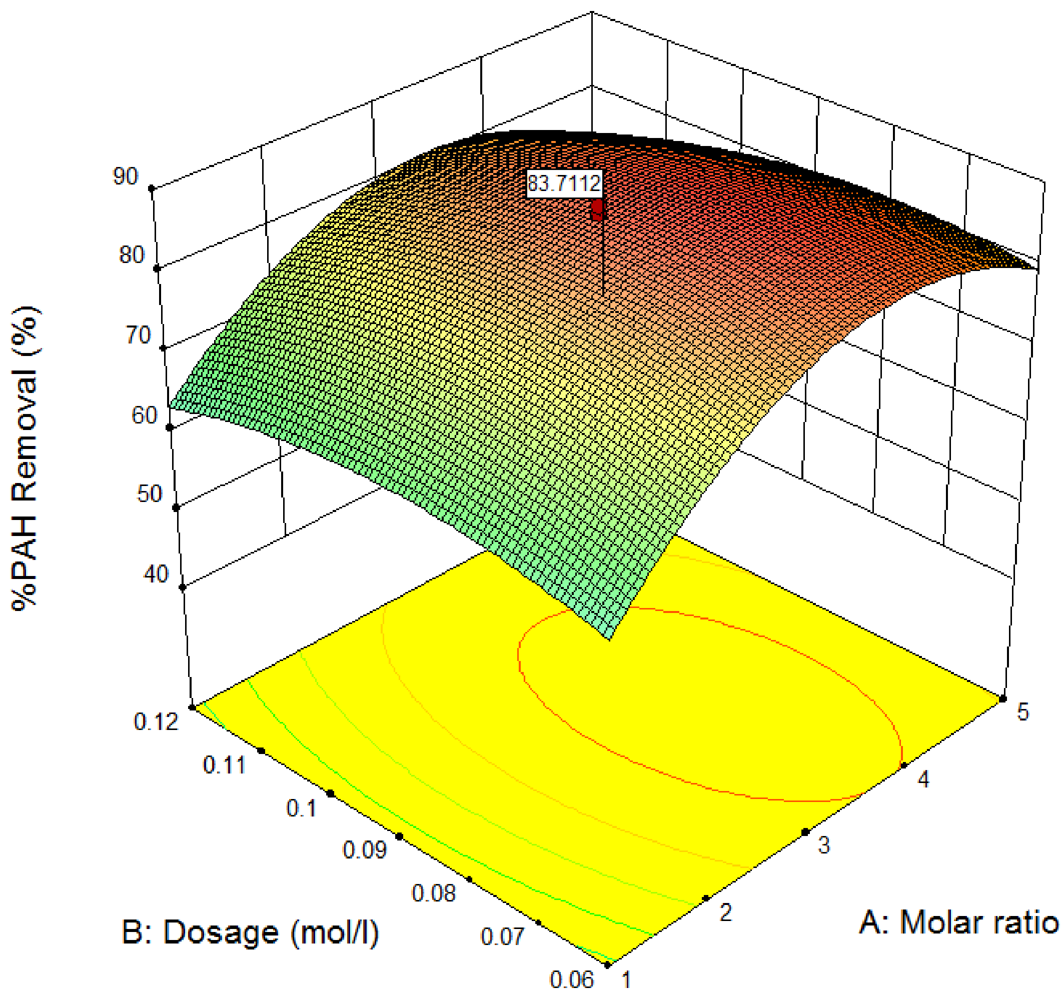

FIGURE 4.4. Dosage & molar ratio vs % PAH Removal

From Figure 4.4 the highest percentage of PAH removal are shown on the red contour of the graph where it lies around molar ratio of 3.8 and dosage of hydrogen peroxide approximately 0.082 mol/L. Dosage that exceed 0.082 mol/L show that the removal of PAH are decreased as excessive hydrogen peroxide scavenge the hydroxyl radicals that act to oxidize the PAH also, the molar ratio have to be optimum to ensure the Fe^{2+} is not excessive as it can scavenge hydroxyl radicals and also not too low in ratio with the hydrogen peroxide so that it have sufficient Fe^{2+} that act as catalyst to help perform the process to its maximum.

