Landfill Leachate Treatment

by

Fithri Natasha Ishak

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

JANUARY 2011

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Rizuan

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CERTIFICATION OF APPROVAL

Landfill Leachate Treatment

by

Fithri Natasha Ishak

A project dissertation submitted to the
Civil Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CIVIL ENGINEERING)

Approved by,

(Prof. Malay Chaudhari)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2011

CERTIFICATION OF ORIGINALITY

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

Natasha

FITHRI NATASHA ISHAK

ABSTRACT

In this study, treatment options for leachate are reviewed and the most suitable and convenient treatment process of all will be identified. The efficiencies of pH adjustment and settling as pre-treatment as well as photo-Fenton process as primary treatment were evaluated based on their ability to remove the Chemical Oxygen Demand (COD) for it to be amenable to further biological treatment.

Response Surface Methodology (RSM) was used to optimize the photo-Fenton process for the removal of COD.

ACKNOWLEDGMENTS

First and foremost, I would like to thank God Almighty for giving me the strength and patience to complete this final year project.

I would also like to express my utmost gratitude to my supervisor, Professor Malay Chaudhuri for offering me guidance and imparting his wisdom to me. I am very grateful to have a mentor who keeps on giving me countless chances to produce a good and reliable project. The highlights of my research were came from his guidance and the errors and mistakes are all entirely my own.

The same goes to Mr. Gan Chin Heng for helping me out with the basis of Response Surface Methodology and providing me with countless advices and tips concerning the experiments. I would also like to extend my gratitude to Dr. Shamsul Rahman Kutty who taught me Water & Wastewater Engineering as well as all the lab technicians for being generous with their time and knowledge.

Last but definitely not least, I would like to thank both my parents, Ishak Ismail and Nuri Supian along with all my friends who have been completely supportive and encouraging during the duration it takes to complete this project.

A million thanks to all of you, without whom I might not be able to make it to the final steps to cross the finish line. I will forever be indebted to each and everyone of you.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Leachate is made out of rain that passes through a landfill site as well as liquids that are generated by the breakdown of the waste within the landfill. Initially, the water that permeates landfills will come in contact with decomposing solid waste. It will then become contaminated and once it flows out of the waste material, it becomes what we know as leachate.

The composition of leachate varies greatly according to a few factors which are :

- Age of landfill
- Types of waste it comes in contact with
- Degree of decomposition that has taken place and
- Physical modification of the waste

However, in general leachate contains suspended solids, high in both organic and inorganic contents and also proven to contain heavy metals (Kouezeli-Katsiri et al, 1999). Due to this, it poses a very detrimental effect on the environment. Besides that, there might also be pathogenic microorganisms as well as other toxic substances such as methane that might be present in the composition of leachate.

The problem arises when the leachate streams to water sources, immediately putting a huge impact on the environment and endangering the populations of sensitive and fragile species. With help from the natural environment cycle, the leachate contaminated water source will then reach us humans and also the flora and fauna. The toxic metals and organics that might be present in the leachate composition might very well lead to chronic toxin accumulation and negatively affect bio-diversity.

Figure 1 : Leachate contaminated pond

Leachates can be assessed by a few factors such as its chemical oxygen demand (COD) and biological oxygen demand (BOD) values, ratio of BOD to COD, its pH, suspended solids as well as other substances such as nitrogen, phosphorus, ammonia and metals.

There are a few treatment methods available to treat leachate problems and it can be classified into two main categories which are the biological methods as well as the chemical and physical methods. (Wiszniowski et al, 2006).

1.2 Problem Statement

The most efficient way to treat landfill leachate is still being mulled over by many. Considering that one method of treatment is not enough to efficiently treat leachates, the best approach is to combine both the physico-chemical methods with the biological ones (Wiszniowski et al, 2006). Preferably, using physicochemical methods as pre and post treatment.

This study serves to investigate the most suitable preliminary treatment method and adequacy of Advanced Oxidation Process (AOP) for treatment of leachate so that it becomes amenable to biological treatment.

For leachate to be permitted to be released into water bodies, it should not contain organic and inorganic matters, heavy metals or any pollutants in high concentration exceeding the limit set by the Department of Environment.

This study serves to investigate the most efficient preliminary and pretreatment method that may change the whole system of how leachates are treated and will in turn, save resources, money as well as energy.

1.3 Objectives and Scope of Study

The objective for this project is to come up with an efficient pre-treatment and primary treatment method to treat landfill leachate using physico-chemical techniques. The scope of the study, on the other hand is planned to act in accordance with the objective mentioned above in the period of two semesters. Research and experiments for this study is spread in the course of Final Year Project 1 and 2.

During FYP 1, work mostly involves research and planning. The research that was held will mostly revolved around the different methods of physico-chemical treatment and in what order these treatment methods should be conducted to achieve the most proficient result.

Experimental and laboratory works are mostly conducted during FYP 2. Initially, basic laboratory experiments such as preliminary characterization of landfill leachate sample in terms of pH, BOD, COD, total suspended solids, ammonia nitrogen and nitrate nitrogen was carried out. This preliminary characterization provides a better outlook on what to expect from the leachate sample and give a result on its basic composition. This is to assist in the imminent physicochemical experiments that follow after.

Work for FYP 2 was carried out in compliance to the work outline stated in the documents from FYP 1. This way, the planning can be thoroughly completed earlier on and it will reflect in a well-organized and precise work and results.

Leachate sample is obtained from Bukit Tagar landfill and research was also done on the ongoing treatment methods used by this landfill on the leachates.

PARAMETER	UNIT	Bukit Tagar Landfill Leachate
Temperature	°C	29 °C
pH	-	6.6
BOD_5 at 20 °C	mg/l	**27000**
COD	mg/l	**59000**
Total Solid, TS	mg/l	1719
NH_3 - N	mg/l	**4300**
Turbidity	FAU	3600
Conductivity	μ^5/cm	670
Salinity	(%)	0.3
Colour	ADMI value	15300
Cadmium (Cd)	mg/l	**11.25**
Arsenic (As)	mg/l	**3.6**
Lead (pb)	mg/l	**15.15**
Zinc (Zn)	mg/l	**17.55**
Copper (Cu)	mg/l	**10.95**
Aluminium (Al)	mg/l	15.75
Calcium (Ca)	mg/l	397.8
Potassium (K)	mg/l	764.4
Iron (Fe)	mg/l	**84.3**
Sodium (Na)	mg/l	803.55
Manganese (Mn)	mg/l	**17.85**
Selenium (Se)	mg/l	1.65
Magnesium (Mg)	mg/l	29.1

Table 1 : Characteristics of raw leachate from Bukit Tagar Sanitary landfill. (Agamuthu et al, 2009)

CHAPTER 2

LITERATURE REVIEW

2.1 Sanitary Landfill and Leachate

Sanitary Landfill is a solid waste disposal site where waste is spread in layers, compacted and covered with soil or other materials in order to minimize pest, disease, air and water pollution problems. Modern sanitary landfills are endowed with leachate collection and monitoring systems. These landfills are operated in accordance with environmental protection standards.

Leachate, on the other hand is water generated by the decomposition of waste and rainwater that has come into contach with waste. It collects contaminants as it trickles through wastes, pesticides, fertilizers and other materials in a landfill. Leachate usually contains both dissolved and suspended material. Thus, if it is allowed to run untreated into a water body, it may result in a big environmental predicament.

Typically, landfill leachate contains a high concentration of nitrogen, iron, organic carbon, manganese and chloride. Other chemicals include solvents and heavy metals may also be present. In the past, before all the technologies, leachates are usually allowed to slowly leak away into the nearby environment, eventually mixing with the groundwater system or any other water source.

Groundwater is the source of drinking water for the population among the area. It was formerly assumed that this source of water was not subject to contamination but recent studies have shown that this water can in fact easily be contaminated by leachates and the materials in its composition.

Therefore, many have conducted research in order to treat these leachates so that it will be apt for disposal without the fear of it contaminating the water sources and intoxicating the population with poisonous substances.

2.2 Leachate Treatment

Execution of leachate treatment methods is dependant on the characteristic of the leachate composition itself. Plenty of technological means have been developed in the science of landfill leachate treatment and they are generally categorized as biological methods and physico-chemical methods.

Whereas biological processes are effective on newly produced leachates, they are not as suitable for the more mature leachates. On the other hand, physico-chemical processes are not a preferance for new leachates (Forgie, 1998).

Biological treatment process are based on controlling the environment required for optimum growth of the microorganisms involved. Microbes are used to convert colloidal, dissolved carbonaceous organic matter as well as inorganic elements into cell tissues or/and various gases (Wiszniowski et al, 2006). In simpler words, these microbes will destroy or at least reduce the toxicity level of a leachate sample.

One of the inorganic elements that are modifed by the microbes is nitrogen and the major biological processes involved in its removal are ammonification, nitrification/denitrification and anammox.

On the other hand, physical treatment methods are used to remove, separate and concentrate perilous elements and compounds. However, landfill leachates with a relatively high COD's often experiences blockage with membranes thus, making it utterly incompatible with membrane related methods such as Electrodialysis and Ultrafiltration.

