TREATMENT OF SANITARY LANDFILL LEACHATE BY ADVANCED OXIDATION PROCESS (FENTON)

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by

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CERTIFICATION OF APPROVAL

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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 continued herein have not been undertaken or done by unspecified sources or persons.

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MAKHARINGE GLORENCE

ABSTRACT

This study was conducted to investigate the potential of Advanced Oxidation Process (AOP) system, Fenton Process in removing Polycyclic Aromatic Hydrocarbon (PAHs) and Chemical Oxygen Demand (COD) in landfill leachate. Resistant and complex organic compounds in leachate such as PAHs formed by incomplete combustion of garbage has detrimental effect on the environmental and human health as PAHs is mutagenic, toxic and carcinogenic. The leachate samples were collected at Jeram Sanitary Landfill, Selangor, Malaysia with average initial COD of 9100mg/L and pH of 8.21.The laboratory experiments were conducted based on the design generated using Design-Expert software with control parameters, initial COD (4900 mg/L-9100 mg/L), H_2O_2/Fe^{2+} (0.5-3.5), reaction time(60 min – 150 min) and H_2O_2 (1000 mg/L-2000 mg/L). Response Surface Methodology (RSM) was applied for optimising the operating conditions. 16 PAHs classified by United States Environmental Protection Agency (US EPA) as the priority pollutants was detected in the leachate sample after the Fenton treatment PAHs concentration were not detected under optimum conditions. The optimum conditions for COD removal were at 7700 mg/L initial COD, 1.5 H_2O_2/Fe^{2+} , 60 minutes reaction time and 1000 mg/L H_2O_2 which resulted in 86.69% COD removal.

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CHAPTER 1: INTRODUCTION

1.1 Background of Study

Continuous population growth and industrial development have led to an increase in waste generation. An increase in knowledge of environmental protection, sustainable developments and global warming, waste management strategies has resulted in legislations which protect the environment. Sanitary landfilling is the primary method used for disposing municipal solid waste in many countries. In Malaysia, primary method of disposal of solid waste is landfilling, sanitary landfill (30.9%) and dumpsites (62.6%), recycling (5.5%) and compost (1%) in 2006. Ghafari, et al. (2009) stated that sanitary landfill leachate a highly polluted industrial wastewater, has been a cause for significant concern with landfilling.

Advanced Oxidation Process (AOP) using Fenton Oxidation for degrading Polycyclic Aromatic Hydrocarbons (PAHs) in landfill leachate is the main objective of this research. . PAHs are resistant and complex organic compounds formed by incomplete combustion of garbage has detrimental effect on the environmental and human health as PAHs is mutagenic, toxic and carcinogenic. It has been reported that PAHs damages the endocrine system in humans. Hermosilla, et al. (2009) states that AOPs achieves high efficiencies for organic compounds removal in leachates compared to other physiochemical technologies.

Leachate is made up of rain that passes through the landfill and liquids that are generated by the breakdown of the waste within the landfill (Wiszniowski, et al., 2006). Large amounts of organic matter, heavy metals, inorganic salts, humic acids, ammonia nitrogen and chlorinated organic form composition of leachate. Disposing leachate without treatment has adverse impact on the environment due to high toxicity of the leachate. (Hermosilla et al., 2009) reported that the landfill characteristics are dependent on the composition of deposited wastes, soil parameters, rainfall patterns and the age of the landfill.

Biologically refractory organic constituents, ammonia, and heavy metals in leachate are three principal issues with regard to treatment and disposal of leachate (Deng & Englehardt, 2006). Moreover, Qasim & Chiang, (1994) clarify that there is a growing concern about the surface and groundwater pollution from leachate as the leachate may percolate through soil and subsoil, causing extensive pollution of streams, creeks and water wells.

According to Renou et al., (2008) Fenton's process is technically simple and there is no mass transfer limitation and both the Fenton's reagent hydrogen peroxide (H_2O_2) and Iron are cheap and non-toxic. Leachate treatment ensures that the discharge standards in terms of the chemical oxygen demand (COD), biochemical oxygen demand (BOD), and suspended solids are met. Several studies have confirmed that AOP can be used to treat old or well stabilised leachate and improves the biodegradability of recalcitrant organic pollutants. In addition, Advanced Oxidation Processes (AOP) and electrochemical oxidation are often used for degradation of recalcitrant compounds.

1.2 Problem Statement

The generation of leachate from landfill site is an inevitable process. When solid waste is disposed in the landfill; the breakdown of the waste material and the liquid that percolates into the landfill in forms of rain forms composition of leachate. The leachate consists of organic and inorganic contaminants therefore leachate treatment is obligatory. Due to the toxicity of leachate, research has shown that failure to effectively treat leachate has detrimental effect on the environment and human health. As a requirement for controlling pollution discharge standards for leachate effluent have been set.

There are many treatment methods available for treating leachate but most of the studies on leachate treatment focus on removal of BOD and COD. However, COD of leachate is usually several thousand mg/L, even high removal efficiencies does not guarantee that the carcinogenic micro pollutants like polycyclic aromatic hydrocarbons (PAHs) will be removed.

For many years, conversional treatment methods such as leachate transfer, recycling, combining leachate treatment with domestic sewage, biodegradation (aerobic and anaerobic process), and chemical and physical process such as chemical oxidation, chemical precipitation, coagulation-flocculation, sedimentation and air stripping were considered to be the appropriate methods for treating leachate effluent. However, on more stabilized leachate from aged landfills (>10 years) biological and chemical-physical treatment processes are not sufficient to reach the level of purification needed for fully reducing the impact of leachate on the environment (Renou et al., 2008).

New treatment methods which make use of membrane processes e.g. reverse osmosis only transfer the pollution and do not eliminate the environmental problems. Advanced oxidation processes (AOPs) such as Fe^{2+}/H_2O_2 (Fenton) and UV/ Fe^{2+}/H_2O_2 (photo-Fenton) have been reported as powerful technologies capable of degrading a wide variety of refractory compounds from stabilized leachate (Hermosilla et al., 2009).

1.3 Objectives

The objectives of conducting the study on Advanced Oxidation Process for landfill leachate treatment are as follows:

1) To identify polycyclic aromatic hydrocarbons (PAHs) in municipal landfill leachate
2) To determine the potential of AOP (Fenton Process) for removal of COD and PAHs.
3) To determine the optimum operating conditions (Fe^{2+}/H_2O_2 dosage , pH, and reaction time) of advanced oxidation process system for effective treatment of leachate.

1.4 Scope of the study

The scope of study is as follows, samples of raw landfill leachate from the landfill site is collected and treated using Fenton oxidation process for determination of Polycyclic Aromatic Hydrocarbons (PAHs) and COD removal efficiencies. The major parts of the carried out for the completion of the research are literature review, laboratory experiments and analysis of the results.

CHAPTER 2: LITERATURE REVIEW

2.1 Advanced Oxidation Process

Advanced Oxidation Processes (AOPs) is defined as the oxidation processes in which the sufficient quantity of hydroxyl radicals (OH) is generated to induce wastewater treatment. Another comprehensive definition states that AOPs refers to a set of chemical treatment procedures designed to remove organic and inorganic wastewater by oxidation (Sharma, et al., 2011). Advanced Oxidation Process is the one of best treatment option for treatment of stabilized leachate because it can effectively remove organic and inorganic compounds (Renou, et al., 2008).

All AOPs systems are characterised by generation of hydroxyl radicals. AOPs have ability to completely oxidise organic contaminants and inorganic ions, the hydroxyl radical is the primary powerful oxidizer in AOPs which reacts with the compounds including aromatic hydrocarbons, unsaturated carbon compound and alcohols (Qasim & Chiang, 1994). Therefore, the hydroxyl radicals act with high efficiency to destroy organic compounds (Sharma et al., 2011). Some of the commonly used AOPs systems include:

- Fenton Reagent: H_2O_2 and Fe^{2+}
- Photo Fenton: H_2O_2, Fe^{2+} and UV light
- H_2O_2 and UV light
- Ozone and H_2O_2
- Ozone and UV light
- Ozone, H_2O_2 and UV light

Application of advanced oxidation process such as UV/Fe^{2+} H_2O_2, UV/ H_2O_2, UV/O_3 and UV/TiO_2 can effectively degrade resistant organic compounds in leachate but application of these processes in large scale treatment of leachate is not economically feasible (Wiszniowski, et al.,2006).

Naddeo et al.,(2011) and Andreozzi et al., (1999) Advanced Oxidation Processes offers the following advantages:

i. High effectiveness in removing resistant organic compounds
ii. Capability of complete mineralization of organic contaminants into carbon dioxide if desired.
iii. Small foot print
iv. Less susceptibility to the presence of toxic substances
v. Biological and chemical processes create sludge, in AOPs there is no creation of sludge.
vi. OH radicals generated in AOPs systems are extraordinary reactive species.
vii. Does not concentrate waste for further treatment as in case of membrane processes

The drawbacks of the AOPs are as follows:

i. Capital intensive
ii. In order to optimise the processes, AOPs are require profound chemistry knowledge.
iii. Quenching of excess peroxide is required in some cases

Hydroxyl radicals attack organic contaminants in two methods which depends on the nature of the organic compound (Renou, et al., 2008). In the first possible method, hydroxyl radical abstracts a hydrogen compounds from water as with alkanes and alcohol. In contrast, when the contaminant is aromatic compounds or olefins the hydroxyl radical add itself to the contaminant. Some of the examples of chemical oxidants for treatment of landfill leachate are photo-Fenton or Fenton reagent, O_3/ H_2O_2, O_3 /UV, H_2O_2/UV, TiO_2/UV (Cortez et al., (2011) .

Deng (2007), illustrates the primary commonly used chemical oxidants and average overall COD removal efficiencies of each oxidant in the Table 2.1. There are few investigations for photocatalytic oxidation (UV/TiO_2) (Heng, 2010). In advanced oxidation technology, under optimum pH, ferrous ions react with hydrogen peroxide to generate the hydroxyl radical in a very simple and cost-effective manner (Cortez et al., 2011).

Table 2.1: Average overall COD removal efficiencies in treatment of landfill leachate by different AOPs

AOPs	UV/H_2O_2	Fenton	O_3	O_3 /UV
Average Overall COD Removal	77%	71%	53%	52%

Source: (Deng, 2007)

It can be observed from Table 2.1 that the COD removal efficiencies are above 50% when different AOPs are applied for treatment of landfill leachate. Hydroxyl radical are produced from single oxidants such as Ozone (O_3), or combination of strong oxidants are Ozone or hydroxide and hydrogen peroxide or ferrous ions with hydrogen peroxide (Cortez et al., 2011).