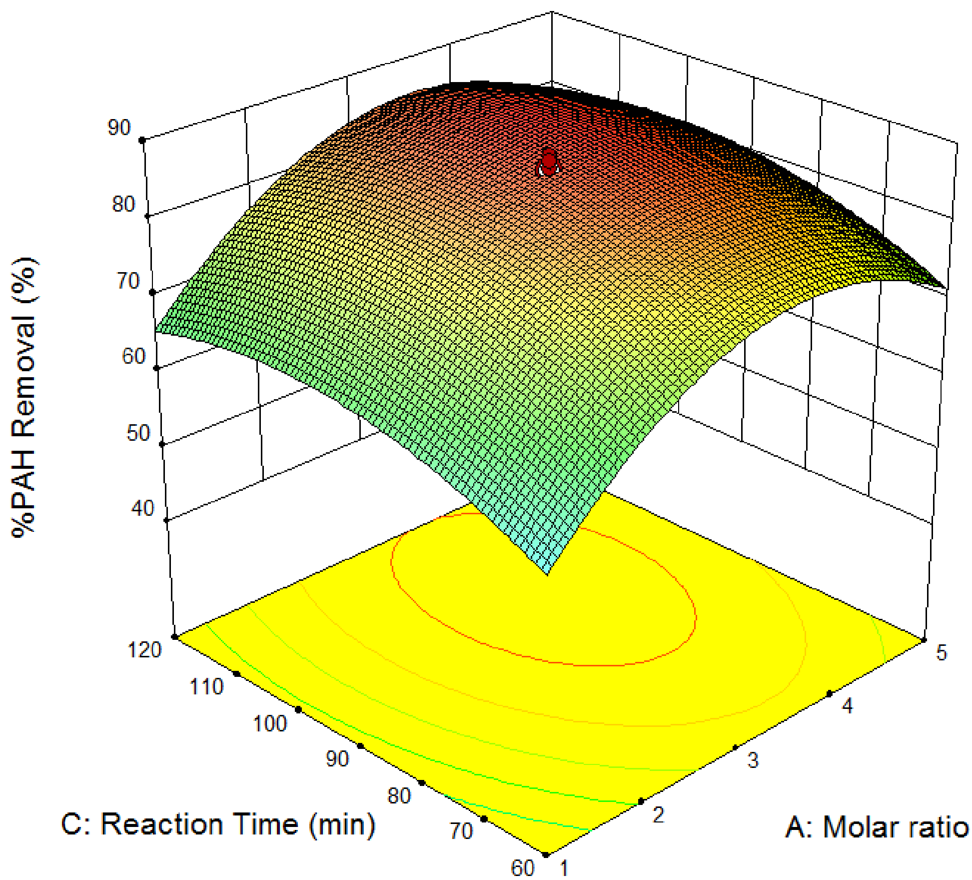

FIGURE 4.5. Reaction time & molar ratio vs % PAH Removal

From Figure 4.5 the highest percentage of PAH removal are shown on the red contour of the graph where it lies approximately around reaction time of 98 minutes and Molar ratio approximately at 3.5. At 98 minutes and above, the Photo-Fenton process were almost completely degrade most of PAH in the leachate, however the molar ratio are at around 3.5 it is the optimum hydrogen peroxide and ferrous sulphate ratio.

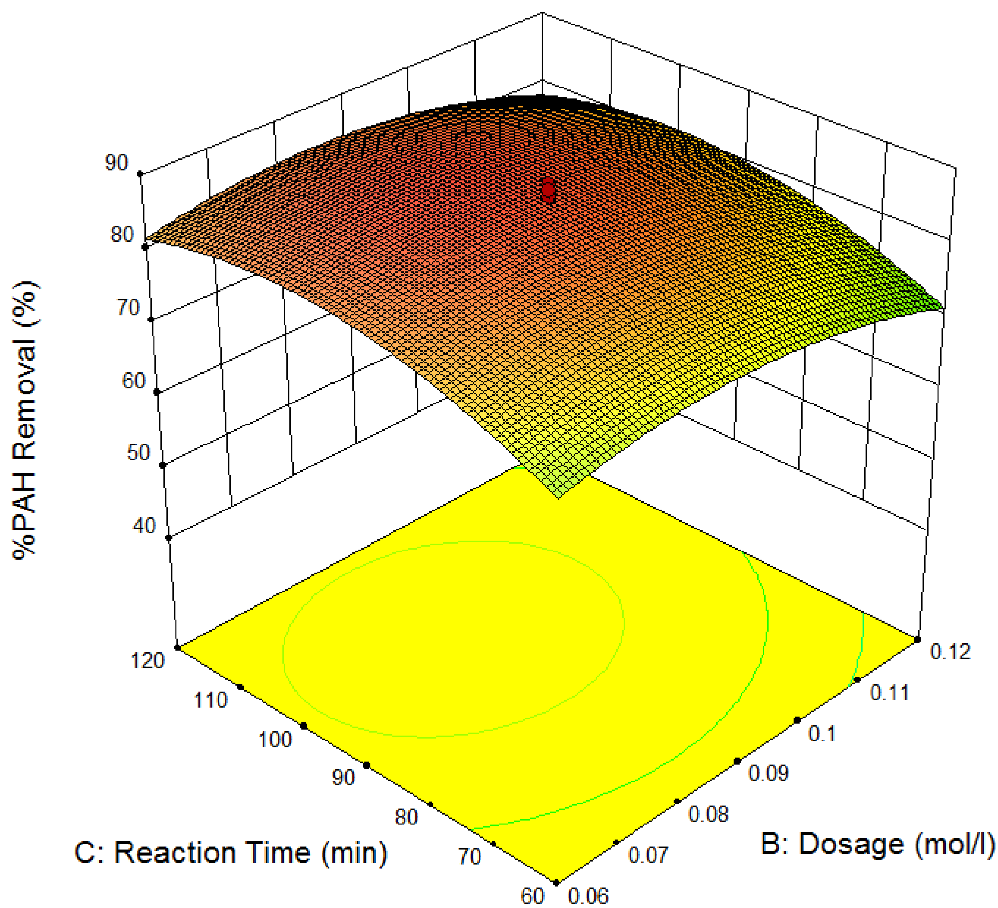

FIGURE 4.6. Reaction time & Dosage vs % PAH Removal

Figure 4.6 the highest percentage of PAH removal are shown on the contour of the graph where it lies approximately around reaction time of 100 minutes and dosage of hydrogen peroxide at 0.085 mol/L. Lower dosage needs more reaction time to degrade PAH and higher dosage results in lower PAH removal because of the scavenging effect of hydrogen peroxide to the hydroxyl radicals.

Data plotted in the 3D graph were analyzed by response surface method and it shows that the highest percentage PAH removal were at 87.66% where PAH in the hazardous leachate were almost completely degraded and the optimal condition to achieve the highest percentage removal is at molar ratio 3.25, time reaction at 98.2 minutes and dosage of hydrogen peroxide and ferrous sulphate at 0.08 and 0.025 mol/L respectively.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

The subject matter which is Polycyclic Aromatic Hydrocarbons indeed have a great impacts to the environment if not be taken seriously. It can cause cancer, cardiovascular disease and give impact on fetal development. This studies were to be conducted to study the efficiency of Photo-Fenton process in removing PAHs in leachate using different reaction time, dosage and molar ratio. The idea of using Photo-Fenton process is because they are most efficient in removing COD in wastewater and to fully utilize them for treatment process. The previous research were to use Photo-Fenton process to remove COD from landfill leachate and this study are taking leachate as sample to remove PAHs. Later, the result and discussion obtained from the test may be collected and compared to find the optimum condition of reaction time, dosage and molar ratio to see the efficiency of Photo-Fenton in removing PAHs from leachate. From the results, it is shown that the optimum molar ratio is at molar ratio 3, the optimum dosage is 3 and the optimum time reaction is at 90 minutes. COD test is used to determine the optimum condition because it will take long timeframe if use GC-MS as PAH removal are almost the same as COD removal as PAH are also organic substances. The results from the COD test are used to test the highest PAH removal from leachate by different condition by using Design Expert software. After conducting 20 runs designs of experiment generated from the software and analyzed the data, the highest percentage of PAH removal is 87.66% and the condition is at molar ratio 3.25, time reaction of 98.2 minutes, and dosage of hydrogen peroxide and ferrous sulphate at 0.08 mol/L and 0.025 mol/L respectively. All results obtained, satisfy the objectives of this research as the molar ratio, time reaction and the dosage of hydrogen peroxide and ferrous sulphate have been determined also the efficiency of Photo-Fenton process method in degrading PAH from hazardous waste landfill leachate have been ascertained.

5.2 Recommendation

From the test that have been conducted before, there are some recommendation the experiment needed for future research .The recommendations are as below:

1. The leachate must be exposed completely with the UV lamp to ensure the Photo-Fenton process are undergo perfectly thus the data obtained from the experiment conducted are much more reliable as a result of Photo-Fenton process and not a Fenton process. Special container for the leachate must be used to make sure the UV lamp light every part of the leachate.
2. The energy consumption of the UV light are need to be varied to determine whether different watt of UV light energy consumption effect the efficiency of PAH removal from hazardous waste landfill leachate.

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