As a result, physiochemical treatments exist not only for removing refractory substances from the leachate, but also, it is considered as a refining pre-treatment which is required before biological treatment is conducted (Ozturk et al, 2003).

Methods of physico-chemical means besides membrane process are coagulation-flocculation, adsorption, air stripping, chemical precipitation, chemical oxidation process and many others (Melike et al, 2007).

Focusing on coagulation-flocculation, this process manipulates the coagulants, experimental conditions, and pH in order to optimize the treatment operation. Jar test experiments were conducted in order to determine the optimum conditions to remove organic matter and colour (Tatsi et al, 2003).

The percentage of COD and TOC removal obtained by this process is 10-25% with young leachates but is at a much higher percentage of 50-60% for mature leachates (Amokrane et al, 1997). Aluminium sulfate (alum), ferrous sulfate and ferric chloride are commonly used as coagulants (Uygur et al, 2004).

Alternatively, chemical oxidation is necessary for the treatment of wastewater containing soluble organic which cannot be eliminated via physical separation, non-biodegradable and/or toxic substance (Marco et al, 1997). Chemical oxidation has the advantage of organic substances being almost completely removed which is something that biological treatment on its own will not be able to achieve. Hydrogen peroxide/UV, ozone and ozone/fixed bed catalyst processes were used to successfully purify pre-treated leachates (Steensen, 1997).

In an experiment done on leachates from Tehran's landfill where coagulation-flocculation and ozonation processes were combined, the result showed that the BOD/COD ratio is increased from 0.36 to 0.45 and the BOD was also successfully increased to 10%. However, the COD profile remained constant as the organic matters in the leachate was hard to oxidize. (Jamali et al, 2009).

Treatment process	Young leachate	Medium leachate	Old leachate	Space utilization	Installation and operational cost	Requiring less skilled personnel
Biological						
Activated sludge	Good	Fair	Poor	Poor	Expensive	No
RBC	Good	Fair	Poor	Good	Expensive	Yes
SBR	Good	Fair	Poor	Good	Less expensive	No
Reed beds	Fair	Fair	Good	Poor	Less expensive	Yes
BAF	Good	Fair	Fair	Good	Expensive	Yes
Lagoons	Good	Fair	Poor	Poor	Expensive	Yes
UASB	Good	Fair	Fair	Good	Less expensive	Yes
AF	Good	Fair	Fair	Good	Expensive	Yes
MBBR	Good	Fair	Poor	Poor	Expensive	No
MBR	Good	Fair	Fair	Poor	Expensive	No
Physicochemical						
Coag. & flocculation	Poor	Fair	Fair	Fair	Less expensive	No
Precipitation	Poor	Fair	Poor	Fair	Less expensive	No
Adsorption	Poor	Fair	Good	Good	Less expensive	No
Flotation	Poor	Fair	Fair	Poor	Expensive	Yes
Chem. Oxidation	Poor	Fair	Fair	Good	Expensive	No
Ammonia stripping	Poor	Fair	Fair	Poor	Expensive	No
Membrane process						
Microfiltration	Poor	Poor	Poor	Good	Expensive	Yes
Ultrafiltration	Fair	Fair	Fair	Good	Expensive	Yes
Nanofiltration	Good	Good	Good	Good	Expensive	Yes
Reverse Osmosis	Good	Good	Good	Good	Expensive	Yes

Table 2 : Comparison of treatment processes available

2.3 Bukit Tagar Landfill

Bukit Tagar Landfill is located 40km north of the Malaysian capital, Kuala Lumpur. Construction began in the year 2004 and the site started operating in April 2005. In the first year of operation, they received about 0.584 Mt of municipal solid waste and generated about 500-700 m^3 of leachate daily (Kortegast et al. 2007).

The landfill has high density polyethylene membrane as the base liner as well as a multilayer system to ensure the complete separation of waste from the ground. The waste disposal in Bukit Tagar Landfill is highly mixed municipal solid waste which is not source separated (Agamuthu et al, 2009).

Figure 2 : Entrance of Bukit Tagar Landfill

Figure 3 : Bukit Tagar Landfill

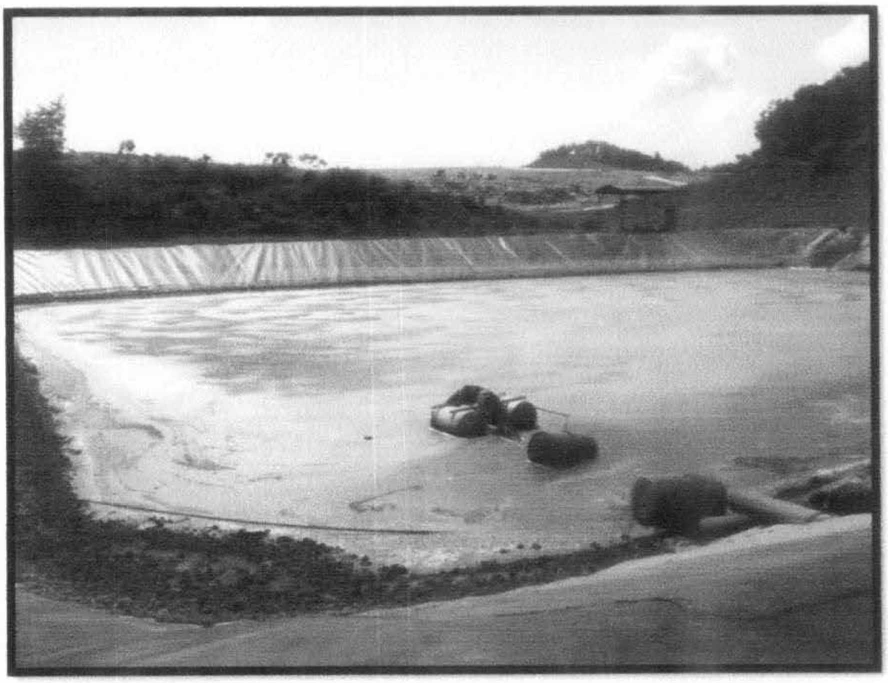


Figure 4 : Leachate pond at Bukit Tagar

2.4 Leachate Treatment at Bukit Tagar Landfill

In Malaysia, discharges of treated wastewaters into surface watercourses are controlled by a set of national quality criteria known as Standards A and B. At Bukit Tagar, Standard B is applied and the treated leachate quality complies with every limit, except that of 100 mg/L for COD.

The treatment that leachates at Bukit Tagar landfill undergoes are :

1) Biological Treatment

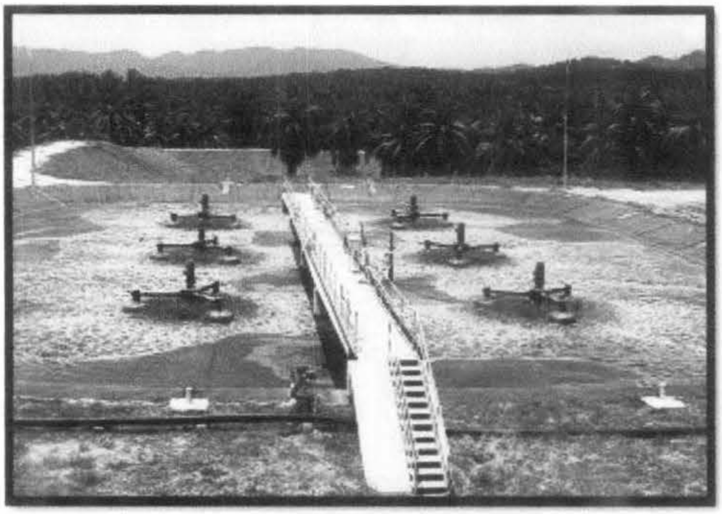


Figure 5 : Floating Surface Aerators in HDPE-lined lagoon.

The picture above shows the six floating surface aerators in each of the 4 HDPE-lined lagoons in Bukit Tagar Landfill. These aerators' function is to provide oxygenation and mixing of solids. It is in these lagoons that the biological removal of biodegradable COD and nitrification of ammoniacal-N will take place.

2) DAF Treatment

Effluent will then pass through a dissolved air flotation (DAF) plant to remove almost all residual suspended solids and some colloidal COD material. On site testing is also conducted by dosing with polyelectrolyte and flocculant solution.

3) Reed Bed Polishing

Effluent from the DAF treatment is then polished by passage through one of two banks of four reed beds. These beds are lined with HDPE and filled with gravel.

Figure 6 : Part of the extensive Reed Bed Polishing System

Figure 7 : Leachate after the Reed Bed Polishing Treatment

4) Effluent Irrigation

Reed bed effluent flows by gravity to a storage lagoon. There, it is pumped into a high level header lagoon which feeds the extensive palm oil irrigation scheme (Kortegast et al, 2007)

Figure 8 : Machine at the HDPE-lined lagoon

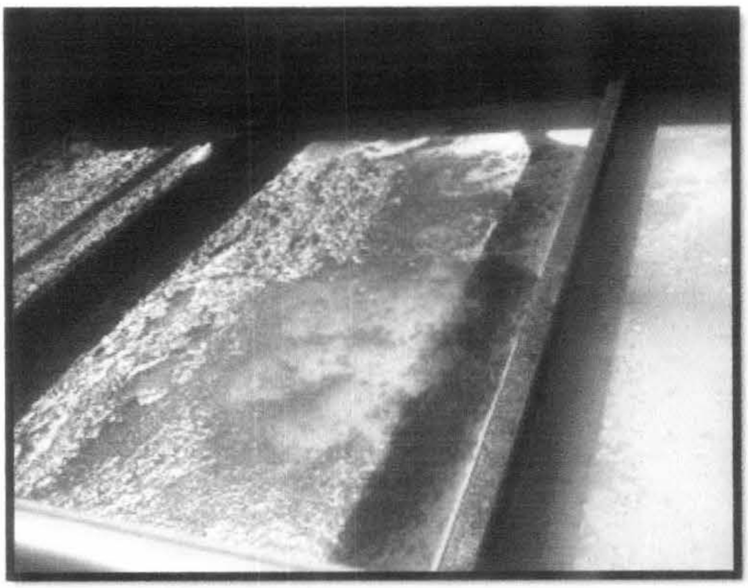


Figure 9 : Processed Leachate

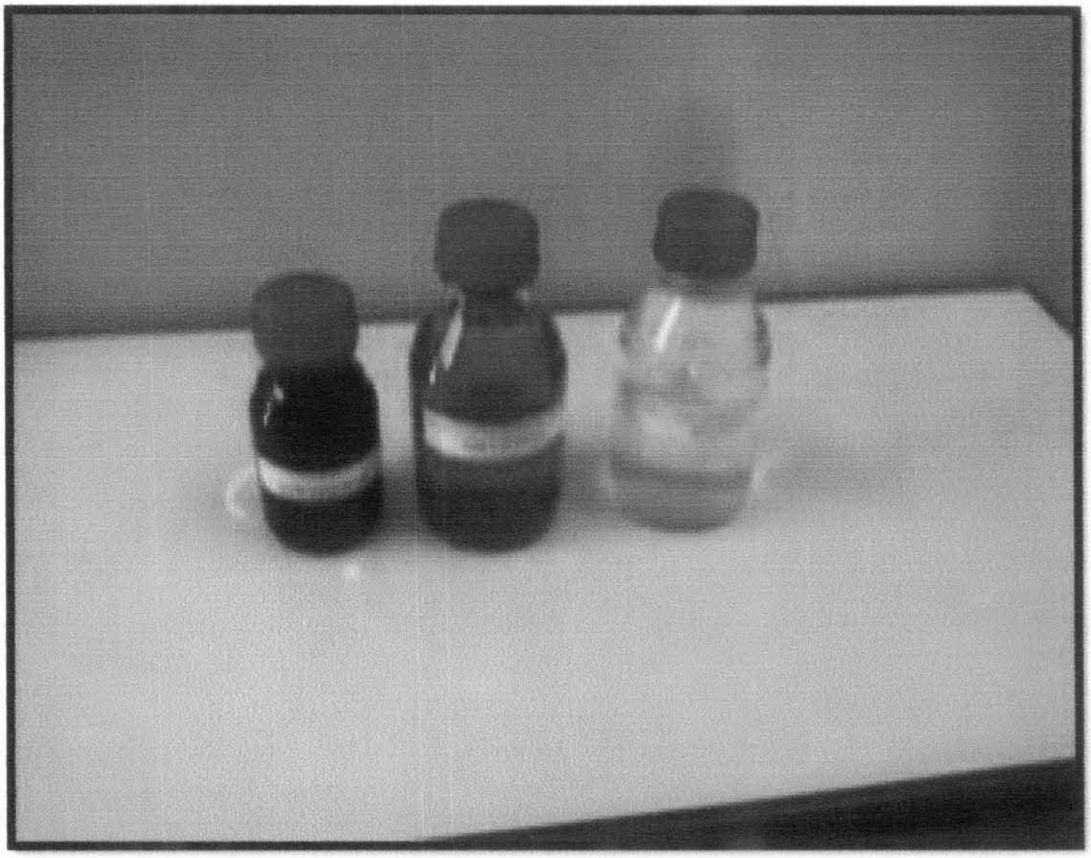


Figure 10 : Leachate sample before, during and after the treatment process

2.5 Advanced Oxidation Process (AOP)

On the other hand, there is also the method of Advanced Oxidation Processes (AOP). AOP is a set of chemical treatment procedures designed to remove organic and inorganic materials in wastewater via oxidation. AOP is a process in which the oxidative capacity of a parent compound is modified in order to make oxidation-reduction reactions more rapid or complete (Mofidi et al. 2002). It is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents and volatile organic compounds. The contaminants will be converted into stable inorganic compounds such as water, carbon dioxide and salts.

By means of AOP, contaminants are oxidized by four different reagents which are ozone, hydrogen peroxide, oxygen and air. The oxidation by these reagents are conducted in precise, pre-programmed dosages, sequences and combinations. The main purpose of AOPs is to enhance chemical oxidation efficiency by increasing generation of hydroxyl radicals (Huang et al. 1993).

AOP offers a powerful treatment solution for the reduction of residual organic compounds as measured by COD, BOD or TOC. As mentioned above, AOP produces hydroxyl radicals. It is these that act with high efficiency to destroy organic compounds.

Oxidizing Agent	EOP (V)
Hydroxyl Radical	**2.80**
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

Table 3 : Oxidizing power of hydroxyl radicals versus other oxidants

The AOP is successfully used to decompose many hazardous chemical compounds to acceptable levels, without producing additional hazardous by-products or sludge which require further handling.

Advantage	Disadvantage
Rapid reaction rates	Capital intensive
Potential to reduce toxicity and possibly complete mineralization of organics treated	Complex chemistry must be tailored to specific application
Does not concentrate waste for further treatment methods such as membranes	
Does not produce materials that require further treatment such as 'spent carbon' from activated carbon absorption	
Does not create sludge	

Table 4 : Advantages and disadvantages of AOP

Several methods are available for generating OH radicals. These include both non-photochemical and photochemical methods (Munter, 2001). They are :

- Ozonation at elevated pH (>8.5)
- Ozone + hydrogen peroxide (O_3/H_2O_2)
- Ozone + catalyst
- O_3/UV
- H_2O_2/UV
- O_3/H_2O_2/UV
- Photocatalytic oxidation (UV/TiO_2)
- Fenton Process (H_2O_2/Fe^{2+})
- Photo-Fenton Process (H_2O_2/Fe^{2+}/UV)

2.5.1 Fenton Process

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

$$Fe^{3+} + H_2O_2 \underset{(a)}{\overset{-H^+}{\rightleftharpoons}} Fe - O_2H^{2+} \underset{(b)}{\rightleftharpoons} Fe^{2+} + HO_2\cdot$$

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + H^+ + O_2$$

(Fenton Process)

In Fenton Process illustrated above, the method requires adjusting the wastewater to pH 3-5, then the addition of iron catalyst as well as hydrogen peroxide.

According to Munter, the rate constant for the reaction of ferrous ion with hydrogen peroxide is high and Fe(II) oxidizes to Fe(III) in a few seconds to minutes in the presence of excess amount of hydrogen peroxide. Hydrogen peroxide decomposes catalytically by Fe(III) and generates hydroxyl radicals yet again as could be seen in the second equation above.

It has been proven that Fenton process is able to annihilate different phenols, nitrobenzene and herbicides in sample as well as reduce COD (Esplugas et al. 1998).

The usage of Fe (II) and hydrogen peroxide as an oxidant is appealing because :

1) Iron is a highly abundant and non-toxic element
2) Hydrogen peroxide is easy to handle and environmentally benign (Munter, 2001).

However, the Fenton process consumes one molecule of Fe^{2+} for each OH radical produced, thus demanding a high concentration of Fe(II).

Photo-Fenton on the other hand, is the combination of Fenton reaction in UV(ultraviolet light) and has been shown to enhance the efficiency of the Fenton Process (Feng et al. 2003).

2.5.2 Photo-Fenton Process

$$Fe^{2+}{}_{aq} + H_2O_2 \Rightarrow Fe^{3+}{}_{aq} + OH^- + OH^\bullet$$

$$Fe^{3+}{}_{aq} + H_2O + h\nu \Rightarrow Fe^{2+}{}_{aq} + H^+ + OH^\bullet$$

(Photo-Fenton Process)

In further detail, the UV irradiation in photo-Fenton process will enhance the reduction of Fe^{3+} to Fe^{2+} and the resulting Fenton reaction, as well as the photolysis of H_2O_2 (hydrogen peroxide) directly to OH (Deng et al. 2006). Photo-Fenton produces more hydroxyl radicals in comparison to the conventional Fenton process, thus promoting the degradation of organic pollutants (Primo et al. 2007).

Photo-Fenton process relies on the UV irradiation to initiate the generation of hydroxyl radical. According to Sun et al, organic pollutants can be mineralized completely with UV/visible irradiation.

The higher production of hydroxyl radicals due to the combination of oxidant compounds and metallic catalysts in presence of UV radiation and the potention applicability of sunlight as UV light resource are sme attractive advantages of this system (Pignatello et al. 2006)

The application of both Fenton and photo-Fenton to landfill leachates will result in a 60-70% decrease in COD value (Sarasa et al. 2006). As this is an important key in the objective of this study, it can be said that photo-Fenton process has a high rate of efficiency.

2.6 Response Surface Methodology

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes (Myers et al, 2002). In RSM, a response of interest is influenced by several variables and the objective is to optimize this response (Montgomery, 2005).

The main principle of RSM is to use a sequence of designed experiments in order to obtain an optimal response. It is useful for the modeling and analysis of programmes in which a response of interest is influenced by several variables and the objective is to optimize this response.

$$y = f(x_1, x_2) + \varepsilon$$

The variables x_1 and x_2 in the equation above are independent variables in which the response y depend on. The dependent variable y is a function of x_1, x_2 and the experimental error team, denoted as ε. The error term represents any measurement error on the response, as well as other type of variations not counted in function f.

In most RSM problems, the true response function f is unknown. In order to develop a proper approximation for f, the experimenter usually starts with a low-order polynomial in some small region. If the response can be defined by a linear function of independent variables, then the approximating function is a first-order model. A first-order model with 2 independent variables can be expressed as :

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon$$

The first-order model is likely to be appropriate when the experimenter is interested in approximating the true response surface over a relatively small region of the independent variable space in a location where there is little curvature in the function (Carley et al, 2004).

However, if there is a curvature in the response surface, then a higher degree polynomial should be used (Bradley, 2007). The approximating function with 2 variables is called a second-order model and can be expressed as :

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_{11}^2 + \beta_{22} x_{22}^2 + \beta_{12} x_1 x_2 + \varepsilon$$

The second-order model is generally more widely used in RSM for a few reasons. First, the second-order model is very flexible. It can take on a wide variety of functional forms, so it will often work well as an approximation to the true response surface. Other than that, it is also easy to estimate the parameters (the βs) in the second-order model. The method of least squares can be used for this purpose (Carley et al, 2004).

Among the known usages of RSM are :

- To determine the factor levels that will simultaneously satisfy a set of desired specifications
- To determine the optimum factors that yield a desired response and describes the response near the optimum
- To determine how a specific response is affected by changes in the level of the factors over the specified levels of interest
- To achieve a quantitative understanding of the system behavior over the region tested.
- To find conditions for process stability

The application of RSM to design optimization is intended to reduce the cost of expensive analysis methods and their associated numerical noise.

CHAPTER 3

METHODOLOGY

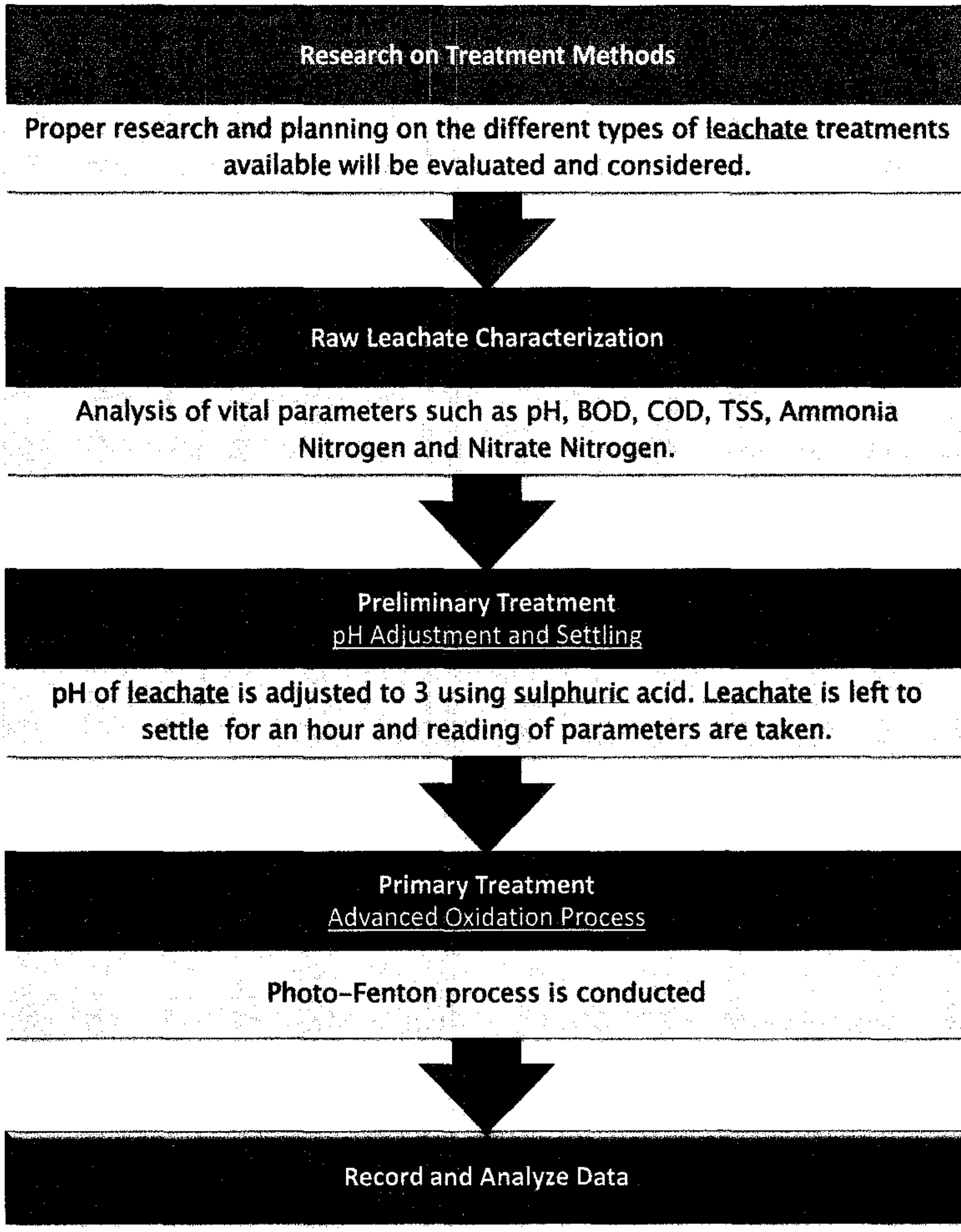


Figure 11 : Flow chart of Methodology

As mentioned in the study scope, proper research and planning on the different types of leachate treatments available will first be evaluated and considered.

The research will center mostly around physico-chemical treatments only as to resolve the objective of this study. Instead of making sure that the effluent from this study adheres to the limit set by DOE, this project focuses more on making the leachate sample amenable to biological treatment as secondary treatment.

When sufficient data and information has been obtained, the landfill leachate sample is then attained from the Bukit Tagar Landfill. This sample will be used in all the experiments that follow.

The preliminary characterization of landfill leachate sample is then conducted in order to analyze the parameters of the leachate sample. Some of the following parameters that will be tested according to methods outlined in Standard Methods (2005) are :

1. pH
2. Biochemical Oxygen Demand (BOD)
3. Chemical Oxygen Demand (COD)
4. Total Suspended Solids (TSS)
5. Ammonia Nitrogen
6. Nitrate Nitrogen

The procedures of the experiments that were done in order to obtain the parameters listed above are explained at length in the methodology parts below :

3.1 PH Test

i) Leachate sample is thoroughly mixed.

ii) PH meter is switched on.

iii) The electrode is thoroughly rinsed with DI water in order to remove all traces of storage solution, process medium, or previous test solution. The electrode is then blotted on a soft tissue to remove the excess of rinse water.

iv) The electrode is inserted in buffer solutions of pH 4, 7 and 10 to ensure precision of data.

v) Electrode is dipped in leachate sample.

vi) PH meter will display the pH reading of sample.

3.2 Biochemical Oxygen Demand (BOD)

i) Samples are poured into BOD bottles, along with blanks and seeds.

ii) The initial DO is measured using the DO probe that was equipped with a stirring mechanism.

iii) The BOD bottles are then placed in the refrigerator at 20°C for 5 days.

iv) After 5 days of incubation, the final DO is measured using the same DO probe that was used for the initial DO.

3.3 Chemical Oxygen Demand (COD)

i) Leachate sample is placed in a tube with pre-measured reagent and is mixed well.

ii) It is then digested for 2 hours at 150°C.

iii) Mixed sample is then left to cool down for 30 mins.

iv) Data is read using a spectrophotometer.

v) COD of sample is obtained.

3.4 Total Suspended Solids (TSS)

i) A 47mm filter disc is placed in the filter holder with the wrinkled surface upwards.

ii) 100ml of well mixed sample is filtered by applying vacuum to the flask.

iii) This is followed by three separate washings with deionized water.

iv) The filter disc is gently removed from the holder and placed on a pan.

v) The filter pan along with the filter are once again measured.

vi) They are then placed in a drying oven at 105°C for an hour.

vii) After drying, they are both weighed once again.

viii) From these data, the result for TSS is obtained.

3.5 Ammonia Nitrogen (NH_3-N)

i) 25mL of leachate sample is filled into a mixing graduated cylinder.

ii) 25mL of deionized water is mixed into another mixing graduated cylinder to act as blank.

iii) 3 drops of Mineral Stabilizer is added to each cylinder. Samples are inverted several times to allow it to mix well.

iv) 3 drops of Polyvinyl Alcohol Dispersing Agent Is added to each cylinder. Samples are inverted several times to allow it to mix well.

v) 1 mL of Nessler Reagent is pipetted into each cylinder. Samples are inverted several times to allow it to mix well.

vi) Leave it for one minute for the sample to react.

vii) Pour 10 mL of both the leachate sample and the blank into respective square sample cell.

viii) After one minute, the blank is inserted into cell holder and the button ZERO is pressed.

ix) After the reading has been zeroed, the leachate sample is inserted and the data is read.

3.6 Nitrate Nitrogen (NO_3-N)

i) A square sample cell is filled with 10mL of sample.

ii) NitraVer 5 Nitrate Reagent Powder Pillow is added to sample.

iii) Sample is shaken vigorously for one minute to react.

iv) The cell is left for five minutes to observe the reaction.

v) An amber colour should develop if nitrate is present in sample.

vi) A blank made of raw leachate sample is used to zero the meter.

vii) Sample is inserted into cell holder and the reading is taken.

Readings were taken consistently and on a steady basis so that the results will be accurate and precise. After each parameter has been characterized, subsequent research plans were made and the most suitable treatment arrangement will be drawn in order to come up with the most efficient combination treatment process yet.

After the raw leachate characterization has been carried out, the preliminary treatment of pH adjustment and settling is then conducted.

According to Heng et al, initially, as a pre-treatment, pH adjustment and settling will be conducted on the leachate sample. In this process, the pH of the sample will first be adjusted to several values, in a pH range of 2.5 - 8. Based on experiments that has been conducted, it was proven that the optimum pH is 3.

Using this fact as a guide, sulphuric acid will be added and the leachate will then be stirred until the pH becomes constant at 3. The sample will then be left to settle for several hours before parameter readings are taken.

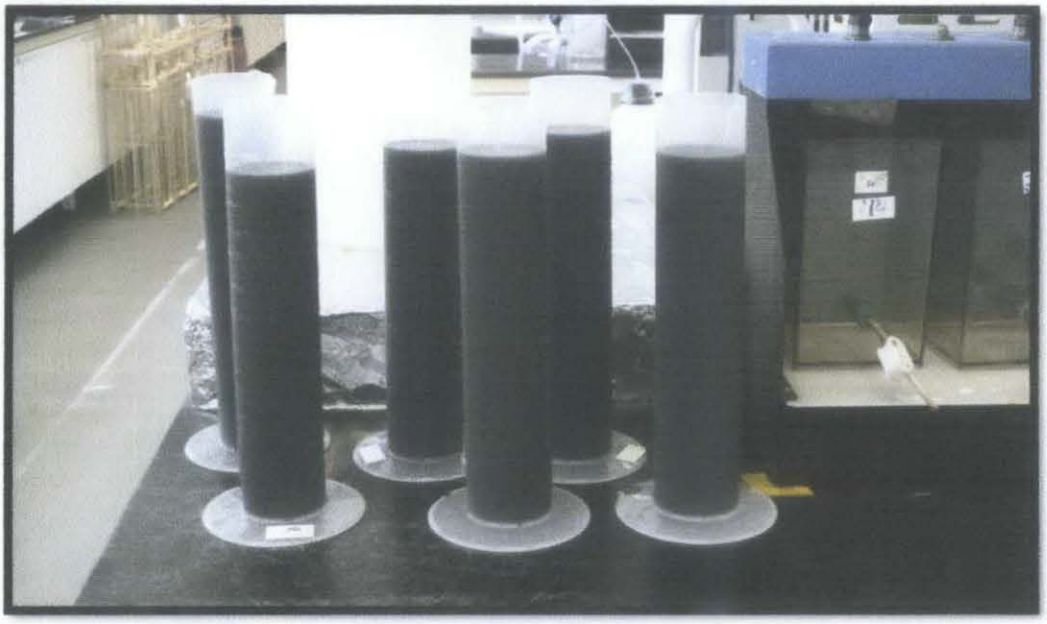


Figure 12 : Leachate that has been left to settle prior to preliminary characterization

Figure 13 : Supernatant being taken out with pipette

Figure 14 : Leachate sample are mixed well

Figure 15 : pH of leachate adjusted to 3 using Sulphuric Acid

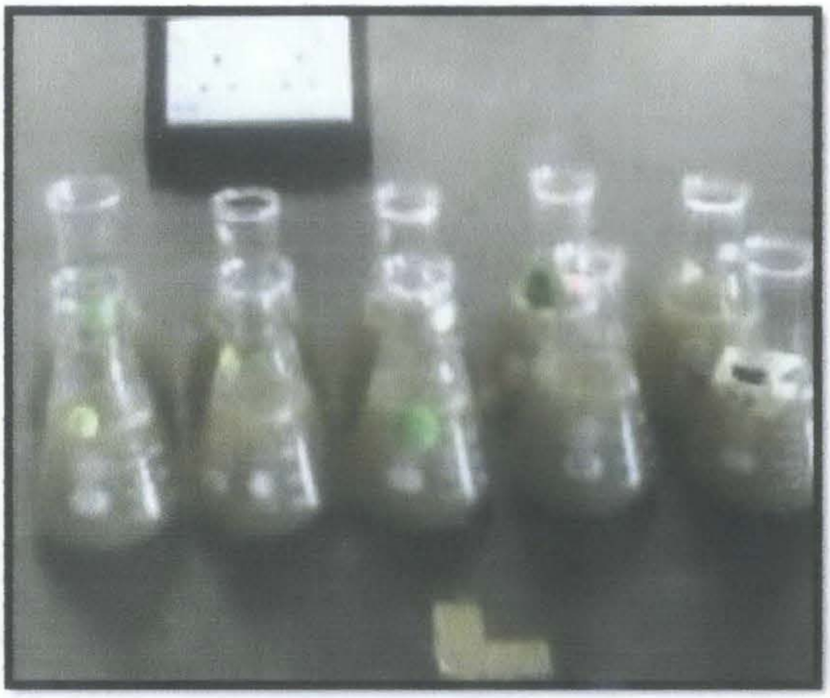


Figure 16: Leachate are left to settle after pH adjustment

Subsequent to this process, photo-Fenton process will be conducted as the primary treatment. For photo-Fenton, hydrogen peroxide and ferrous sulphate are added to the leachate that has gone through the preliminary treatment. It is then exposed under UV light to get an optimum result.

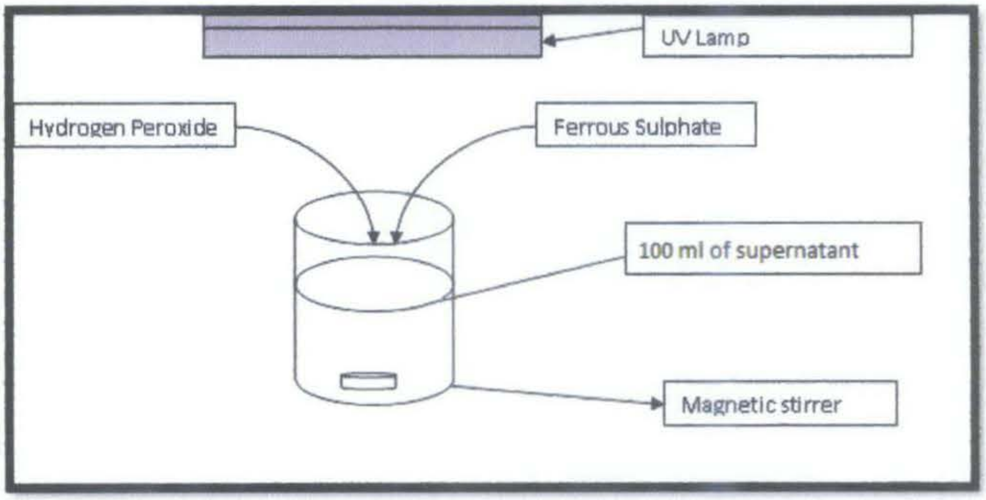


Figure 17 : Diagram of Photo-Fenton process

3.7 Photo Fenton Procedure

i. 100mL of preliminary treated leachate samples that has been adjusted to pH ~ 3 are placed in a 1000mL Pyrex reactor using

ii. Ferrous Sulphate ($FeSO_4.7H_2O$) and Hydrogen Peroxide (H_2O_2) are added to the leachate according to the selected H_2O_2 : COD and Fe^{2+} : H_2O_2 ratio (refer to Topic 3.8 : Response Surface Methodology).

iii. The mixture are continuously stirred to ensure complete homogeneity during reaction.

iv. At the same time, the sample are irradiated with a UV lamp that emits radiation of wave length ≈ 365 nm.

v. After the pre-selected reaction time is over, the pH of the sample is adjusted to be above 10 using sodium hydroxide and are mixed well.

vi. Sample are left overnight to settle.

vii. COD value of sample is measured.

Figure 18 : Photo Fenton process

3.8 Response Surface Methodology

In order to obtain the statistical design of experiments and data analysis, a software called Design Expert 6.0 is used. Response Surface Methodology was applied with the aim of optimizing the parameters which are the ratio of H_2O_2/COD, the ratio of H_2O_2/Fe^{2+} as well as the reaction time.

As mentioned in topic 2.6, the second-order model is more widely used in RSM for reasons that have been previously stated. Thus, a total of 20 experiments were prepared and the data were fixed to the second-order model of a suitable degree for the optimum conditions of leachate treatment using the photo-Fenton process.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_{11}^2 + \beta_{22} x_{22}^2 + \beta_{12} x_1 x_2 + \varepsilon$$

Relating the equation above to this particular research, with A as the ratio of H_2O_2/COD, B as the ratio of H_2O_2/Fe^{2+} and C as the reaction time, the equation can then be written as :

$$y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC$$

Exp	A : H_2O_2/COD	H2O2 volume (mL/0.1L sample)	B : H_2O_2/Fe^{2+}	FeSO4 volume (g/0.1L sample)	C : Reaction Time (Hour)
1	3	14.238	1.59	109.357	1.5
2	3	14.238	18.41	9.445	1.5
3	4.68	22.211	10	27.125	1.5
4	2	9.492	5	23.184	1
5	1.32	6.265	10	7.651	1.5
6	4	18.983	5	46.367	2
7	4	18.983	15	15.456	2
8	2	9.492	5	23.184	2
9	3	14.238	10	17.388	1.5
10	4	18.983	5	46.367	1
11	3	14.238	10	17.388	0.66
12	2	9.492	15	7.728	1
13	2	9.492	15	7.728	2
14	4	18.983	15	15.456	1
15	3	14.238	10	17.388	2.34
16	3	14.238	10	17.388	1.5
17	3	14.238	10	17.388	1.5
18	3	14.238	10	17.388	1.5
19	3	14.238	10	17.388	1.5
20	3	14.238	10	17.388	1.5

Table 5 : Experiment conditions set by Design Expert 6.0 Software

CHAPTER 4

RESULT

Parameters	Raw Leachate
COD	22600
BOD	13800
TSS	1100
Ammonia Nitrogen	2050
Nitrate Nitrogen	180
pH	7.4

Table 6 : Parameters of Raw Leachate

Parameters	Leachate after Preliminary Treatment
COD	14300
BOD	7370
TSS	639
Ammonia Nitrogen	1290
Nitrate Nitrogen	310
pH	3.0

Table 7 : Parameters of Leachate after Preliminary Treatment

Central Composite Design

To construct an approximation model that can capture interactions between N design variables, a full factorial approach (Montgomery, 2005) may be necessary to explore all possible combinations. A factorial experiment is a strategy wherein design variables are varied together instead of one at a time.

The lower and upper bounds of each N design variables in the optimization problem needs to be defined. The allowable range is then discretized at different levels. An experimental design is called 2^N full factorial when each of the variables are defined at the lower and upper bounds only. If the midpoints are also included, the design is called 3^N full factorial.

A second-order model can be constructed efficiently with central composite designs (CCD) (Montgomery, 2005). CCD are first-order designs enhanced by additional centre and axial points to allow estimation of the tuning parameters of a second-order model.

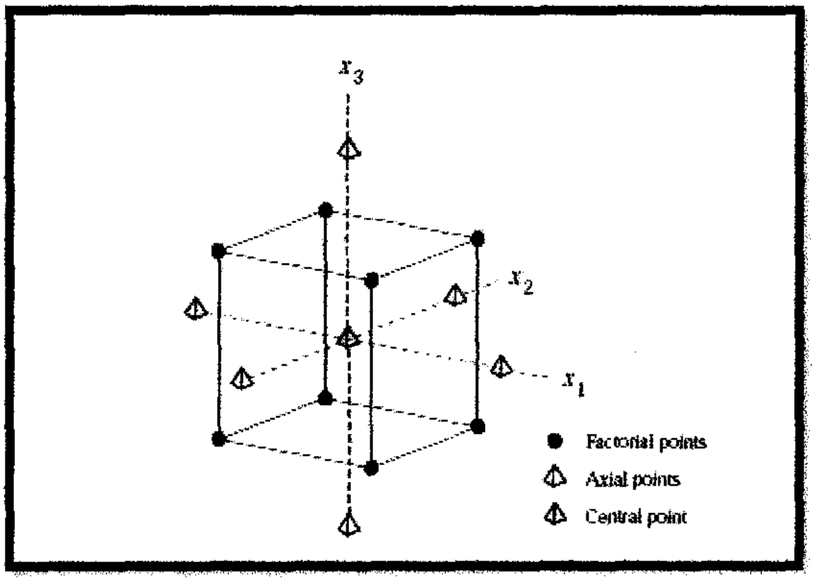


Figure 19 : Central composite design for 3 design variables at 2 levels

This CCD stands as an alternative to 3^N designs in the construction of second-order models because the number of experiments is reduced in comparison to a full factorial design. Instead of 27 experiments in a full-factorial design, only 15 experiments are conducted with and additional 5 experiments that act as replicates of the central point.

Run	Block	Factor 1 A:H2O2/COD	Factor 2 B:H2O2/Fe2+	Factor 3 C:Reaction Time Hour	Response 1 COD Removal %
1	Block 1	3.00	1.59	1.50	76.9
2	Block 1	3.00	18.41	1.50	52.4
3	Block 1	4.68	10.00	1.50	61
4	Block 1	2.00	5.00	1.00	68.5
5	Block 1	1.32	10.00	1.50	29.7
6	Block 1	4.00	5.00	2.00	72.3
7	Block 1	4.00	15.00	2.00	50.1
8	Block 1	2.00	5.00	2.00	62.2
9	Block 1	3.00	10.00	1.50	65.1
10	Block 1	4.00	5.00	1.00	63.6
11	Block 1	3.00	10.00	0.66	51.8
12	Block 1	2.00	15.00	1.00	38
13	Block 1	2.00	15.00	2.00	54.4
14	Block 1	4.00	15.00	1.00	52
15	Block 1	3.00	10.00	2.34	64.7
16	Block 1	3.00	10.00	1.50	60.4
17	Block 1	3.00	10.00	1.50	66.5
18	Block 1	3.00	10.00	1.50	60.9
19	Block 1	3.00	10.00	1.50	54.7
20	Block 1	3.00	10.00	1.50	74.7

Table 8 : Central Composite Design (CCD) for The Operating Conditions of Photo-Fenton Process

FACTOR	NAME	RANGE
A	H_2O_2/COD	1.32 – 4.68
B	H_2O_2/FE^{2+}	1.59 – 18.41
C	Reaction Time	0.66 – 2.34

Table 9 : Range of Parameters

ANOVA Table

Analysis of Variance (ANOVA) is a statistical test used to determine if more than two population means are equal. The test uses the F-distribution (probability distribution) function and information about the variances of each population and grouping of populations to help decide if variability between and within each populations are significantly different.

The ANOVA table that has been produced by the Design Expert Software gives a Model F-value of 3.75 and Prob > F values that are less than 0.05 which gives an indication that the model terms are significant. The 'Lack of Fit F value' of 1.54 implies that the Lack of Fit is not significant relative to the pure error.

The coefficient of determination (R^2) is defined as the ratio of the sum of squares. It refers to the proportion of the variation in the dependent variable accounted for by the independent variable. If R^2 is equal to 0, then there is no linear relationship between the dependent and independent variables. If it is equal to 1, the relationship is perfect and all values of the dependent and independent variables lie on a straight line.

The R^2 value obtained is 0.7714 which basically indicates that 77.14% of the variance of either variable is shared with the other variable.

Adequate precision (A.P) evaluates and compares the range of the predicted values at the design points to the average prediction error. It is essentially a measurement of the signal to noise ratio. A ratio greater than 4 (> 4) is desirable as it is an indication of adequate model discrimination. The value obtained for A.P is 7.678 which means that this model can be used to navigate the design space.

The coefficient of variance (C.V.) is the ratio of the standard error of estimate to the mean value of the observed response.

Response	R^2	Adequate Precision (A.P.)	Probability of Lack-of-Fit (PLOF)	Coefficient of Variance (C.V.)
	0.7714	7.678	0.3231	12.98

Table 10 : ANOVA for Response Surface Quadratic Model

The final equation in terms of actual factors tabulated by Design Expert Software is :

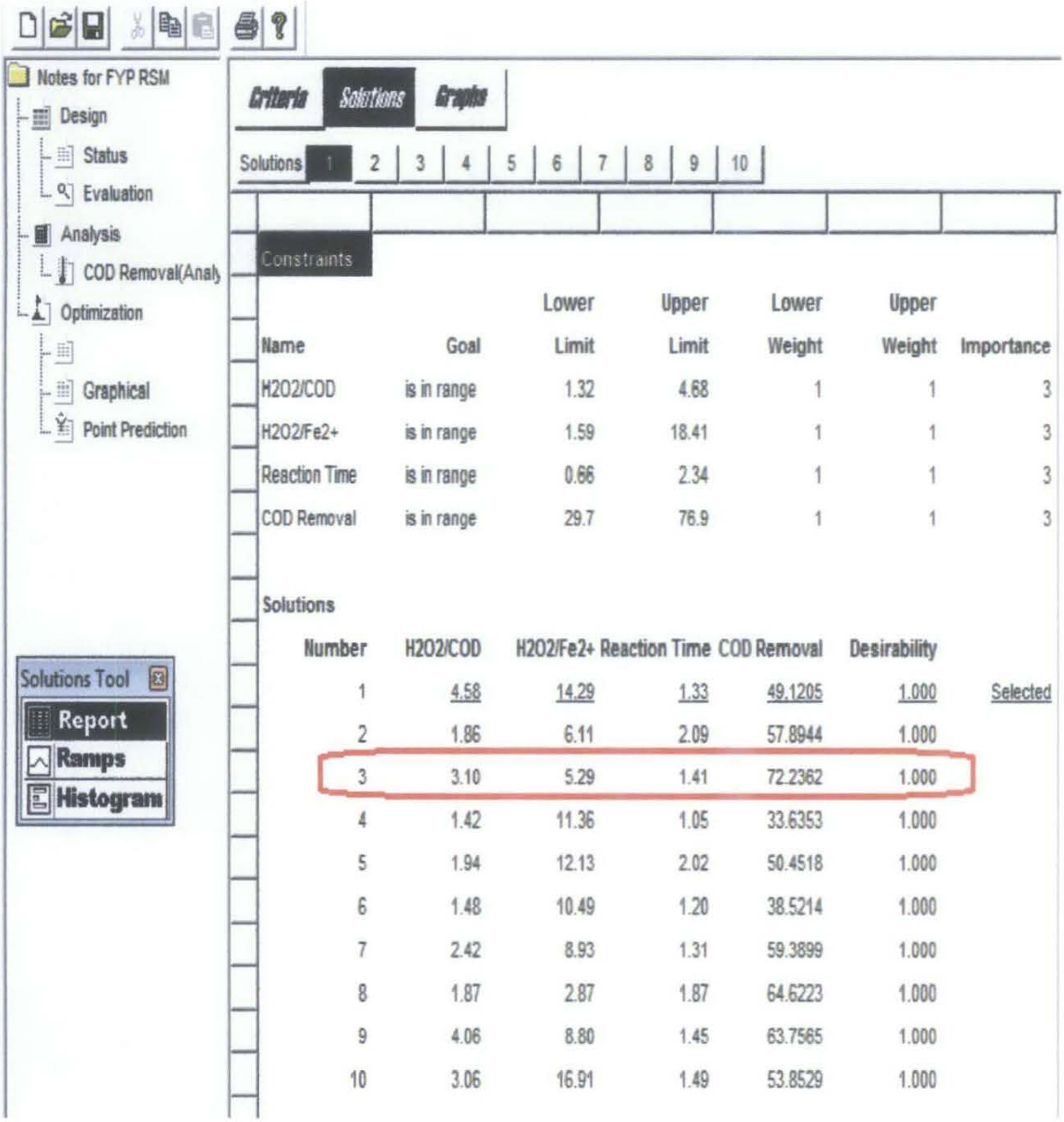
COD Removal = +0.45769 + (41.51650 * H_2O_2/COD) – (3.51141 * H_2O_2/Fe^{2+}) + (20.14825 * Reaction Time) – (6.07637 * H_2O_2/COD^2) + (0.030360 * H_2O_2/Fe2+^{2}) – (6.02317 * Reaction Time^2) + (0.11250 * H_2O_2/COD * H_2O_2/Fe^{2+}) – (0.82500 * H_2O_2/COD * Reaction Time) + (0.60500 * H_2O_2/Fe^{2+} * Reaction Time)

In simpler terms,

COD Removal = +0.45769 + 41.51650A - 3.51141B + 20.14825C - 6.07637(A^2) + 0.030360(B^2) - 6.02317(C^2) + 0.11250AB - 0.82500AC + 0.60500BC

Optimum Conditions

The optimum conditions for maximum value of the response were credited to H_2O_2/COD ratio, H_2O_2/Fe^{2+} ratio as well as the reaction time. The optimum points that give maximum response are 3.10 for H_2O_2/COD ratio, 5.29 for H_2O_2/Fe^{2+}, and 1.41 hours of Reaction Time to give 72.24% of COD Removal.



Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
H2O2/COD	is in range	1.32	4.68	1	1	3
H2O2/Fe2+	is in range	1.59	18.41	1	1	3
Reaction Time	is in range	0.66	2.34	1	1	3
COD Removal	is in range	29.7	76.9	1	1	3

Solutions

Number	H2O2/COD	H2O2/Fe2+	Reaction Time	COD Removal	Desirability	
1	4.58	14.29	1.33	49.1205	1.000	Selected
2	1.86	6.11	2.09	57.8944	1.000	
3	3.10	5.29	1.41	72.2362	1.000	
4	1.42	11.36	1.05	33.6353	1.000	
5	1.94	12.13	2.02	50.4518	1.000	
6	1.48	10.49	1.20	38.5214	1.000	
7	2.42	8.93	1.31	59.3899	1.000	
8	1.87	2.87	1.87	64.6223	1.000	
9	4.06	8.80	1.45	63.7565	1.000	
10	3.06	16.91	1.49	53.8529	1.000	

Figure 20 : Print Screen of Optimum Conditions

Response Surface Plots

The response surface plots for COD removal are shown in the form of two-dimensional contour plots.

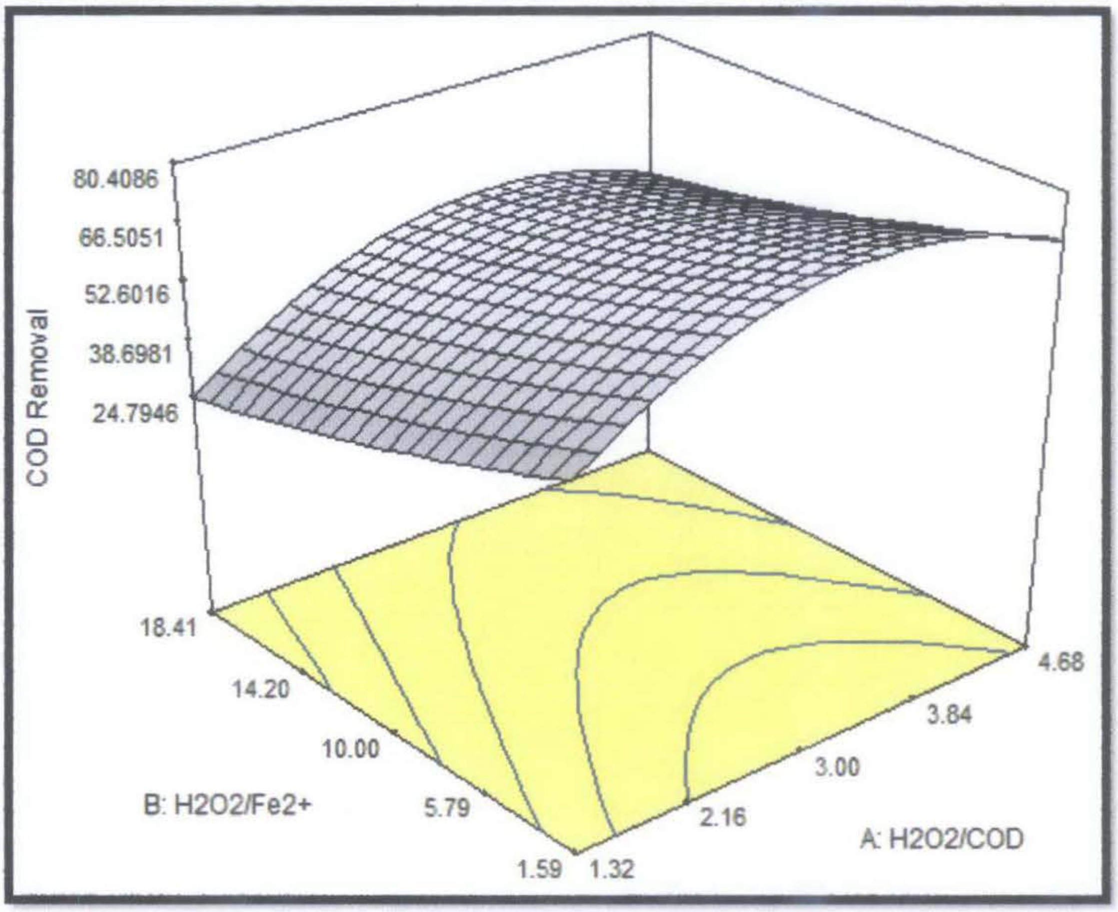


Figure 21 : Response (COD removal) on the H_2O_2/COD ratio and H_2O_2/Fe^{2+} ratio

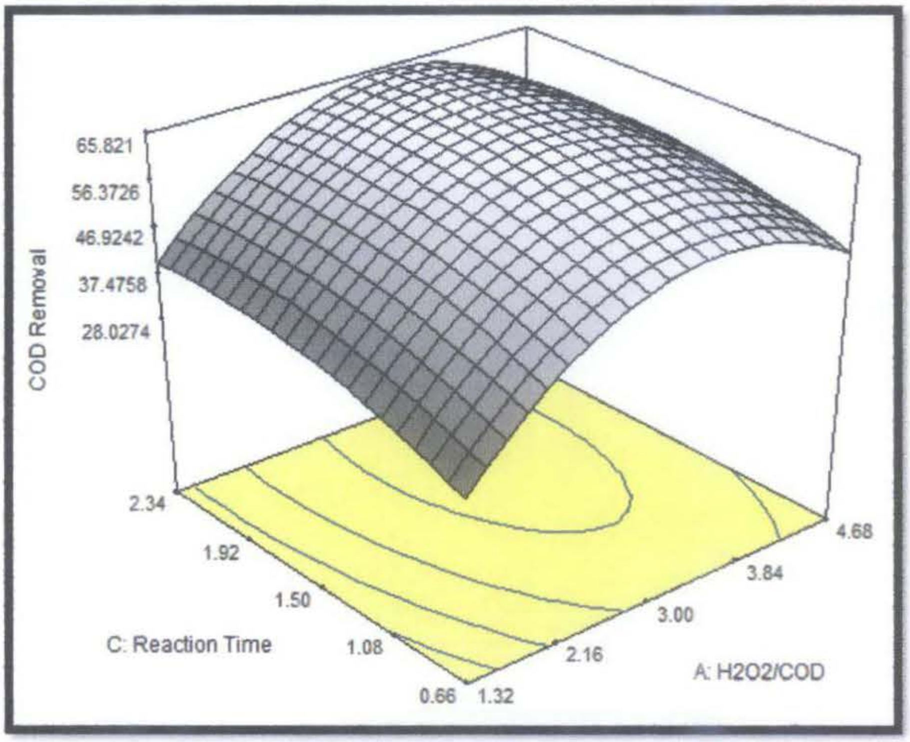


Figure 22 : Response (COD removal) on the H_2O_2/COD ratio and Reaction Time

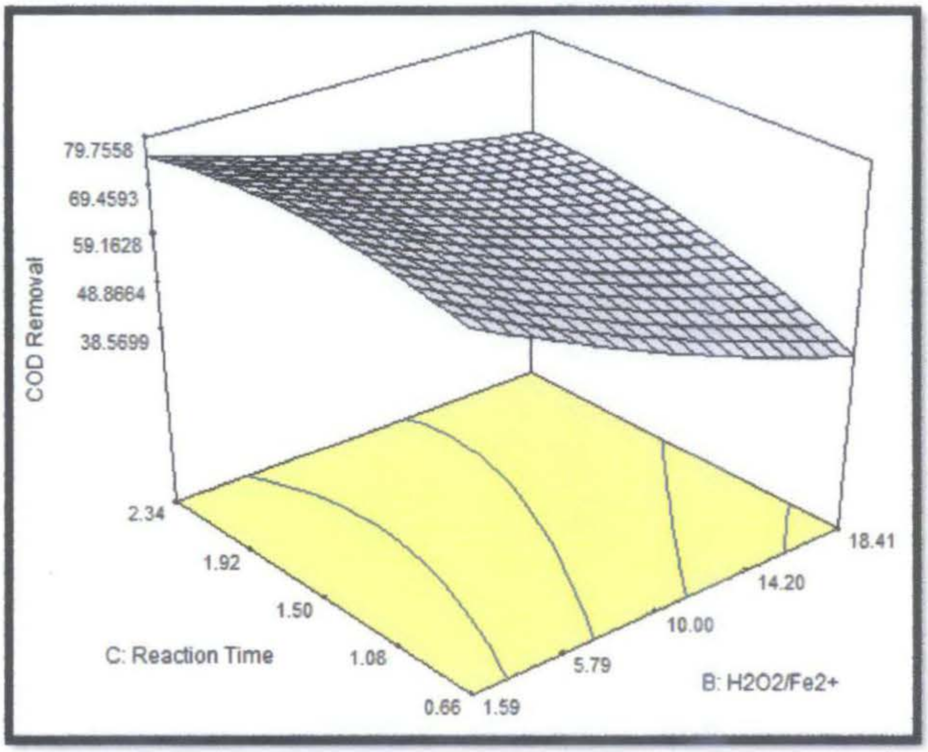


Figure 23 : Response (COD removal) on the H_2O_2/Fe^{2+} ratio and Reaction Time

CHAPTER 5

CONCLUSION

The problem concerning leachate is obviously a hazard to humankind, animals as well as plants. Therefore, proper treatment approaches has to be taken to curb this problem from turning into a bigger crisis.

It has been acknowledged that the two methods available for leachate treatment which are the biological methods and physical and chemical methods are simply insufficient to solve this problem when it is standalone. The combination of biological and physico-chemical treatment methods are bound to be more effective than if it was done singularly.

For example, the leachate in Bukit Tagar is solely biologically treated and the final effluent still shows a COD of more than 100. This clearly shows that it does not adhere to the limit set by the Department of Environment.

The preliminary and primary treatment suggested will enable the sample to be further treated biologically. Seeing as the removal percentage of COD is already high, it can be said that with the combination of preliminary, primary and biological treatment will make the leachate effluent amenable to biological treatment.

CHAPTER 6

ECONOMIC BENEFITS

This research is experiment-based and thus the expenses are largely allocated for equipment and apparatus. Other than that, a portion of the expenditure also gave to the travelling cost to obtain the sample needed for this research.

Initially, the project requires leachate sample collection from Bukit Tagar Landfill which is quite far from the premise of Universiti Teknologi Petronas. The breakdown of the expenses is as shown below :

Petrol : RM80 (two ways UTP – Bukit Tagar)

Toll : RM40 (two ways UTP – Bukit Tagar)

Container for Leachate : RM80.40 (3 containers)

Total cost : RM 200.40

As for the leachate itself, no expense were necessary as the sample was provided generously by the management of Bukit Tagar Landfill itself. Other than that, no of the expenditures were needed as the experiments were conducted in the Environment Lab of Civil Department and all the materials and apparatus used are already available.

The purpose of this research is to find efficient treatment methods that will make it amenable to biological treatment. In terms of business, this is important as it might bear a solution that will increase the efficiency of current leachate treatment.

Currently, there are plenty of options for treatment methods but its efficiency varies with the combination of procedures done. This research will add on to the combination that will hopefully enhance the technological growth of known leachate treatment methods.

REFERENCES

1. Agamuthu, P., Al-Abdali, S. N. A. (2009). "Physico-chemical treatment of Bukit Tagar sanitary landfill leachate using P-Floc775 and Ferric Chloride." Malaysian Journal of Science 28 : 2 : 187-195

2. Amokrane, A., Comel, C., Veron, J. (1997). "Landfill Leachate Pretreatment by Coagulation-Flocculation." Water Research 31 : 11 : 2775-2782

3. Bradley, N. (2007). "The Response Surface Methodology." Department of Mathematical Sciences, Indiana University of South Bend

4. Carley, K. M., Kamneva, N. Y., Reminga, J. (2004) "Response Surface Methodology ." CASOS Technical Report, School of Computer Science, Carnegie Mellon University, CMU-ISRI-04-136

5. Deng, Y., Englehardt, J. D. (2006). "Treatment of Landfill Leachate by the Fenton Process." Water Research 40 : 3683-3694

6. Esplugas, S., Marco, A., Chamarro, E. (1998). "Use of Fenton Reagent to Improve the Biodegradability of Effluents". Proceedings of International Registry Conference of Ozonation and AOPs in Water Treatment, Poitiers, France.

7. Feng, J., Hu, X., Yue, P. L., Zhu, H. Y., Lu, G. Q. (2003). "Discoloration and Mineralization of Reactive Red HE-3B by Heterogeneous photo-Fenton Reaction." Water Research 37 : 15 : 3776-3784

8. Forgie, D.J.L. (1988). "Selection of the Most Appropriate Leachate Treatment Methods. Part 2: A review of recirculation, irrigation and potential physical-chemical treatment methods." Water Pollution Research Journal of Canada, 23: 2 : 329-341

9. Huang, C. P., Dong, C., Tang, Z., (1993). "Advanced Chemical Oxidation: Its present role and potential future in hazardous water treatment." Waste Management 13 : 361-377

10. Heng, G. C., Elmolla, E. S., Chaudhuri, M. (2009) "Physicochemical Pretreatment of Landfill Leachate." In : Second International Conference on Engineering Technology (ICET 2009), 8-10 December 2009, Kuala Lumpur.

11. Jamali, H. A., Mahvi, A. H., Nabizadeh, R., Vaezi, F., Omrani, G. A. (2009). "Combination of Coagulation-Flocculation and Ozonation Processes for Treatment of Partially Stabilized Landfill Leachate of Tehran." World Applied Sciences Journal Volume 5 (Special Issue for Environment) : 9-15

12. Kortegast, A. P., Eldridge, S. F., Richards, B. A., Yong, S., Chock, E. T., Bryce, A., Robinson, H., Carville, M. (2007) "Leachate Generation and Treatment at the Bukit Tagar Landfill, Malaysia." Eleventh International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy.

13. Kouezeli-Katsiri, A., Bosdogianni, A., Christoulas, D. (1999). "Prediction of Leachate Quality from Sanitary Landfills." Environment International 29 : 15 : 593-600

14. Laitinen, N., Luonsi, A., Vilen, J. (2005). "Landfill Leachate Treatment with Sequencing Batch Reactor and Membrane Bioreactor." Desalination 191 : 1-3 : 86-91

15. Marco, A., Esplugas, S., Saum, G. (1997). "How and Why Combine Chemical and Biological Processes for Wastewater Treatment." