ADVANCED OXIDATION OF LANDFILL LEACHATE USING THE FENTON PROCESS TO REMOVE PAHs

KAGISANO SEFOLO

CIVIL ENGINEERING

UNIVERSITI TEKNOLOGI PETRONAS

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BY

KAGISANO SEFOLO

Dissertation submitted in partial fulfilment of the requirements for the Bachelor of Engineering (Hons) (Civil Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Kagisano Sefolo

A project dissertation submitted to the Department of Civil Engineering, Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the Bachelor of Engineering (Hons) (Civil Engineering)

Approved:

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A.P Dr Mohamed Hasnain Isa

UNIVERSITI TEKNOLOGI PETRONAS TRONOH, PERAK

May semester 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am the person responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements.

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Kagisano Sefolo

ABSTRACT

The contents of this report are a study of the approach taken in the advanced oxidation of municipal landfill leachate using the Fenton process. This process is used for the effective reduction in concentration of organic contaminants in municipal landfill leachate. The study will be looking at the aspects of the advanced oxidation process, indicating the significances of each of the components towards the treatment of the municipal landfill leachate. The efficiencies for this process are measured by the reduction of COD and five day BOD. The study will however focus on the removal effect of the Fenton process on xenobiotic organic compounds. The xenobiotic organic compounds referred to in this study are polycyclic aromatic hydrocarbons (PAHs). These xenobiotic substances are known to be found in leachate in trace levels. The study will be looking into how different chemical reactions contribute to essentially treating the municipal landfill leachate.

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I am thankful to God who has blessed me with the opportunity to study civil engineering up to this level and has guided me throughout to reach use my full potential. I am also thankful to A.P. Dr Mohamed Hasnain Isa (my supervisor) for the guidance they provided me with throughout this project.

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ABREVIATIONS AND NOMENCLATURES

List of abbreviations

Abbreviation	Full meaning
4NP	4 nonylphenol
4tOP	4-t octylphenol
AOP	advanced oxidation process
AP	associate professor
BBP	butyl benzyl phthalate
BOD	biological oxygen demand
BPA	bisphenol A
COD	chemical oxygen demand
DBP	dibutyl phthalate
DEHP	diethylhexyl phthalate
Dr.	Doctor of philosophy
FYP	final year project
GC-MS	gas chromatography – mass spectrometry
PAH	polycyclic aromatic hydrocarbons
PPB	part per billion
RPM	revolutions per minute
SEDEX	science and engineering design exhibition

CHAPTER 1:
INTRODUCTION

1.1 Project Background

Land filling is currently the most widespread and most economical method for waste disposal, up to 95% of solid waste generated worldwide is currently disposed in landfills [1]. A problem associated with the use of landfills is the production of leachate. Leachate discharges can lead to serious environmental problems as it can percolate through soils and sub soils, it contains various pollutants which can be harmful to the human body [1]. Leachate can be characterized as either young or old leachate, these characterizations have an effect on how biodegradable the leachate is. The proper treatment of leachate has been found to be one of the biggest environmental challenges in many countries all over the world [2]. Old leachates have a lower biodegradability because they contain various pollutants which can be harmful to the human body [1]. Polycyclic aromatic hydrocarbons are some of the toxic pollutants that can be found in leachate which are known to cause bodily harm to humans. The presence of toxic substances such as PAHs plays a big role in hampering the biological treatment of leachate [2]. Advanced oxidation processes have been reported to be highly effective techniques capable of degrading the vast range of organic matter found in leachates [3]. Due to the organic carbon content present in the particles found in these pollutants they are readily attached on to the solids found in the leachate and tend to interact to some extent with the particulate matter in the leachate [2]. PAHs can be transported over long distances in wet and dry conditions, together with being found at minute levels, this makes them very harmful.

1.2 Problem statement

Old municipal landfill leachates cannot be effectively treated by biological treatment because they have low biodegradability, xenobiotic organic compounds are not sufficiently removed by the biological treatment and thus require advanced processes to remove them. The organic matter in municipal landfill leachate can be harmful as it can permeate into the ground polluting ground water and soil, it can also mix with and pollute surface water. Polycyclic aromatic hydrocarbons are problematic because they are harmful even in the small fractions in which they found in leachates.

1.3 Objectives

The objectives of this study are:

(i) To measure the effect of the Fenton process with regard to the removal of harmful xenobiotic compounds namely polycyclic aromatic hydrocarbons.