Studies have shown that degradation of pollutants by the Fenton process is most effective in acidic environments due to higher production of hydroxyl free radicals (Cortez et al., 2011). Furthermore, many studies have confirmed that a pH of 3 has high removal efficiencies for COD and BOD on mature landfill leachate (Deng et al.,2006).

Advanced Oxidation process offer a powerful tool for treatment of leachate and wastewater, but it also has drawbacks. Most advanced oxidation systems are characterised by making use of hydrogen peroxide or ozone, and these reactants are expensive (Andreozzi et al., 1999). Therefore, it has been suggested for Advanced Oxidation process to be combined with other treatment process such as biological processes to reduce operating costs (Oller, et al.,2011). The strength and weakness of several treatment processes are illustrated in Table 2.2.

Table 2.2: Strengths and weaknesses of some treatment methods for landfill leachate

Treatment Process	**Strength**	**Weakness**	**Reference**
Advanced Oxidation Process	Effective for degrading a variety of resistant organic compounds	Not economically feasible for large-scale effluents, combination with other treatment methods is necessary	Andreozzi et al., (1999)
Coagulation	Applicable for mature landfill leachate	Not applicable for young landfill leachate	Wiszniowski et al., (2006)
Reverse Osmosis	COD and NH_3-N high removal	Costly and extensive pre-treatment is required.	Renou et al., (2008)

2.2 Leachate Characteristics

Research on treatment of landfill leachate shows that AOPs is an attractive treatment method which can eliminate colour, reduce the organic load and improve the biodegradability of recalcitrant contaminants of mature leachate (Abu Amr,et al., 2013; Cortez et al., 2011). Chemical oxidants improve the destruction of persistent contaminants such as Polycyclic Aromatic Hydrocarbons (PAHs).

The characteristics of the landfill leachate can usually be represented by the basic parameters of chemical oxygen demand (COD), biochemical oxygen demand (BOD), BOD/COD ratio, pH, total suspended solids (TSS), ammonia-nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN) and heavy metals (Heng, 2010). Table 2.3 illustrates basic parameters of landfill leachate ranges which differ depending on the age of landfill.

Previous studies have detected a variety of heavy metals in landfill leachate such as zinc, copper, lead, nickel, chromium, cadmium and mercury.

Table 2.3: Landfill Leachate Characterisation

Parameter	**Unit**	**Young**	**Medium age**	**Old**
Age	year	<5	5-10	>10
COD	mg/L	1870-70900	1180-9500	100-3460
BOD	mg/L	90-26800	331-1436	3-150
BOD/COD	-	0.05-0.07	0.07-0.33	0.04-0.11
TSS	mg/L	950-5000	480-784	130-1600
NH_3	mg/L	10-11000	743-5500	0.2-1522
pH	-	5.8-9.0	6.9-9.0	7.0-9.4

Source: (Kabdasli & Arslan, 2010)

Age of landfill has been reported to play a major role in affecting leachate characteristics (Ahmadian et al., 2013). In addition, Bilitewski, et al., (1996) and Wiszniowski et al., (2006) state that nearly all wastewater treatment methods currently in use or any combination can be used for treating landfill leachate. However, conventional treatment methods are ineffective and expensive for removing micro pollutants from more stabilized leachate. Biological processes have been reported to be effective in treating young leachates and ineffective in treating old leachates (Hermosilla et al., 2009). Better understanding of leachate composition and characteristics helps to determine the appropriate treatment method.

The United States Environmental Protection agency states that leachate characteristics are a source of essential information with regard to design and operation of leachate treatment facilities. Moreover, characterisation of leachate provides important information that facilitates risk analysis of leachate impact on the environment when there liner leaks.

Leachate from different landfill site has varying characteristics due to many factors. Kabdasli & Arslan-Alaton (2010) and Renou et al., (2008) states the contributing factors to variable leachate characteristics as follows:

1) The type of waste received
2) Operating practices encompassing shedding
3) Daily cover and capping
4) Soil properties
5) Compaction of layers
6) Depth of fill
7) Annual precipitation or rainfall patterns
8) Age of Landfill
9) Refuse moisture content
10) Landfill design
11) Landfill operation
12) Rate of water infiltration

Knowledge of the quantity and composition of leachates is essential in achieving high organic and inorganic compounds. Quantity and composition of leachate usually gives an insight into selecting an appropriate, effective and sustainable treatment method.

The Department of Environment in Malaysia has environmental regulations and requirements for discharge of landfill leachate into water bodies. The environmental regulations enforces prevention control and abatement of pollution through the Environmental Quality Act legislation. Table 2.4 shows the acceptable standards or conditions for discharge of leachate. Therefore, leachate needs to be treated to meet the standards before it can be discharged into the environment and Fenton treatment is a powerful technology which can effectively treat leachate of varying ages and leachate with high organic contaminants

Table 2.3: Acceptable standards for discharge of leachate in Malaysia.

Parameter	**Unit**	**Standard**
Temperature	^{o}C	40
pH value	-	6.0 – 9.0
BOD_5 at $20^{o}C$	mg/L	20
COD	mg/L	400
Suspended Solids	mg/L	50
Ammoniacal Nitrogen	mg/L	5
Mercury	mg/L	0.005
Cadmium	mg/L	0.01
Chromium, Hexavalent	mg/L	0.05
Chromium, Trivalent	mg/L	0.20
Arsenic	mg/L	0.05
Cyanide	mg/L	0.05
Lead	mg/L	0.10
Copper	mg/L	0.20
Manganese	mg/L	0.20
Nickel	mg/L	0.20
Tin	mg/L	0.20
Zinc	mg/L	2.0
Boron	mg/L	1.0
Silver	mg/L	5.0
Selenium	mg/L	0.02
Barium	mg/L	1.0
Fluoride	mg/L	2.0
Formaldehyde	mg/L	1.0
Phenol	mg/L	0.001

Sulphide	mg/L	0.50
Oil and Grease	mg/L	5.0
Color	ADMI	100

2.3 Fenton Process

The Fenton process was reported by Fenton in 1884 for maleic acid oxidation (Naddeo et al., 2011). Moreover, In the Fenton process, ferrous iron is the catalyst of the reaction and hydrogen peroxide is the powerful oxidant for organic contaminants. In the Fenton Process, a powerful, non- selective chemical oxidant, hydroxyl radicals are generated in sufficient quantity and act rapidly with organic compounds confirms (Lille, 2001). The Fenton reaction has been successfully utilised for treatment of organic compounds such as PAHs (Deng & Englehardt, 2006).

(Naddeo et al., 2011 and Oller et al., 2011) states that many researches have demonstrated that the Fenton process is capable of degrading different phenols and reduces chemical oxygen demand in wastewater. Furthermore, Ahmadian et al., (2013) explains that the Fenton process has been successfully utilized for treatment of slaughterhouse, food, olive oil wastewater, industrial wastewater and landfill leachate.

Zhang, et al., (2005), explains that the two major chemicals, iron and hydrogen peroxide used in the Fenton process determines the operation cost and efficiency of the reaction. (Naddeo et al., 2011) further states that the overall efficiency of degradation of organic compounds is independent on the initial state (Fe^{2+} / Fe^{3+}) of iron used. The use of Fenton reagents for degradation of landfill leachate heavily depend on the chemical composition of leachate (Sharma et al., 2011).

The Fenton reactions which received attention in most of the studies are mentioned in the Table 2.5. Fundamental research has been conducted on the Fenton reaction types for treatment of landfill leachate. Most of these studies focused on pH range and Fenton reagents for optimum removal of COD, and organic compounds such as the PAHs.

Table 2.4: Fenton Reaction types

Fenton reaction types	Reagents	pH
Classic Fenton or Fenton Reaction	Fe^{2+},H_2O_2	2-4
Fenton like	Fe^{3+},H_2O_2 H_2O_2, Iron	2-4
Photo-Fenton	H_2O_2, Iron complex, free iron ion	Acidic to Neutral
Heterogeneous Fenton	H_2O_2, solid iron oxide	Wide pH range
Electro-Fenton	Electro-generated H_2O_2, electro-generated Fe^{2+}	2-4
Heterogeneous photo-Fenton	H_2O_2, solid iron oxide	Wide pH range
Heterogeneous photoelectro-Fenton	Electro-generated H_2O_2, solid iron oxide	Wide pH range

Hermosilla et al. (2009) reported that the Fenton process can achieve 60–90% of COD removal in the treatment of landfill leachate. Fenton oxidation has been extensively studied for the treatment of mature landfill leachate (Cortez et al., 2011; Renou et al., 2008) Fenton and photo-Fenton processes allow COD decrease efficiency of, respectively, 45–75% and 70–78%. In term of biodegradability improvement, BOD/COD ratios close to 0.5 after oxidation have been reported in recent works using Fenton process (Renou et al., 2008).

A study conducted on mature landfill with dosages of 2438 mg/L H_2O_2 and 56 mg/L Fe^{2+} and achieved 70% COD removal (Heng, 2010). The optimum H_2O_2 concentration, Fe (II) concentration, pH and reaction time were 0.033 mol/L, 0.011 mol/L, 3 and
145 min, respectively, resulted in 58.3% COD in a study conducted by Mohareji et al., (2011).
The main reactions occurring during the Fenton process is described in the following equations (Hermosilla et al., 2009).

1. $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$
2. $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\cdot}_2 + H^+$
3. $H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^- + H_2O$
4. $Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^-$
5. $Fe^{2+} + HO_2 \rightarrow Fe^{2+} + O\ {}_2H^+$
6. $Fe^{2+} + HO^{\cdot}_2 + H \rightarrow Fe^{3+} + H_2O_2$
7. $2HO^{\cdot}_2 \rightarrow H_2O_2 + O_2$

Hydroxyl radicals are rapidly generated in the first reaction of the Fenton Process. During the reaction cycles from Fe^{2+} and Fe^{3+}. The next sequence of reaction is the decomposition of H_2O_2 into water and O_2.

Fenton Oxidation is the combination of Fe^{2+} and H_2O_2 (Ahmadian et al., 2013) states that the reaction between hydrogen peroxide and ferrous ion is performed because hydrogen alone is not strong factor capable of oxygen transfer and oxidation of organic materials. OH radicals generated by Fenton treatment has the potential to destroy and degrade organic pollutants.

The major role or major advantage of the Fenton process is the ability or capability of the process to remove refractory and toxic organic compounds states and increases the degradability of resistant organic compounds states (Ahmadian et al., 2013). Furthermore, the Fenton treatment is able to degrade resistant organic matter without production of toxic by-products. It has been reported that more organic matter are removed faster because oxidation and flocculation processes takes place simultaneously (Ahmadian et al., 2013).

A non-toxic, abundant element, Iron which is used in the Fenton treatment makes the Fenton Process to be an attractive system for degradation of recalcitrant organic compounds. Moreover, the oxidant, hydrogen peroxide is environmentally friendly and can be easily handled (Andreozzi et al., 1999).

2.3.1 Dosages of Fenton Reagent

The dosages of Fenton reagents play a major role in determining the operating and treatment efficiencies for organic compounds and COD removal (Deng & Englehardt, 2006). Increasing the concentration of hydrogen peroxide or iron salt increases the COD removal efficiencies and degradation of organics in a Fenton process (Renou et al., 2008). However, after reaching optimum conditions, further increase in hydrogen peroxide result in low degradation efficiency as the hydrogen peroxide act as a free-radical scavenger (Mohajeri et al., 2011). Thus, it is important to optimise the concentration of the hydrogen peroxide as it determines the efficiency of the degradation of the Fenton process and plays the operational cost depends on the quantities of the hydrogen peroxide utilized.

2.3.2 Effect of pH

The Fenton process has a preferable pH in which the hydroxyl radicals are produced in high amounts, it has been reported that the Fenton process favours acidic pH. Zhang et al., (2005) reported that an acidic pH of range 2-4 has been found to be the most effective in yielding higher hydroxyl radicals but pH of 2.5 yielded a higher COD removal efficiency. A study conducted by (Ahmadian et al., 2013) shows that the optimum pH for removal of recalcitrant organic compounds and COD is at a pH of approximately 3 for Fenton oxidation.

A study on effects of reaction conditions on the oxidation efficiency in the Fenton process by Kang & Hwang (2000) shows similar results of acidic pH resulting in higher efficiency of the Fenton Process. At a pH higher than 4, studies have shown that there is an unstable and uncontrolled transformation of Fe^{2+} ions into Fe^{2+} ions.

Consequently, there will be formation complications with hydroxyl radicals and H_2O_2 will be reduced to water and oxygen because H_2O_2 loses its oxidation power.

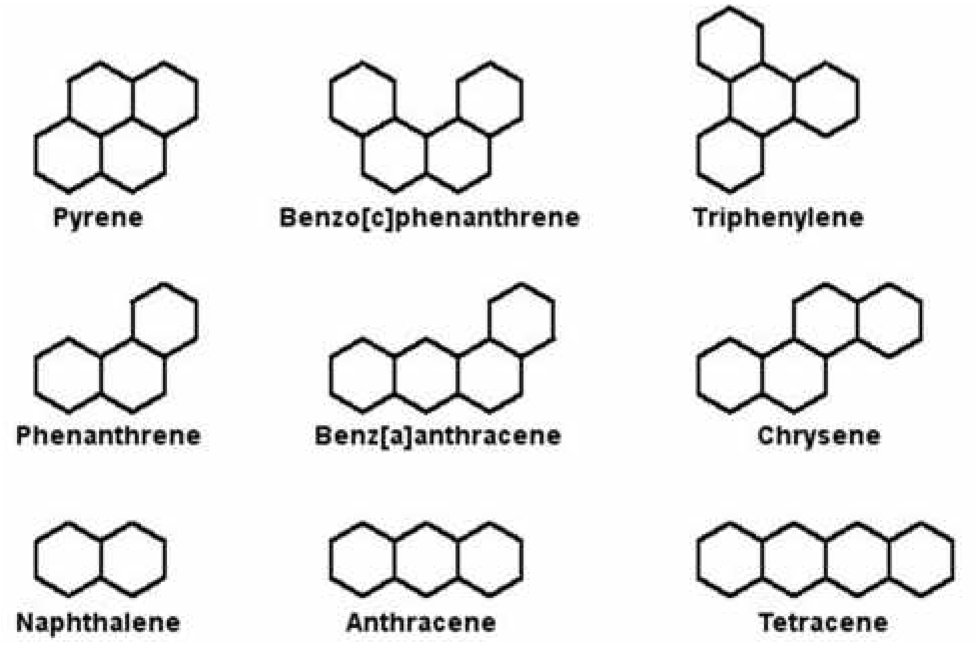
2.4 Polycyclic Aromatic Hydrocarbons

PAHs are composed of two or more fused benzene and are classified as highly toxic. Polycyclic Aromatic hydrocarbons are mutagenic, toxic and complex organic compounds formed by incomplete combustion of coal, gas and garbage (Ravindra,et al., 2008) and may cause certain types of cancer (Trapido, 1999).

Conventional physical and biological processes used for wastewater treatment have only a limited ability to degrade a broad range of organic dye compounds (Assaf-Anid et al., 2001). PAHs are classified as among the most persistent pollutants and are known to be toxic, mutagenic and carcinogenic (Dabestani & Ivanov, 1999). Approximately 16 PAHs are classified as priority by both the US and Environmental Protection Agency (US EPA), these priority polluted in illustrated in Table 2.6. Some of the priority PAHs compound structures are illustrated in the Figure 2.1.

Studies have shown that efficiencies in degrading PAHs vary due to the different physico-chemical properties of PAHs states (Rashid, 2013). Hydrocarbons which are less toxic will therefore be degraded quicker than those that are more toxic.

Figure 2.1: PAHs Compound structures



Polycyclic aromatic hydrocarbons (PAH) are also known as polynuclear aromatic hydrocarbons or polyarenes, constitute a large class of organic compounds (Dabestani & Ivanov, 1999), and PAHs are quite resistant to degradation (Trapido, 1999). In addition, (Trapido, 1999) explains that the presence of PAH compounds in the environment has detrimental effects on public health. Furthermore, PAHs contaminants are found in soil and leachates from precipitation which was already contaminant by PAHs emitted into the atmosphere. However, PAHs can originates from plants that produce synthetic fuels such as coal or oil shale (Josephson, 1981).

Table 2.5: PAHs identified as priority pollutants

Compound	**Abbreviation**	**Formula/ MW**	**No. of rings**
Acenaphtylene	AC	$C_{10}H_8$/128	2
Acenaphthene	CAN	$C_{10}H_8$/152	3
Fluorene	FL	$C_{10}H_{10}$/154	3
Phenanthrene	PHE	$C_{13}H_{10}$/166	3

Anthracene	AN	$C_{13}H_{10}$/178	3
Fluoranthene	FA	$C_{13}H_{10}$/178	3
Pyrene	PY	$C_{16}H_{10}$/202	4
Benzo [a] Anthracene	B[a]A	$C_{16}H_{10}$/202	4
Chrysene	CHR	$C_{18}H_{12}$/228	4
Benzo [b] Fluoranthene	B[b]F	$C_{18}H_{12}$/228	4
Benzo [k] Fluoranthrene	B[k]F	$C_{20}H_{12}$/252	5
Benzo [a] Pyrene	B[a]P	$C_{20}H_{12}$/252	5
Indeno[1,2,3-cd] Pyrene	IP	$C_{20}H_{12}$/252	6
Dibenzo[ah] Anthracene	D[ah]A	$C_{22}H_{12}$/276	6
Benzo[ghi] Perylene	B[ghi]P	$C_{22}H_{12}$ /278	6

The process to that degrades recalcitrant products such as PAHs involves the production of hydroxyl radical (Cortez et al., 2011). Moreover, hydroxyl radicals can quickly react with most organic compounds some organic substances such as acetic acid, acetone, carbon tetrachloride, chloroform, maleic acid, malonic acid, methylene chloride, oxalic acid, n-Paraffins, trichloroethane, and tetrachlorethane are not amenable by oxidation (Lehmann, 2007).

2.5 Gas Chromatography- Mass Spectrometry (GC-MS)

GC_MS is a technique which is characterised by combination of the detection power of mass spectrometry and gas chromatography. Mikhail Semenovich Tsvett discovered the Gas Chromatography as a separation technique for separating compounds in 1900s, in the 1950's development of the GC-MS was undertaken after James and Marin originated with the device in 1952. GC-MS separates, identifies and quantifies different substances present in a test sample and it has been applied to detect PAHs compounds in water, soil or leachate. Applications of GS-MS are diverse and has been widely used in drug detection, fire investigation, and identification of unknown samples and detection of substances by airport security. Advancement in technology had made GS-MS devices not be available only in the laboratory settings. Gas chromatograph and mass spectrometer form the major building blocks of GC-MS instrument.

GC-MS devices are different due to different applications purposes. Nevertheless, GC-MS instrument generally consist of an injection port and a detector. For GC-MS analysis, injection of the sample into the GC inlet is carried out. In the GC inlet the sample is vaporised and transferred onto a chromatographic column by the carrier gas, the carrier gas is inert or non-reactive. Helium is the commonly used carrier gas, other carrier gases such as argon, hydrogen, nitrogen and hydrogen have also been used. The drawbacks of GC are that, one of the requirement is for the analyte to have significant vapour pressure between 30 and 300 ^{o}C and there are no definitive proof of the nature of the detected compounds, identification of the compounds is merely based on the retention time matching and this might lead to inaccuracy or misleading. However, GC-MS is still considered to be the best method for separating and analysing PAHs.

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

The flow chart in Figure 3.1 represents the methodology used in this study in order to achieve the objectives of this study and to facilitate this study. Sampling and Characterisation comprises of analytical methods for determination of initial of pH, COD, and PAHs. Research methodologies which focus on AOPs, Fenton Process, PAHs degradation, pH adjustments, COD removal efficiencies and reaction time and hydrogen peroxide and ferrous iron dosages were reviewed from previous literature for the experiment design and experimental procedure, data analysis and results.

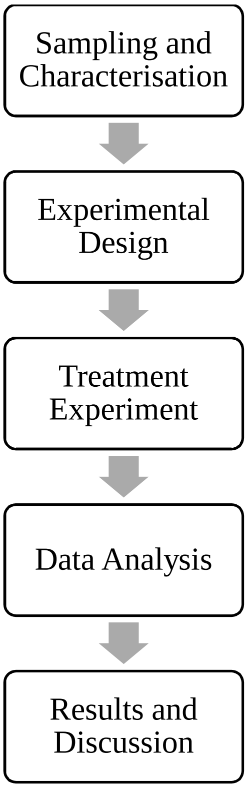


Figure 3.1: Flowchart for the research methodology

3.2 Leachate Sampling and Characterization

The leachate samples were collected from Jeram Sanitary landfill in Selangor, Malaysia which has been operating for 7 years beginning January 2007 and has a design capacity of 6 million tons of waste. The collected samples will be preserved in the refrigerator. Initial characteristics of the leachate readings such as pH, COD, and total concentrations of PAHs compound was measured, recorded and tabulated.

3.3 Analytical Methods

The amounts of pH, COD and PAHs were examined in the laboratory following standard methods.

3.3.1 pH

The pH readings was determined using HACH model 51910 pH meter. To ensure accurate results the pH probe will first be calibrated before the pH measurements are taken.

3.3.2 COD

Chemical Oxygen Demand (COD) concentration of landfill leachate was determined using HACH DR 2800 spectrophotometer under program 430. The spectrometer was calibrated to zero by inserting a blank sample prepared from distilled water. Thereafter, the COD measurement of the supernatant proceeded by putting the 2 mL of supernatant into a vial which was at diluted by a dilution factor of 50. The sample was placed in Thermolyne Maxi Mix II 37600 rotator or mixer for about a minute.

The sample will therefore be inserted into the digester where it will be heated at 150^{o}C for 2 hours. The sample was taken out from the heater after 2 hours and allowed to cool for 15 - 20 minutes, after cooling the science wipes was used to wipe the vial externally. The COD readings were taken by first placing the vial into the spectrometer and reading the results to determine COD readings. COD experiments were performed in triplicate to ensure accurate results are taken. COD removal in percentage, R was determined using the equation:

$$R = \frac{\text{COD initial} - \text{COD residual}}{\text{COD initial}}$$

3.3.3 Gas Chromatography-Mass Spectrometry (GC-MS)

In order to meet the objective of identifying polycyclic aromatic hydrocarbons (PAHs) in municipal landfill leachate, Polycyclic Aromatic Hydrocarbons concentration was determined using Gas Chromatography Mass Spectrometry.

GC-MS separates chemical mixtures, identifies and quantifies the chemicals. The sample containing PAHs is injected into GC inlet, vaporisation of the sample will occur in the GC device followed by separation and analysis of the substances present in the sample. For this study, for analysis of GC-MS of PAHs, Perkin Elmer Clarus 600 Mass Spectrometry (MS) detector will be used and incorporated with Clarus 600 Gas Chromatography. The data from the GC-MS is sent to the computer, the system is controlled by the PerkinElmer TurboMass GC-MS software. Analysis PAHs in samples will be performed by comparison of modified peak areas of PAHs in a standard mixture with internal standards.

3.4 Experimental Design

The Design Expert software was be used for statistical design the experiments and for data analysis of Fenton oxidation process. The statistical design reduces the number of experiments by narrowing the range of reagents does, pH and reaction time., In the past experimental procedures were carried out by changing one variable at the time while the other variable are kept unchanged, this method is time consuming and the interaction among variables was neglected. The design layout used in this study in shown in Table 3.2

Response Surface Methodology (RSM) will be applied for optimising the operating conditions (Initial concentration of Fe^{2+} and H_2O_2, pH and reaction time) in this study. RSM is a technique used for the design of experiments, RSM is a favourable tool used by researchers for building models and evaluating the effects of several factors to achieve optimum conditions. Heng (2010) states that RSM has been effectively used to optimise Advanced Oxidation processes for the treatment of landfill leachate. ANOVA, short for Analysis of Variance will be used for graphical analysis of the date to obtain interaction between the variables and responses.

The Central Composite Design (CCD) summary from design expert inputs are shown in Table 3.1. The number of experiments carried out for this study were 30 with two responses, COD removal and PAH removal.

Table 3.1: Independent Variables Input parameters for the Design Expert Software

Independent Variable	**Code**	**Unit**	**Low**	**High**	**Low Coded**	**High Coded**
Initial COD	A	mg/L	4900	7700	-1	1
H_2O_2/Fe^{2+}	B	mg/L	1.5	3.5	-1	1
Reaction Time	C	mins	60	150	-1	1
H_2O_2	D	mg/L	1000	2500	-1	1

Table 3.2: Design layout generated by Design Expert Software

Run	**Factor A** **Initial COD** mg/L	**Factor B** **H_2O_2/Fe^{2+}**	**Factor C** **Reaction Time** min.	**Factor D** **H_2O_2** mg/L
1	6300	2.5	105	3250
2	6300	2.5	15	1750
3	4900	1.5	60	2500
4	6300	2.5	105	1750
5	4900	1.5	150	1000
6	4900	3.5	60	2500
7	7700	3.5	150	2500
8	7700	3.5	60	2500
9	6300	0.5	105	1750
10	6300	2.5	195	1750
11	7700	1.5	150	1000
12	4900	1.5	150	2500
13	6300	2.5	105	1750
14	7700	3.5	60	1000

15	4900	3.5	60	1000
16	7700	1.5	150	2500
17	4900	1.5	60	1000
18	6300	2.5	105	1750
19	4900	3.5	150	1000
20	7700	1.5	60	2500
21	6300	2.5	105	1750
22	6300	2.5	105	1750
23	6300	2.5	105	1750
24	3500	2.5	105	1750
25	4900	3.5	150	2500
26	6300	4.5	105	1750
27	7700	1.5	60	1000
28	6300	2.5	105	250
29	9100	2.5	105	1750
30	7700	3.5	150	1000

3.5 Experiment Procedure

3.5.1 Fenton Treatment

To investigate the efficiency of the Fenton process in degrading PAHs and COD removal, the chemical oxidation experiments were conducted at the lab with the 500ml beakers as batch reactors. The operating conditions were pH 3, H_2O_2 range of 1000 mg/L–2500 mg/L, H_2O_2/Fe^{2+} ratios of 0.5-3.5 and reaction time in minutes of 15-195.

1. Required amounts of leachate were prepared in beakers at ambient temperature and pressure. In this study, the initial COD of the leachate was high, the concentration of COD was lowered to obtain the initial COD readings in the statistical design. The equation illustrated below was used to calculate the required amounts of leachate (X) to be poured into 500ml beaker. Thereafter, distilled water was poured into the beaker containing

samples leachate to top the leachate to 500mL. Table 3.3 shows the amount of leachate in a better for different Initial COD.

$$\frac{\mathrm{X}}{500\mathrm{ml}} = \frac{\text{Initial COD in design layout}}{9100\mathrm{mg/L}}$$

Table 3.3: Amounts of leachate poured into a beaker

Initial COD (mg/L)	**Leachate Amount (mL)**	**Distilled Water (mL)**
9100	500	0
7700	423	27
6300	346	154
4900	269	231
3500	192	308

2. Adjust the pH to a targeted pH of 3 by addition H_2SO_4 or N_aOH. In this study H_2SO_4 was pipetted into the sample to adjust the pH to 3.

3. Required amounts of reagents are added according to the statistical design. $FeSO_4.7H_2O$ powder in mg/500mL of sample was measured in a petri dish and poured into the sample, required amounts of H_2O_2 in mg/500mL was measured using graduated pipette. For stock preparation, amounts of reagents calculated considered the following specifications.

   For Ferrous Ion (Fe^{2+})

   - $FeSO_4.7H_2O$ = 278 g/L and 1M Fe = 56 g/L

   For Hydrogen Peroxide (H_2O_2)

   - 1M H_2O_2 = 34 g/L & H_2O_2 concentration purity is 30% thus = 300 g/L

4. Gently stir the mixture during reaction and allow for selected reaction time. The reaction time for this study ranged from 15 min to 195min

5. Adjust the pH above 10 with NaOH to stop the reaction.

6. Allow the solution to settle for 20-30 min

7. Draw the supernatant for analysis or measurement of COD.

3.5.2 Liquid-Liquid Extraction

In order to determine the concentration of PAHs in the leachate, the leachate samples were subject to liquid-liquid extraction using dichloromethane following separatory funnel liquid-liquid extraction SW-846 Method 3510 C. The 500mL sample was first filtered using a filter flask and filter paper. Thereafter, filtrate samples were placed on two 250ml conical flasks, 31.25mL of dichloromethane was added in both the samples. The sample was shaken thoroughly to ensure that the dichloromethane and leachate mixes. The sample was then put into two separator funnels of 250mL which were placed on a stand. An empty flask was put underneath the separatory funnel, after the separatory funnel has rested undisturbed on the stand, and the layers on the separatory funnel could be clearly distinguished the stopcock is opened carefully and slowly to drain the lower or bottom layer into the flask.

The separation process was repeated two times following the standards that is for 250mL sample, 31.25 mL of dichloromethane was added at the first stage. The process is repeated by addition of 12.5 mL of dichloromethane twice.

After the separation was completed and the extracted samples were collected from the funnel, sodium sulphate was added to the sample to absorb any solids which might have leaked during the separation process. The extracted sample was then put into a vibratory evaporator where only 1ml of the unevaporated sample was put in a vial and sent into the GC-MS lab for PAHs concentration analysis.

3.6 Chemicals and Reagents

The following chemicals were utilised for the experiments.

- $FeSO_4.7H_2O$ powder
- Dichloromethane, CH_2Cl_2
- Anhydrous Sodium Sulphate (Solid)
- 98% Pure H_2SO_4 solution
- 30% H_2O_2 solution
- NaOH powder

3.7 Gantt chart

The Gantt charts shown illustrates the project tasks allocation and the duration of each task throughout the project for FYP1 and FYP2

3.7.1 FYP1

No.	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	🟧	🟧												
2	Preliminary Research Work		🟧	🟧	🟧	🟧									
3	Submission of Extended Proposal						⬟								
4	Proposal Defence								🟧	🟧					
5	Project Work continues										🟧	🟧	🟧		
6	Submission of Interim Draft Report													⬟	
7	Submission of Interim Report														⬟

⬟ Suggested Milestone 🟧 Process

3.7.2 FYP 2

No.	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues	🟧	🟧	🟧	🟧	🟧	🟧	🟧								
2	Submission of Progress Report							⬟								
3	Project Work Continues								🟧	🟧	🟧	🟧	🟧			
4	Pre-SEDEX										⬟					
5	Submission of Draft Final Report											⬟				
6	Submission of Dissertation (Soft Bound)												⬟			
7	Submission of Technical Paper												⬟			
8	Viva													⬟		
9	Submission of Project Dissertation (Hard Bound)															⬟

⬟ Suggested Milestone 🟧 Process

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Data Gathering and Analysis

Laboratory experiments were conducted to determine the optimum conditions (H_2O_2, Fe^{2+}, H_2O_2/Fe^{2+} and reaction time) for COD and PAHs removal and the efficiency of the Fenton treatment to remove the PAHs and COD in leachate from Jeram sanitary landfill site, Selangor, Malaysia. The sample characteristics before treatment and after treatment are measured to determine the removal efficiency of the Fenton treatment. The responses under consideration in this study, PAHs removal and COD removal were analysed using Response Surface Methodology. The results of the experiments are indicated and discussed in this section.

4.1.1 Sample Characterisation

The average initial characteristics of the leachate as follows:

Table 4.1: Characteristics of leachate

Parameter	**Average**
pH	8.21
COD (mg/L)	9100

The PAHs compounds present in the leachate were Napthalene, Acenaphtylene Acenaphthene, Fluorene, Phenanthrene, Anthracene, Carbazole, Fluoranthene, Pyrene, Benzo [a] Anthracene, Chrysene, Benzo [k] Fluoranthene, Benzo [a] Pyrene, Indeno[1,2,3-cd] Pyrene, Dibenz[ah] Anthracene and Benzo[ghi] Perylene. Napthalene had the highest concentration of 3.03ppb and Carbazole had the lowest concentration of 2.19 ppb, the concentration of the other compounds are illustrated in Table 4.2.

Table 4.2: Concentration of 16 PAHS found in sample

Compound	**Concentration (ppb)**
Napthalene	3.03
Acenaphtylene	2.59
Acenaphthene	2.56
Fluorene	2.55
Phenanthrene	2.56
Anthracene	2.57
Carbazole	2.19
Fluoranthene	2.55
Pyrene	2.54
Benzo [a] Anthracene	2.57
Chrysene	2.57
Benzo [k] Fluoranthene	2.57
Benzo [a] Pyrene	2.58
Indeno[1,2,3-cd] Pyrene	2.65
Dibenz[ah] Anthracene	2.62
Benzo[ghi] Perylene	2.62
Total PAHs	41.32

The results show 16 PAHs compounds were detected in the leachate, all the compounds detected are among the PAHs classified as priority pollutants by US EPA. The total concentration of PAHs was 41.32ppb. Jeram Sanitary Landfill has been in operation for only 7 years the low PAHs concentration detected suggest that at this stage the formation of PAHs in the landfill is minimal as the leachate is of medium age. However, PAH results was detected at trace elements and PAH concentration are still very harmful even at low levels.

Bauer et al. (1998) found that the presence of organic macromolecules in leachate may enhance the migration of hydrophobic substances such as PAH. The low PAH found in this current study may confirm this hypothesis. In contrast, the PAH in landfill leachate obtained on a study by Jaries et al., (2005) varied between 0.10 and 0.40 ppm with an average value of 0.29ppm which is much higher than the current study. Other factors such as degradation patterns, climatic conditions and combustion of organic material might have contribute to the varying results.

4.2. COD removal

The highest COD removal achieved for the study is 86.69% with the lowest removal being 29.59%. The removal efficiencies of all the Fenton experiments conducted are shown in Table 4.3.

It evident from the results that there was a strong correlation between COD removal efficiency and the operating conditions, reaction time, H_2O_2/Fe^{2+} and concentration of H_2O_2. In cases where the same concentration of H_2O_2 and H_2O_2/Fe^{2+} was used for the Fenton treatment with varying reaction time a higher reaction time yielded higher percentage COD removal as in the case of Run 3 and Run 16 in Table 4.3. Thus a higher reaction time allows for further destruction of the organic and inorganic compounds.

High removal efficiencies are generally associated with high concentration of the Fenton reagents (Deng & Englehardt, 2006). In this study, the trend for high COD removal efficiency was achieved when reaction time is short, high ratio of H_2O_2/Fe^{2+} are utilized. Another method which result in high COD removal was when the reaction time is longer with low ratio of H_2O_2/Fe^{2+}. However, when any of the operating conditions are too low or too much the reaction efficiency is affected. For example, when hydrogen peroxide is in excess, the hydrogen radicals undergo scavenging of $OH^{\cdot}$ by H_2O_2 resulting in low COD removal efficiency.

Table 4.3: COD removal efficiency

Run	Factor A Initial COD mg/L	Factor B H_2O_2/Fe^{2+}	Factor C Reaction Time mins	Factor D D:H202 mg/L	Response 1 COD removal mg/L	COD Removal %
1	6300	2.5	105	3250	1250	80.16
2	6300	2.5	15	1750	4000	36.51
3	4900	1.5	60	2500	3450	29.59
4	6300	2.5	105	1750	3300	47.62
5	4900	1.5	150	1000	2950	39.80
6	4900	3.5	60	2500	2300	53.06
7	7700	3.5	150	2500	3450	55.19
8	7700	3.5	60	2500	1800	76.62
9	6300	0.5	105	1750	1975	68.65
10	6300	2.5	195	1750	3475	44.84
11	7700	1.5	150	1000	1100	85.71
12	4900	1.5	150	2500	1875	61.73
13	6300	2.5	105	1750	1600	74.60
14	7700	3.5	60	1000	1025	86.69
15	4900	3.5	60	1000	2600	46.94
16	7700	1.5	150	2500	1650	78.57
17	4900	1.5	60	1000	2175	55.61
18	6300	2.5	105	1750	3200	49.21
19	4900	3.5	150	1000	3225	34.18
20	7700	1.5	60	2500	3000	61.04
21	6300	2.5	105	1750	1000	84.13
22	6300	2.5	105	1750	1650	73.81
23	6300	2.5	105	1750	1900	69.84
24	3500	2.5	105	1750	800	77.14
25	4900	3.5	150	2500	1675	65.82
26	6300	4.5	105	1750	1775	71.83
27	7700	1.5	60	1000	4775	37.99
28	6300	2.5	105	250	3250	48.41
29	9100	2.5	105	1750	2650	70.88
30	7700	3.5	150	1000	3975	48.38

4.2.1 Optimum Operating Conditions

The operating conditions for Fenton Process are pH, reaction time, H_2O_2 and Fe^{2+}, previous study on the Fenton process explain that an acidic pH of 3 favours pH therefore for this study, the Fenton treatment was conducted at a pH of 3. Reaction time and H_2O_2 were found to be insignificant for optimum conditions to be achieved. The optimum conditions for the COD removal were H_2O_2/Fe^{2+} of 1.5 and influent COD of 7700 mg/L, reaction time of 60 minutes and H_2O_2 of 1000 mg/L.

4.2.1.1 Optimum Molar Ratio of Fenton Reagents

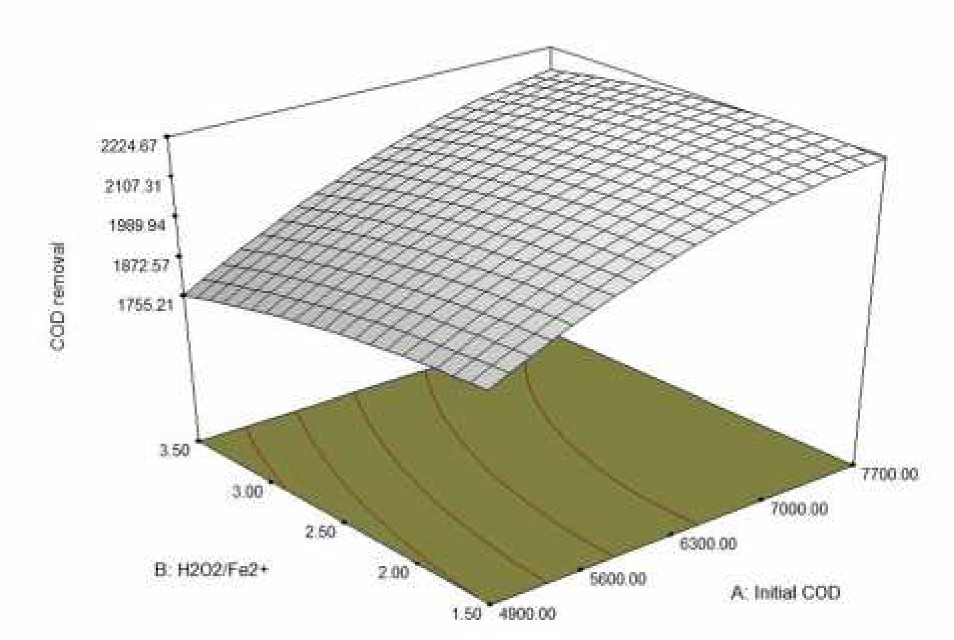


Figure 4.1: 3D plot for Optimum Hydrogen Peroxide and Ferrous ion ratio

The Fenton treatment was conducted to determine the optimum molar ratio, H_2O_2/Fe^{2+} that yields the high COD removal. In this study, the optimum H_2O_2/Fe^{2+} was ^{at} 1.5, the peak is not clear as the optimum value was the lowest molar ratio of H_2O_2/Fe^{2+} for this study. Figure 4.1 illustrates hydrogen peroxide and ferrous ion ratio for this study. Both iron and hydrogen peroxide are play an important role in the Fenton process but hydrogen peroxide is more important as it affects the degradation efficiency (Mohajeri et al., 2011)

4.2.1.2 Optimum Hydrogen Peroxide and Ferrous Ion

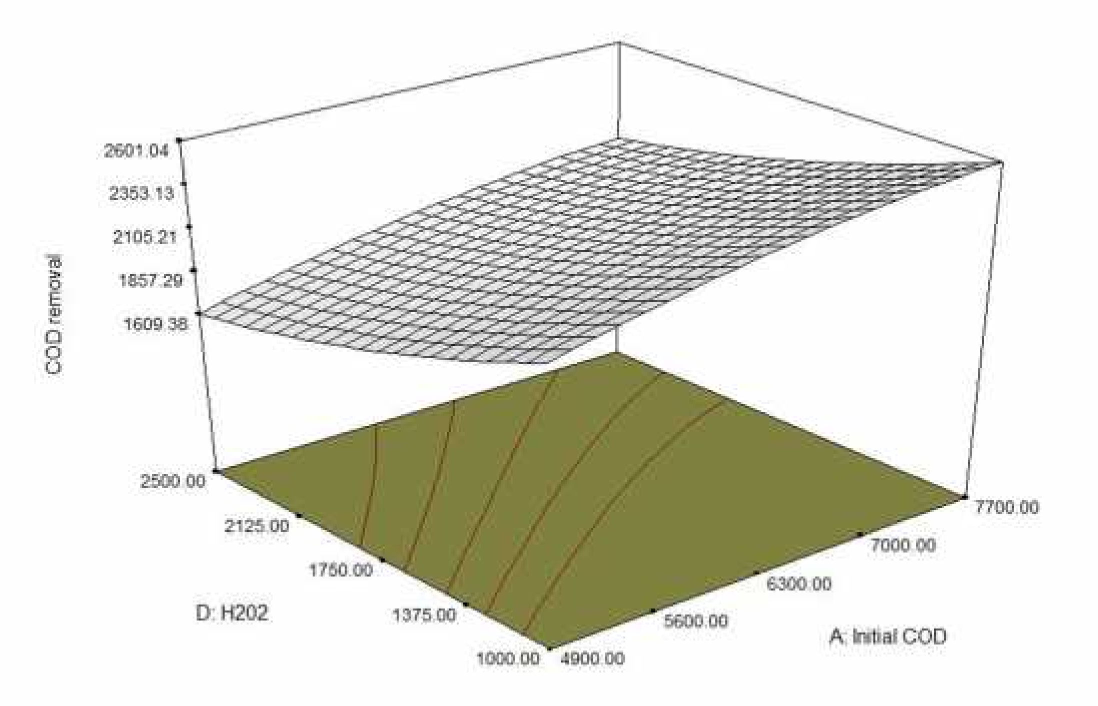


Figure 4.2: 3D plot for Optimum Hydrogen Peroxide dose

The Fenton treatment was conducted to determine the optimum concentration of H_2O_2 that yields the high COD removal. In this study, the optimum H_2O_2 was 1000mg/L. To determine the optimum H_2O_2, H_2O_2 was varied from 1000mg/L to 2500mg/L. The peak is not clear as this value was the lowest concentration of H_2O_2 from the lab experiments. As shown in Figure 4.2 COD removal efficiency is decreasing with an increasing concentration of H_2O_2. This means at H_2O_2 of greater than 1000mg/L the concentration of H_2O_2 was in excess resulting in minimal or no change in toxicity level of the leachate and COD removal efficiency decreases.

At an optimum condition of H_2O_2 of 1000mg/L and H_2O_2/Fe^{2+} of 1.5 and 286mg/L Fe^{2+}. Ferrous Ion acts as a catalyst for the reaction to take place. Many studies have indicated that in the absence of ion, the hydrogen radicals are not generated, thus there will be no reduction in the concentration of organic or inorganic compounds found in the leachate. In this study, when ferrous ion greater than 286mg/L is added, a reaction begins and increases until adding more ferrous ion is not efficient as it does not result in any further changes in the Fenton treatment.

4.2.1.3 Optimum Reaction Time

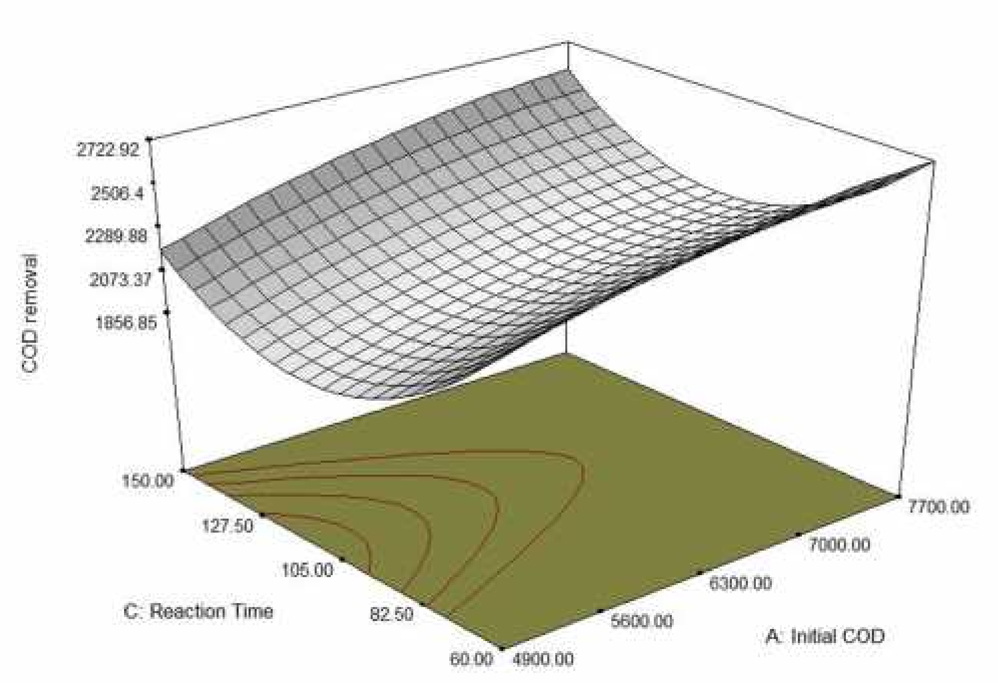


Figure 4.2: 3D plot of Optimum Reaction Time (min)

The reaction time for the Fenton reaction to be optimum depends on the concentration of H_2O_2 and the molar ratio H_2O_2/Fe^{2+}. In this study the optimum reaction time was 60 minutes for highest COD removal yielded. This current study optimum reaction time is in contrast with a study by Mohajeri et al., (2011) which obtain optimum reaction 145minutes for treatment of high strength landfill leachate by the Fenton Process. As mentioned previously, optimum operating conditions for Fenton treatment such as reaction time, H_2O_2 concentration and H_2O_2/Fe^{2+} for vary due to different leachate characteristics. In contrast, leachate of similar ages from varying landfills will more likely to have similar treatment efficiency. In addition, optimum pH for the Fenton treatment is in the acidic state and ranges from pH of 2-4 (Zhang et al., 2005) regardless of age of landfill.

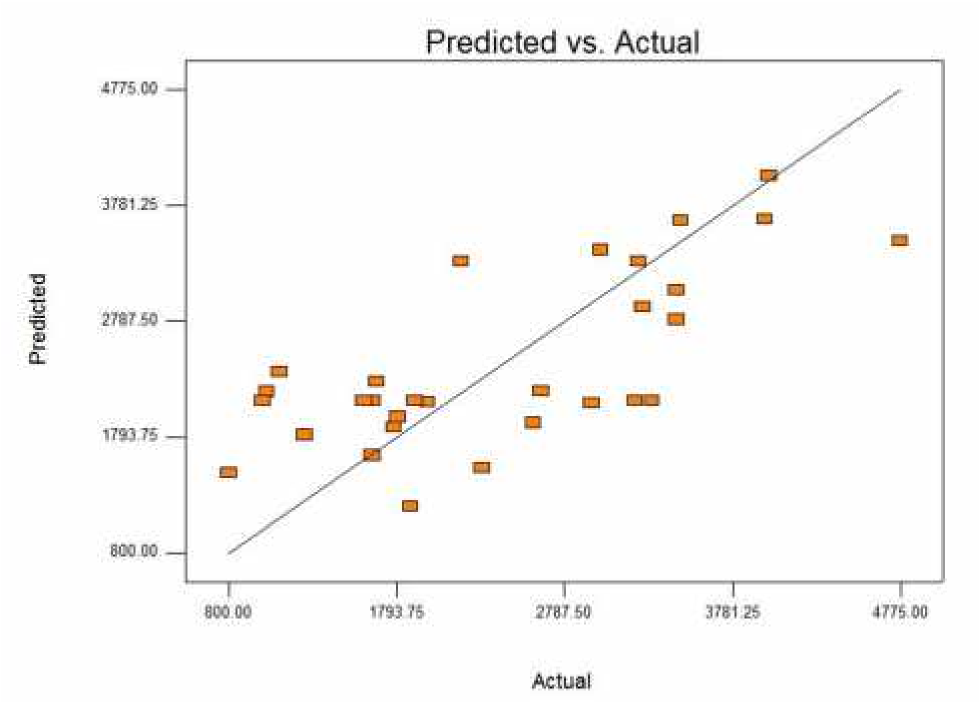


Figure 4.4: Predicted vs. actual COD removal Design-expert plot

A good prediction of the results should have the results scattered along the 45^o line, the results of the COD removal indicates that some of the points are poor prediction while other points show better prediction. Figure illustrates the predicted vs. actual COD removal obtained from Design- Expert software.

4.2.2 Analysis of Variance

The analysis for variance (ANOVA) was carried out to determine the models which are significant for this study. The COD removal statistical details for the analysis of results are shown in Table 4.4. The significant models have a P-value or probability of less than 0.05 and significant models indicate that a model is a good fit.

The influent COD and H_2O_2/Fe^{2+} ratio was found to be significant in COD removal from Analysis for Variance (ANOVA). Lack of fit model is insignificant as the P-value>5 this illustrates that there is a significant model correlation between the responses and the independent variables.

The significant model for COD removal = $2108.33 + 435.1C^2 + 651.56(BC)$

Table 4.4: ANOVA for Surface Quadratic Model

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**
Model	1.60E+07	14	1.14E+06	1.15	0.0937
A	7.44E+05	1	7.44E+05	0.75	0.4402
B	73151.04	1	73151.04	0.074	0.0789
C	2.16E+05	1	2.16E+05	0.22	0.0647
D	1.83E+06	1	1.83E+06	1.84	0.1946
A2	1.27E+05	1	1.27E+05	0.13	0.0725
B2	25463.17	1	25463.17	0.026	0.0874
C2	5.19E+06	1	5.19E+06	5.24	0.0371
D2	1.10E+05	1	1.10E+05	0.11	0.7439
AB	8789.06	1	8789.06	8.86E-03	0.9263
AC	8789.06	1	8789.06	8.86E-03	0.9263
AD	28476.56	1	28476.56	0.029	0.8677
BC	6.79E+06	1	6.79E+06	6.85	0.0194
BD	20664.06	1	20664.06	0.021	0.8872
CD	4.14E+05	1	4.14E+05	0.42	0.5278
Residual	1.49E+07	15	9.92E+05		
Lack of Fit	1.05E+07	10	1.05E+06	1.21	0.4416
Pure Error	4.35E+06	5	8.70E+05		
Cor Total	3.09E+07	29			
Std. Dev.	995.9553621		R-Squared	0.51797	
Mean	2428.333333		Adj R-Squared	0.068075	
C.V.	41.01394765		Pred R-Squared	-1.1674	
PRESS	66901500		Adeq Precision	4.033565	

4.3 PAH analysis

The concentration of PAH in the leachate was analysed using the GC-MS in order to determine the efficiency of the Fenton process in degrading aromatic organic compounds such a PAH. The leachate samples contained 16 PAHs which are classified as priority pollutant by US EPA, Figure 4.4 shows the list of 16 PAH detected, their concentration and the PAH removed. After Fenton Treatment conducted on 30 leachate samples, the PAH in all the samples were analysed, Figure 4.5 to Figure 4.7 shows the results. Appendix C shows the PAH concentration before and after treatment of all the samples analysed.

The optimum conditions for the PAH removal were H_2O_2/Fe^{2+} of 1.5 and influent COD of 7700mg/L, reaction time of 60 minutes and H_2O_2 of 1000mg/L. Under these conditions, the concentration of PAH was no longer detected, meaning that it was 100% removed from the leachate. (Figure 4.4).

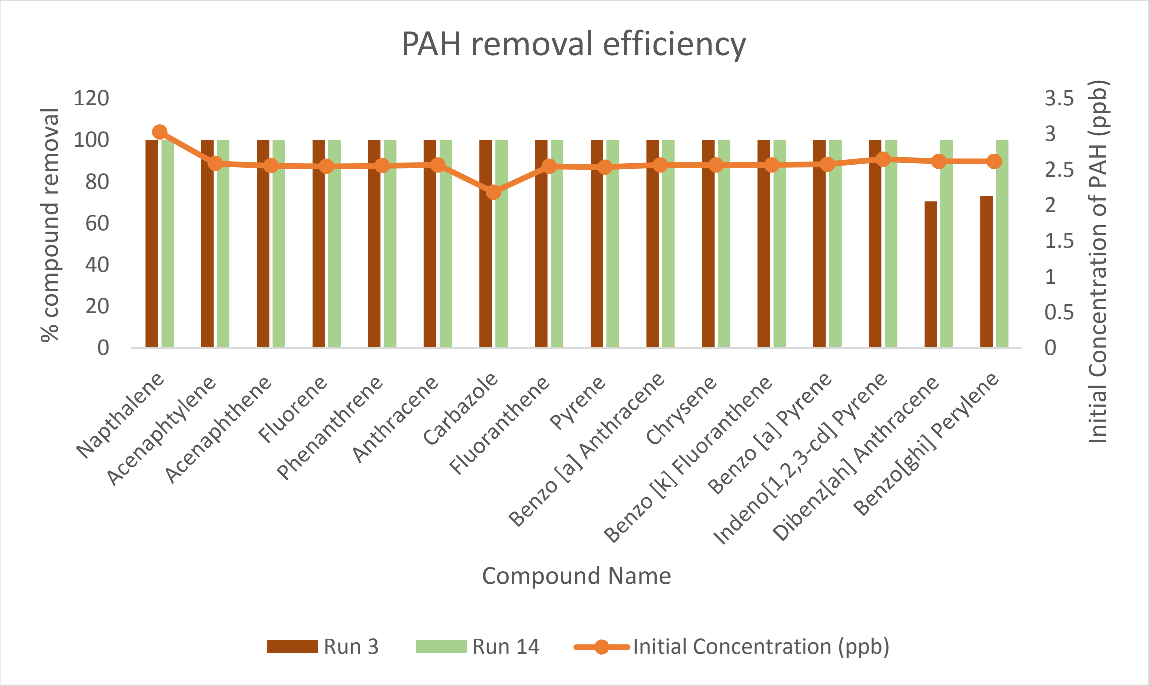


Figure 3.5: List of PAH compounds detected and PAH removal efficiency

14 PAH were detected in leachate after experiment/ run 3 which yielded the lowest COD removal of 29.69% but Dibenz[ah] Anthracene and Benzo[ghi] Perylene was detected and at a removed 70.6% and 73.3% respectively. Dibenz[ah] Anthracene and Benzo[ghi] Perylene have 6 benzene rings and therefore have a high molecular weight compared to the other PAH compounds which was 100% removed. High moleculer weight compounds degradation is much harder than when degrading low molecular weight compounds.

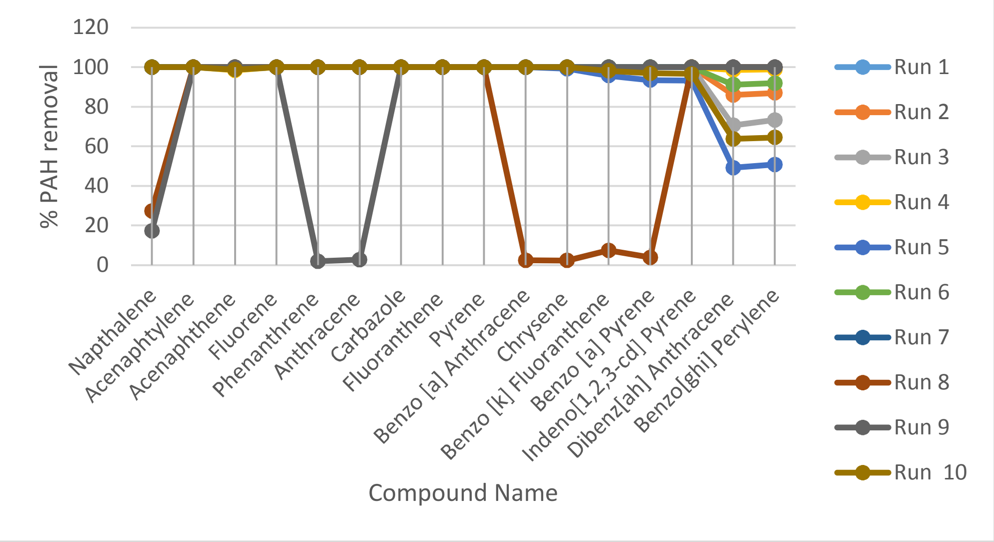


Figure 4.5: % PAH removal for experiment 1-10

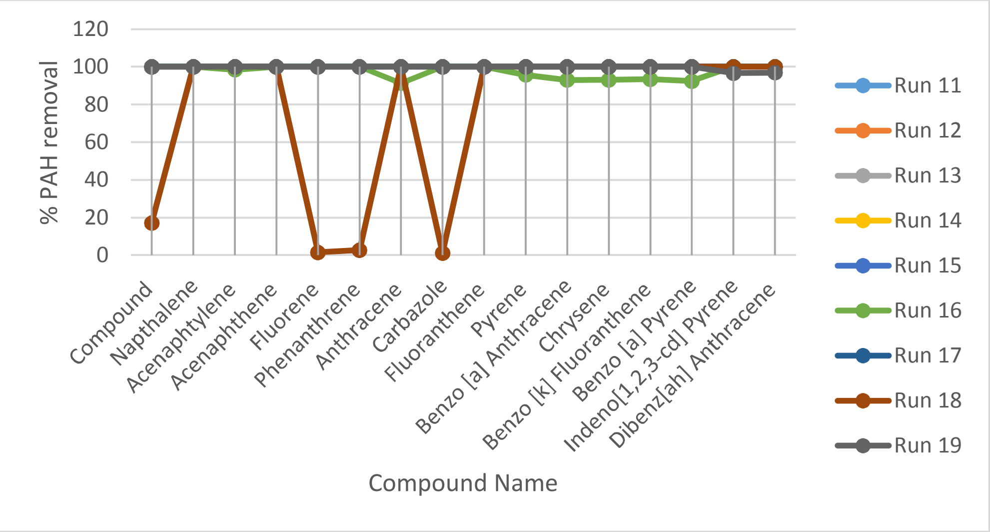


Figure 4.6: % PAH removal for experiment 11-19

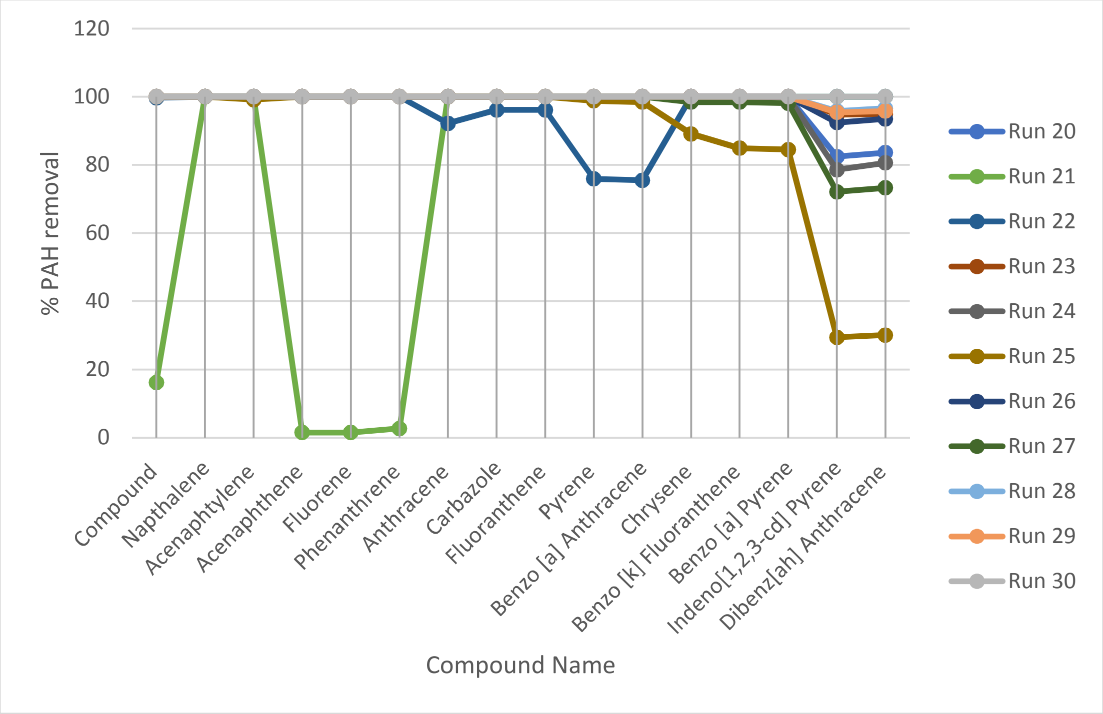


Figure 4.7: % PAH removal for experiment 20-30

In total, PAH concentration found in leachate is 41.32 ppb, the PAH compounds were detected in trace elements meaning that they are toxic to the environment and humans in even in minimal amounts. In conclusion, GC-MS was successfully able to detect the PAH in leachate samples before and after Fenton Oxidation. This study has also proven that the Fenton Treatment can effectively reduce PAH in municipal landfill leachate.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

The chemical treatment methods characterised by the production of hydroxyl radicals for degrading resistant organic compounds is known as Advanced Oxidation Processes. The potential of AOPs (Fenton Process) for the treatment of landfill leachate in degrading Polycyclic Aromatic Hydrocarbons and removing COD was researched in this study and was found to be effective in removing recalcitrant organic compounds. Sample Characterisation shows that the leachate had a high COD of 9100mg/L, the Fenton treatment has resulted in highest COD removal of 86.69% at optimum conditions H_2O_2/Fe^{2+} of 1.5, H_2O_2 of 1000 mg/L, reaction time of 60 minutes and influent COD of 77000 mg/L at a pH of 3. Concentration of PAH was identified in municipal leachate, 16 PAHs detected before Fenton Process were 100% removed under optimum conditions.

Advanced Oxidation Process has received high attention because it can effectively degrade organic and organic compounds in mature or old leachate. The Fenton process was chosen to treat municipal landfill leachate in this study because biological processes and physico-Chemical processes are ineffective in treatment old leachates due to the presence of biorefractory compounds such as PAHs.

In a nutshell, the results of this study indicate that the Fenton process can be for effective treatment of municipal landfill leachate and eliminates the detrimental effect of leachate effluents on the environment.

There have been intensive studies on Fenton and photo-Fenton processes on old and biologically treated landfill leachate in order to enhance the treatment efficiencies for removing recalcitrant organic molecules (Kabdasli & Arslan, 2010). Hydrogen peroxide and ferrous iron at acidic pH level were the primary literature focus on many studies. Great scope of works should be used in the future to ensure that a wide range of parameters found in landfill leachate are taken into consideration.

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APPENDICES

Appendix A: Triplicate COD readings

Run	Reading 1	Reading 2	Reading 3	Average COD	Dilution Factor	Final COD
	mg/L	mg/L	mg/L	mg/L		mg/L
1	27	23	46	25	50	1250
2	72	88	29	80	50	4000
3	77	102	61	69	50	3450
4	139	77	55	66	50	3300
5	111	68	50	59	50	2950
6	47	50	41	46	50	2300
7	70	68	91	69	50	3450
8	30	85	42	36	50	1800
9	39	40	18	39.5	50	1975
10	61	78	103	69.5	50	3475
11	20	46	24	22	50	1100
12	42	24	33	37.5	50	1875
13	23	30	43	32	50	1600
14	22	19	69	20.5	50	1025
15	35	51	53	52	50	2600
16	127	36	30	33	50	1650
17	100	44	43	43.5	50	2175
18	37	60	68	64	50	3200
19	67	101	62	64.5	50	3225
20	53	84	67	60	50	3000
21	23	20	16	20	50	1000
22	29	40	30	33	50	1650
23	21	39	54	38	50	1900
24	16	18	99	16	50	800
25	75	33	34	33.5	50	1675
26	20	39	32	35.5	50	1775
27	100	41	91	95.5	50	4775
28	50	77	68	65	50	3250
29	47	59	76	53	50	2650
30	90	99	74	79.5	50	3975

Appendix B: Fenton reagents amount added in leachate

Run	Initial COD (mg/L)	Initial COD (mmol/L)	H_20_2 (mg/L)	H_2O_2/COD	H_20_2 mL/L	H_20_2 (mL/500mL)	H_20_2/Fe^{2+}	Reaction Time (mins)	Fe^{2+}	X (mg/L)	X (mg/500mL)	X (g/500mL)
1	6300.00	196.88	1750.00	0.28	6.20	3.10	2.50	105.00	700.00	3475.00	1737.50	1.74
2	4900.00	153.13	1000.00	0.20	3.54	1.77	3.50	150.00	285.71	1418.37	709.18	0.71
3	6300.00	196.88	1750.00	0.28	6.20	3.10	1.50	105.00	1166.67	5791.67	2895.83	2.90
4	6300.00	196.88	1750.00	0.28	6.20	3.10	2.50	105.00	700.00	3475.00	1737.50	1.74
5	6300.00	196.88	1750.00	0.28	6.20	3.10	4.50	15.00	388.89	1930.56	965.28	0.97
6	9100.00	284.38	1750.00	0.19	6.20	3.10	2.50	105.00	700.00	3475.00	1737.50	1.74
7	4900.00	153.13	1000.00	0.20	3.54	1.77	2.50	60.00	400.00	1985.71	992.86	0.99
8	7700.00	240.63	2500.00	0.32	8.85	4.43	3.50	60.00	714.29	3545.92	1772.96	1.77
9	7700.00	240.63	1000.00	0.13	3.54	1.77	2.50	60.00	400.00	1985.71	992.86	0.99
10	4900.00	153.13	2500.00	0.51	8.85	4.43	3.50	150.00	714.29	3545.92	1772.96	1.77
11	7700.00	240.63	1000.00	0.13	3.54	1.77	1.50	60.00	666.67	3309.52	1654.76	1.65
12	6300.00	196.88	1750.00	0.28	6.20	3.10	1.50	105.00	1166.67	5791.67	2895.83	2.90
13	4900.00	153.13	2500.00	0.51	8.85	4.43	1.50	60.00	1666.67	8273.81	4136.90	4.14
14	7700.00	240.63	1000.00	0.13	3.54	1.77	1.50	150.00	666.67	3309.52	1654.76	1.65
15	6300.00	196.88	250.00	0.04	0.89	0.44	2.50	105.00	100.00	496.43	248.21	0.25

Run	Initial COD (mg/L)	Initial COD (mmol/L)	H_20_2 (mg/L)	H_20_2 /COD	H_20_2 mL/L	H_20_2 (mL/500mL)	H_20_2 /Fe^{2+}	Reaction Time (mins)	Fe^{2+}	X (mg/L)	X (mg/500mL)	X (g/500mL)
16	7700.00	240.63	2500.00	0.32	8.85	4.43	3.50	150.00	714.29	3545.92	1772.96	1.77
17	6300.00	196.88	3250.00	0.52	11.51	5.76	2.50	105.00	1300.00	6453.57	3226.79	3.23
18	7700.00	240.63	2500.00	0.32	8.85	4.43	1.50	60.00	1666.67	8273.81	4136.90	4.14
19	6300.00	196.88	1750.00	0.28	6.20	3.10	2.50	105.00	700.00	3475.00	1737.50	1.74
20	4900.00	153.13	2500.00	0.51	8.85	4.43	2.50	60.00	1000.00	4964.29	2482.14	2.48
21	7700.00	240.63	1000.00	0.13	3.54	1.77	0.50	150.00	2000.00	9928.57	4964.29	4.96
22	3500.00	109.38	1750.00	0.50	6.20	3.10	3.50	105.00	500.00	2482.14	1241.07	1.24
23	4900.00	153.13	2500.00	0.51	8.85	4.43	2.50	150.00	1000.00	4964.29	2482.14	2.48
24	7700.00	240.63	2500.00	0.32	8.85	4.43	1.50	150.00	1666.67	8273.81	4136.90	4.14
25	4900.00	153.13	1000.00	0.20	3.54	1.77	2.50	150.00	400.00	1985.71	992.86	0.99
26	6300.00	196.88	1750.00	0.28	6.20	3.10	2.50	105.00	700.00	3475.00	1737.50	1.74
27	6300.00	196.88	1750.00	0.28	6.20	3.10	3.50	195.00	500.00	2482.14	1241.07	1.24
28	6300.00	196.88	1750.00	0.28	6.20	3.10	3.50	105.00	500.00	2482.14	1241.07	1.24
29	4900.00	153.13	1000.00	0.20	3.54	1.77	3.50	60.00	285.71	1418.37	709.18	0.71
30	6300.00	196.88	1750.00	0.28	6.20	3.10	1.50	105.00	1166.67	5791.67	2895.83	2.90

*X= $FeSO_{4.}7H_2O$ in g/500mL

Appendix C: PAHs concentrations before and after treatment

Compound	Initial Conc. (ppb)	After Fenton Treatment (ppb)														
		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14	Run 15
Napthalene	3.03	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.51	2.51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Acenaphtylene	2.59	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Acenaphthene	2.56	N.D.	N.D.	N.D.	0.04	N.D.	N.D.	0.03	N.D.	N.D.	0.03	N.D.	N.D.	N.D.	N.D.	N.D.
Fluorene	2.55	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Phenanthrene	2.56	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Anthracene	2.57	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Carbazole	2.19	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Fluoranthene	2.55	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Pyrene	2.54	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo [a] Anthracene	2.57	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.52	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Chrysene	2.57	N.D.	N.D.	N.D.	N.D.	0.02	N.D.	N.D.	2.51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo [k] Fluoranthene	2.57	N.D.	N.D.	N.D.	N.D.	0.11	N.D.	N.D.	2.5	N.D.	0.05	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo [a] Pyrene	2.58	N.D.	N.D.	N.D.	N.D.	0.17	N.D.	N.D.	2.48	N.D.	0.08	N.D.	N.D.	N.D.	N.D.	N.D.
Indeno[1,2,3-cd] Pyrene	2.65	N.D.	N.D.	N.D.	N.D.	0.18	N.D.	N.D.	N.D.	N.D.	0.09	N.D.	N.D.	N.D.	N.D.	N.D.
Dibenz[ah] Anthracene	2.62	N.D.	0.37	0.77	0.04	1.33	0.23	N.D.	N.D.	N.D.	0.95	N.D.	N.D.	N.D.	N.D	N.D.
Benzo[ghi] Perylene	2.62	N.D.	0.34	0.7	0.03	1.29	0.21	N.D.	N.D.	N.D.	0.93	N.D.	N.D.	N.D.	N.D	N.D.

Compound	**Initial Conc. (ppb)**	**After Fenton Treatment (ppb)**														
		Run 16	Run 17	Run 18	Run 19	Run 20	Run 21	Run 22	Run 23	Run 24	Run 25	Run 26	Run 27	Run 28	Run 29	Run 30
Napthalene	3.03	N.D.	N.D.	2.51	N.D.	N.D.	2.54	0.01	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Acenaphtylene	2.59	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Acenaphthene	2.56	0.04	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	N.D.	N.D.	N.D.	N.D.	N.D.
Fluorene	2.55	N.D.	N.D.	N.D.	N.D.	N.D.	2.52	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Phenanthrene	2.56	N.D.	N.D.	2.52	N.D.	N.D.	2.52	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Anthracene	2.57	N.D.	N.D.	2.5	N.D.	N.D.	2.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Carbazole	2.19	0.19	N.D.	N.D.	N.D.	N.D.	N.D.	0.17	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Fluoranthene	2.55	N.D.	N.D.	2.52	N.D.	N.D.	100	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Pyrene	2.54	N.D.	N.D.	N.D.	N.D.	N.D.	100	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo [a] Anthracene	2.57	0.11	N.D.	N.D.	N.D.	N.D.	100	0.62	N.D.	N.D.	0.03	N.D.	N.D.	N.D.	N.D.	N.D.
Chrysene	2.57	0.18	N.D.	N.D.	N.D.	N.D.	100	0.63	N.D.	N.D.	0.04	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo [k] Fluoranthene	2.57	0.19	N.D.	N.D.	N.D.	N.D.	100	N.D.	N.D.	N.D.	0.28	N.D.	0.04	N.D.	N.D.	N.D.
Benzo [a] Pyrene	2.58	0.17	N.D.	N.D.	N.D.	N.D.	100	N.D.	N.D.	N.D.	0.39	N.D.	0.04	N.D.	N.D.	N.D.
Indeno[1,2,3-cd] Pyrene	2.65	0.2	N.D.	N.D.	N.D.	N.D.	100	N.D.	N.D.	N.D.	0.41	N.D.	0.05	N.D.	N.D.	N.D.
Dibenz[ah] Anthracene	2.62	5.43	N.D.	N.D.	0.09	0.46	100	N.D.	0.14	0.56	1.85	0.2	0.73	0.11	0.12	N.D.
Benzo[ghi] Perylene	2.62	3.94	N.D.	N.D.	0.08	0.43	100	N.D.	0.12	0.53	1.84	0.17	0.7	0.09	0.11	N.D.