(ii) To measure the efficiency of the Fenton process in treating municipal landfill leachate in terms of COD.

1.4 Scope of study

The scope of this project covers treatment of municipal landfill leachate by advanced oxidation process, the process undertaken is closely analysed. The project covers the different constituents of municipal landfill leachate before and after treatment. The process used in treating the municipal landfill leachate involves different chemical reactions in which there are different measures of elements yielding a particular treatment product. The treatment used in this project falls under the scope of wastewater engineering. The scope of the study will be focusing on the efficiency of Fenton process to remove harmful xenobiotic organic compounds.

CHAPTER 2
LITERATURE REVIEW

Municipal landfill leachate is liquid that moves through a landfill extracting dissolved organic matter and inorganic compounds from the solid waste that the landfill is comprised of. The liquid may result from the contents of the landfill or be a result of precipitation such as rainfall infiltrating the landfill [4]. The solid waste contained in the landfill can comprise of objects such as food waste, which is a good source for organic substances, and paper, plastic and metallic substances [2]. It is from these objects that the liquid is contaminated and turned into leachate. The pollutants contained by the leachate are biodegradable, non-biodegradable and inorganic in nature [1].

Landfills of ages between one and two years can be efficiently treated using biological treatment yielding significantly high BOD_5/COD ratios [1]. Biological treatment is however not sufficient for leachate found in landfills that are aged above two years and having low BOD_5/COD ratios, this is because it contains a greater proportion of organic compounds some of which might be xenobiotic [1]. Xenobiotic organic compounds are substances that contain chemicals which have been induced as a result of human activities. They are found in trace levels which is what causes the greatest challenge in their treatment capacity [5].

Polycyclic aromatic hydrocarbons are potent atmospheric pollutants that can also be found in landfills. They are aromatic rings that formed due incomplete combustions of various materials which have variants in solid wastes [6]. PAHs can be found in two types:

Table 2.1: Two types of PAHs [7]

Petrogenic	Pyrogenic
From crude and refined petroleum	From the combustion of fossil fuels

Polycyclic aromatic hydrocarbons are introduced into landfills along with petroleum hydrocarbon residues and depositions from the atmosphere which can attach to the surfaces of the solids found in the leachates [6]. They are known to be very harmful in the sense that they can cause cancers and mutations. PAHs have been found in studies in concentrations ranging between (485.2 to 1188.2 ng/L) [6]. PAHs have the ability to remain in the environment for long periods of time due to their high degree of link formation and aromaticity, they are defined by two or more aromatic benzene rings [8].

The purpose of the advanced oxidation of municipal landfill leachate is to effectively remove such organic substances present in the leachate. Advanced oxidation by the Fenton process is a good treatment option because it makes use of hydrogen peroxide and ferrous iron to generate hydroxyl radicals [9]. The hydroxyl radicals have a high oxidation potential to improve the biodegradability of the remaining organic substances by oxidizing them to their highest stable oxidation states [1]. The Fenton process favours low pH because the hydroxyl radicals along with ferric ions are produced at acidic levels [2]. The initial pH, dosage of reagents, final pH and temperature have an influence on the final treatment efficiency. COD removal has been found to increase with increasing temperature and increasing hydrogen peroxide (H_2O_2) up to a certain limit [9].

The Fenton advanced oxidation process is studied using the jar test apparatus [2]. There are four significant stages which are procured. The pH is adjusted to the optimum level suitable for the process to produce hydroxyl radicals. The next stage is the oxidation process itself. To make the treatment more efficient, coagulation is the next step undertaken to clump together the remaining solids which have not been oxidized. This is to prepare them for the next stage which is sedimentation [10].

The propagation of the Fenton to Fenton-like process is described by the chemical formula that follows [9]:

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

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^{+}$

$OH + H_2O \rightarrow HO_2 + H_2O$

$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + O_2H^{+}$

$Fe^{2+} + HO^{\bullet} + H^{+} \rightarrow Fe^{3+} + H_2O_2$

$2HO^{\bullet}_2 \rightarrow H_2O_2 + O_2$

Hydrogen peroxide is added to the leachate with ferrous iron, which initiates and acts as a catalyst to generate hydroxyl radicals and high valence iron species [2]. The ferrous iron is too slowly regenerated after the conversion to ferric iron which essentially inhibits the propagation of the Fenton process thus more ferrous iron dosage is needed for the generation of the hydroxyl radicals. [9].

The Fenton processes can be further energetically enhanced by introducing the photo Fenton process. The photo Fenton process uses ultraviolet radiation to enhance the reduction of ferric ions to ferrous ions while also generating hydroxyl radicals, this is helpful to reduce the production of iron sludge [3].

Studies have reported the removal efficiencies of COD by the Fenton process to range from 45% to 85% [9]. It was found in one study that the coagulation stage has a key role to the removal of COD contributing to 80% [9].

The reasons for the preferred use of the Fenton process according to studies are as follows:

- Less expensive in comparison to other AOPs [9].
- Effects chemical destruction rather than pollutant transfer from one phase to another [9].
- Has a greater simplicity [10].
- Nontoxic nature [2]

CHAPTER 3

METHODOLOGY

3.1 Flow chart

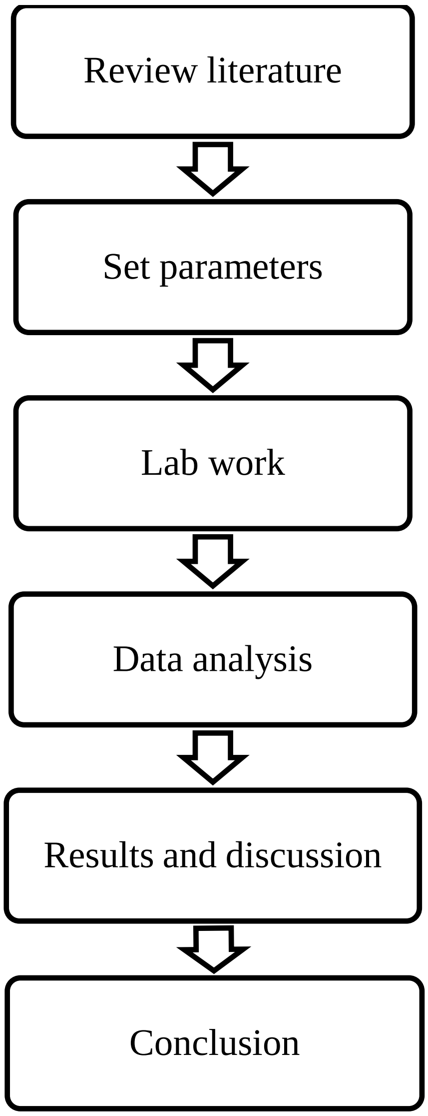

Figure 3.1: Methodology used during the project

3.2 Project activities

3.2.1 Research project material

a. Searching through the internet.
b. Reading through other peoples journals.

3.2.2 Perform laboratory experiments:

1. Sample characterization:
   a. Measure initial pH of leachate sample.
   b. Measure initial COD.
   c. Measure initial PAH concentration.

2. Preparation of stock solution:

H_2O_2:

1M H_2O_2 = 34g/l

2M H_2O_2 = 68g/l

H_2O_2 concentration purity is 30% thus = 300g/l

Using M1V1 = M2V2:

(34g/l)(100ml) = (300) V2

V2 = 11ml/L

Fe^{2+}:

$FeSO_4.7H_2O$ = 278g/l

1M Fe =56g/l

Thus, $FeSO_4.7H_2O = \frac{278}{56} \times 28$

= 139g/500ml

=13, 9/100ml

3. <u>Fenton process:</u>
    a. Add Fenton reagents hydrogen peroxide and ferrous iron to the leachate sample.
    b. Commence rapid mixing for 60 minutes at (120 rpm).
    c. Increase pH to neutral range by adding sodium hydroxide.
    d. Commence flocculation for 30 minutes at (60 rpm).
    e. Allow sedimentation for 30 minutes.

4. <u>Measure effect of pH:</u>

The pH was adjusted in the range from 2 to 6 using sodium hydroxide to increase and sodium chloride to decrease. The Fenton process was then run with 100ml of sample at the various pH levels in different beakers. After the experiment, 2ml of the sample from each beaker was used to measure COD at a dilution factor of 50. The pH level that yields the highest COD removal is the optimum to be used for the experiment.

5. <u>Determine optimum of hydrogen peroxide/ ferrous iron ratio:</u>

Hydrogen peroxide was kept at 1mole while varying the amount of ferrous iron from 0.5 mole to 2mole in increments of 0.5mole. The Fenton to process was run using magnetic stirrers. After the experiment, 2ml of the sample from each beaker was used to measure COD at a dilution factor of 50. The ratio with the highest COD removal will be the optimum to be used for the experiment.

6. <u>Determine optimum hydrogen peroxide dose:</u>

The pH was kept constant as the hydrogen peroxide was increased from 0.5 mole to 2.5 mole at increments of 0.5 mole. The ferrous iron is increased according to the corresponding ratio. The Fenton process was run using mag etic stirrers. After the experiment, 2ml of the sample from each beaker was used to measure COD at a dilution factor of 50. The dose of H_2O_2 with the highest COD removal was the optimum to be used for the experiment.

7. Measure final COD:
    a. COD is measured using a DR 2800 spectrophotometer.
    b. The pH needs to be adjusted to 10 to reduce the interference of hydrogen peroxide.

8. Measure final PAH concentration:
    a. PAH concentrations are measured using GC-MS at the Unviversti Teknologi Petronas central analytical laboratory.

3.2.3 Data analysis and assessment:

a. Discuss and draw conclusions from the results obtained.

3.3 Gantt chart and key milestones

Table 3.1: FYP 1 Gantt chart

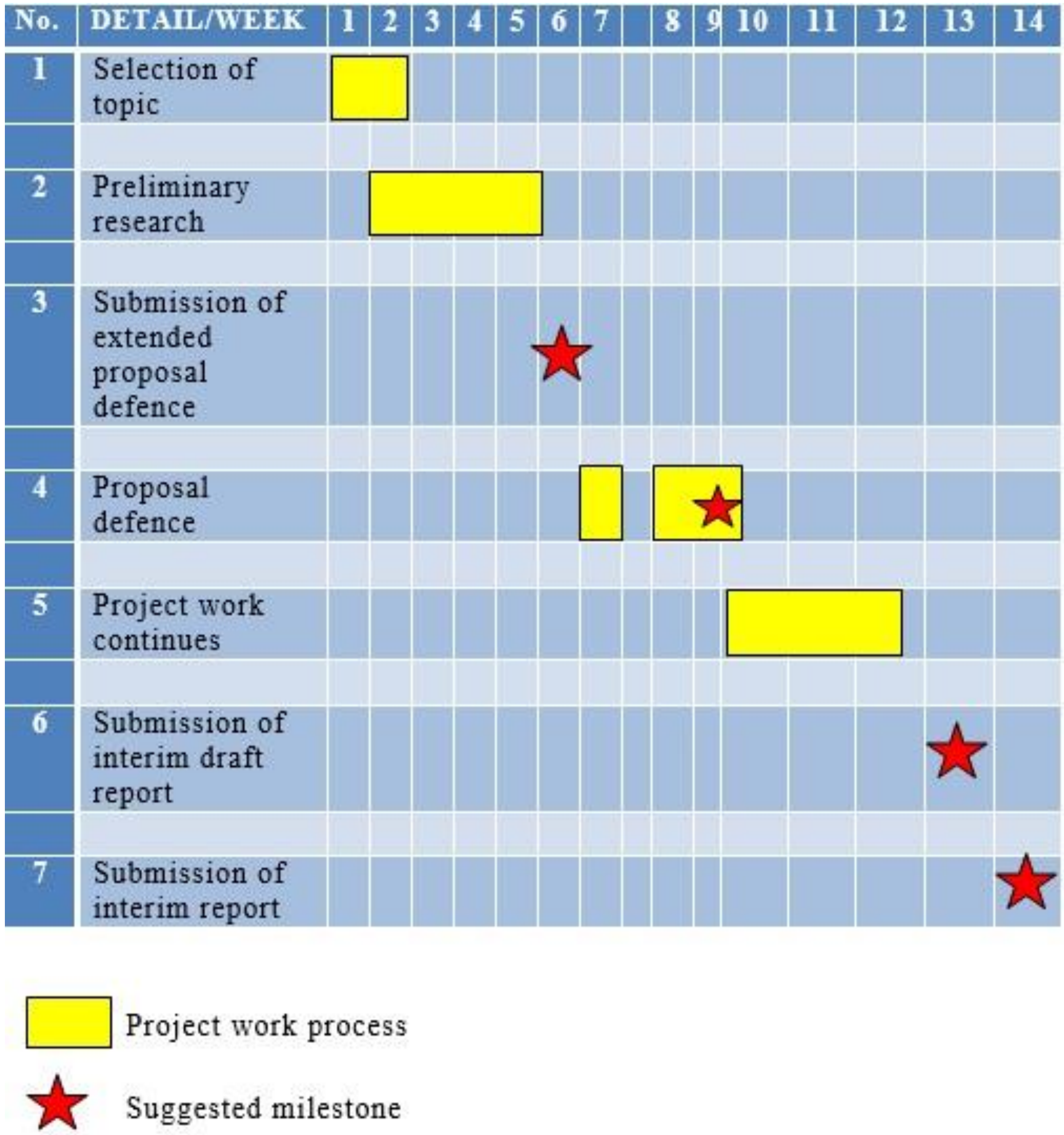

Table 3.2: FYP 2 Gantt chart

No.	DETAIL/ WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project work continues	■	■	■	■	■	■	■								
2	Submission of progress report									★						
3	Project work continues									■	■	■	■	■		
4	Pre-SEDEX												★			
5	Submission of draft report													★		
6	Submission of dissertation (soft bound)														★	
7	Submission of technical paper														★	
8	Oral presentation															★
9	Submission of project dissertation (hard bound)															

■ Project work process

★ Suggested milestones

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Introduction

This section presents the results obtained from the laboratory experiment conducted to test the efficiency of the Fenton process to remove PAHs from a sanitary landfill leachate from Jeram in Kuala Lumpur by showing the initial and final characteristics of the leachate sample. The efficacy of the Fenton process is determined based on its COD removal efficiency. The effectiveness is derived by determining the optimum concentrations of the Fenton reagents (hydrogen peroxide and ferrous iron) which are used in the experiment at the most effective pH process to achieve the highest COD removal. The concentration and pH yielding the highest COD removal is the one which is used for the final experiment to treat PAHs from the leachate sample.

4.2 Sample characterization

- Initial pH: 8.07
- Initial COD: 4063 mg/L

4.3 Determination of optimum hydrogen peroxide and ferrous iron doses

4.3.1 Effect of pH and H_2O_2 / Fe^{2+} ratio

The experiment is run to determine the H_2O_2 / Fe^{2+} ratio that yields the highest COD removal and at what pH value this optimum condition is reached.

Table 4.1: COD removal at various pH ranges and H_2O_2 / Fe^{2+} ratios

pH	H_2O_2 / Fe^{2+} ratio	COD removal (mg/L)	COD removal (%)
2	0.5	1556	38.3
	1.0	2613	64.3
	1.5	2661	65.5
	2.0	2364	58.2
3	0.5	1914	47.1
	1.0	2462	60.6
	1.5	2812	69.2
	2.0	2153	53
4	0.5	1507	37.1
	1.0	1962	48.3
	1.5	2613	64.3
	2.0	2413	59.4
6	0.5	2113	52
	1.0	2413	59.4
	1.5	2613	63.1
	2.0	2563	69.1

The results obtained from the experiments to determine the optimum H_2O_2 / Fe^{2+} ratios at various pH levels, the results are plotted on the same axis using Microsoft excel as shown in Figures 4.1 and 4.2 below.

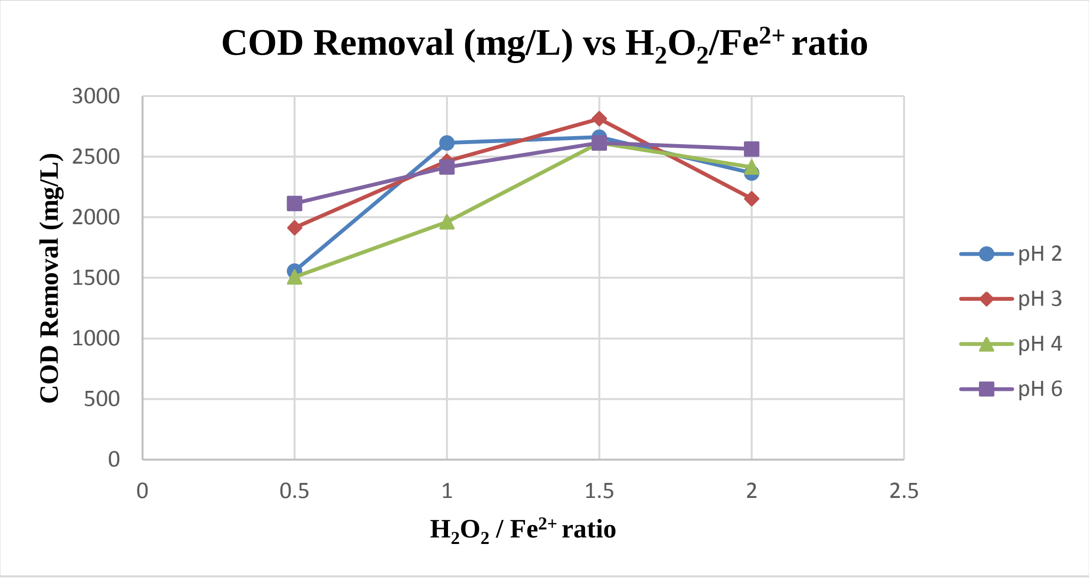

Figure 4.1: COD removal (mg/L) vs. H_2O_2/Fe^{2+} ratio

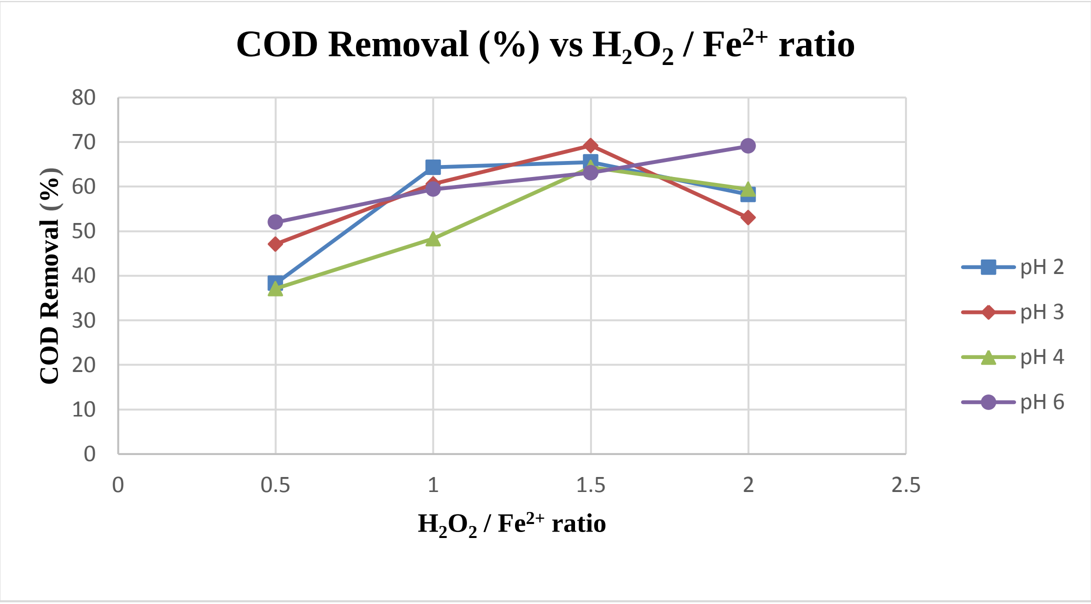

Figure 4.2: COD removal (%) vs. H_2O_2 / Fe^{2+} ratio

4.3.2 The optimum H_2O_2 dose

The experiment was run to determine the optimum dose of hydrogen peroxide that can be used for the Fenton process to remove the most COD and ultimately to remove the most PAHs. This experiment was run at the optimum H_2O_2 / Fe^{2+} ratio of 1.5 and the pH level of 3.

Table 4.2: COD removal at various H_2O_2 doses

	H_2O_2 dose (mol)				
	0.5	1.0	1.5	2.0	2.5
COD removal (mg/L)	1361	1613	1662	3454	3413
COD removal (%)	33.5	39.7	40.9	85	84

The results from the experiment to determine the optimum H_2O_2 dose are plotted on a graph using Microsoft excel as shown in Figure 4.3 and 4.4 below.

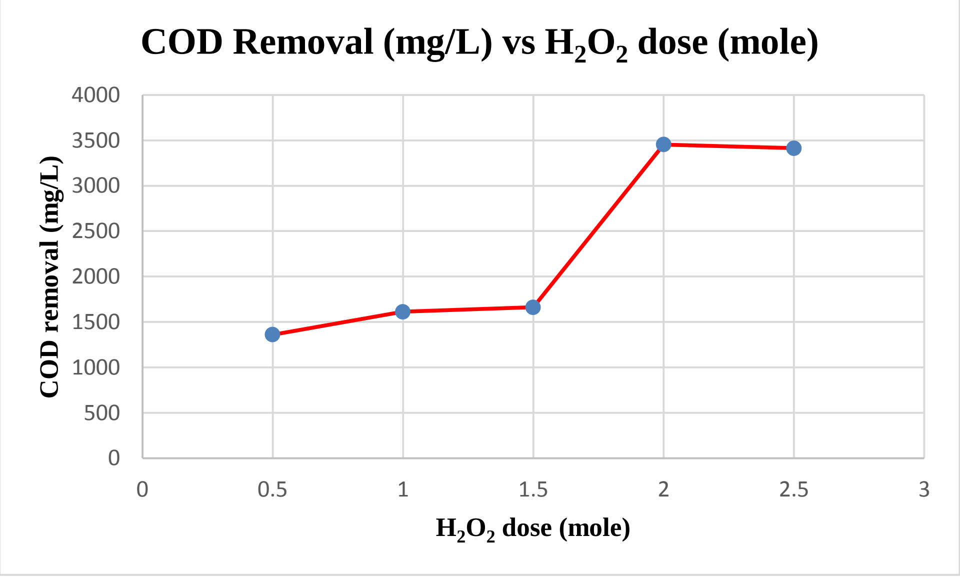

Figure 4.3: COD Removal (mg/L) vs. H_2O_2 dose (mole)

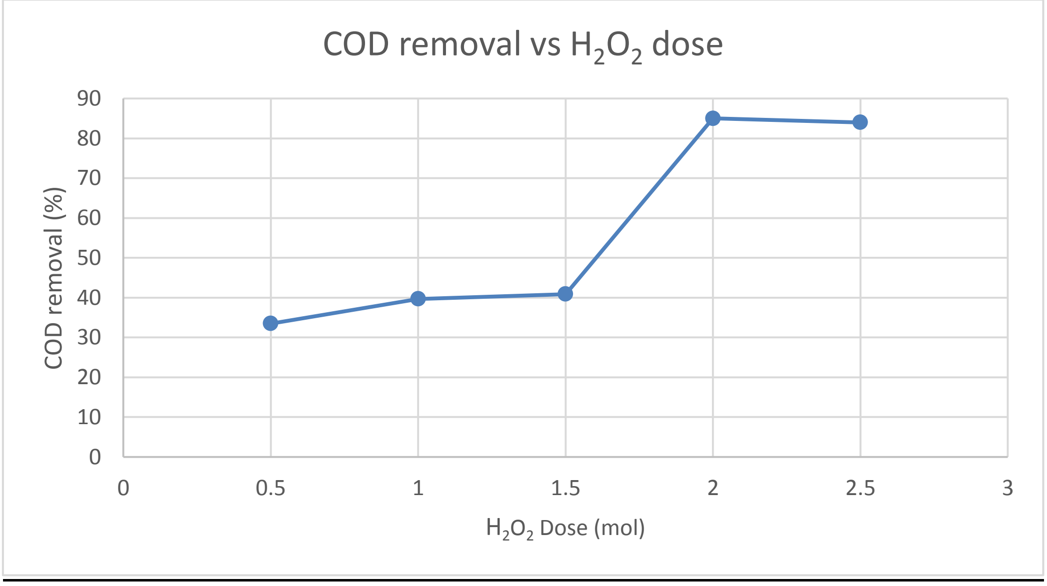

Figure 4.4: COD removal (%) at various H_2O_2 doses

4.4 Analysis of PAHs

The results for the PAH concentrations before and after the leachate has been treated, obtained from the GC-MS analysis, are shown in the table below.

Table 4.3: PAH removal

Compound name	Initial concentration (ppb)	Final concentration (ppb)	Compound removal (%)
Naphthalene	5.84	4.34	25.68
Acenaphtylene	1.03	0.06	94.17
acenaphthene	0.58	ND	100
Fluorene	1.94	ND	100
Phenanthrene	1.75	2.96	-
Anthracene	2.27	ND	100
Carbazole	2.01	ND	100
Fluoranthene	0.3	2.51	-
Pyrene	0.39	ND	100
Benzo (a) anthracene	1.89	ND	100
Chrysene	2.12	ND	100
Benzo (b) fluoranthene	2.16	0.26	87.96
Benzo (k) fluoranthene	1.47	0.26	1.21
Benzo (a) pyrene	1.28	1.26	1.5
Indenol ,2,3 (cd) pyrene	1.58	0.10	93.37
Dibenzo (a,h) anthracene	0.56	0.20	64.3
Benzo (g,h,i) perylene	2.61	0.33	87.36

The results showing the removal of each detected PAHs are plotted in a graph using Microsoft Excel shown in Figure 4.5 below.

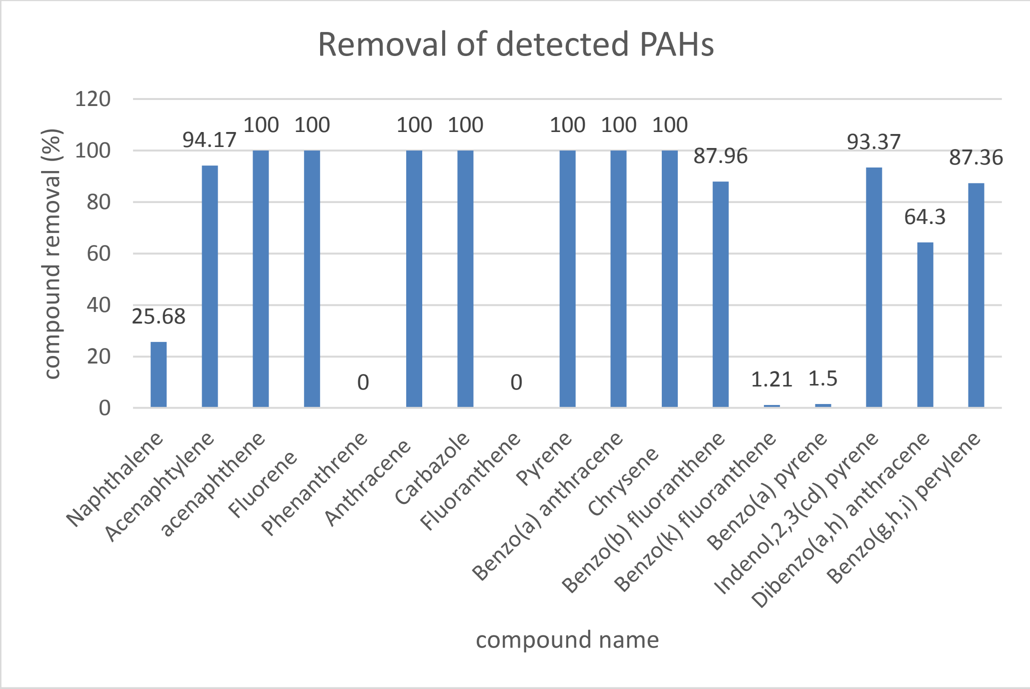

Figure 4.5: PAH removal

4.5 Discussion

In order to ensure that the experiment is as effective as it can be, it is important to use the most optimal doses of the reagents. As can be observed on Figure 4.1 the optimum H_2O_2/Fe^{2+} ratio is 1.5 at a pH of 3. As has been mentioned before, the Fenton process works better at acidic levels however when the experiment is run at too low acidic levels this can inhibit the production of hydroxyl radicals. Once the optimum ratio has been determined the amount of H_2O_2 and Fe^{2+} to be used in the experiment are also determined, as can be observed in Figure 4.2 the optimum H_2O_2 dose to remove the most organic substances was found to be 2 moles which means that the amount of Fe^{2+} to be used is 3 moles based on the ratio determined in section 4.3.1.

Figure 4.3 shows the PAHs which have been detected in the leachate sample by using GC-MS. A total number of 17 PAHs was detected in the sample. These toxic substances were found at trace levels. These trace levels are what makes them difficult to be removed in landfill leachate and as has been mentioned before they are very harmful at these very low levels. Once the optimum doses of the Fenton reagents was determined the experiment was conducted. Due to the high doses of Fe^{2+} a relatively large amount of sludge was produced and observed during the sedimentation stage.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The Fenton process was successful in removing 85% of the COD found in the leachate, 41% of the detected PAHs completely and 29% of the PAHs in the 60 – 95 percent removal range. This shows that the Fenton process can effectively treat landfill leachate and remove harmful substances to a significant amount.

5.2 Recommendations

The performance of the Fenton process can be enhanced by introducing the photo Fenton process which uses ultraviolet radiation to enhance the reduction of ferric ions to ferrous ions while generating hydroxyl radicals. This can result in removing more of the PAHs.

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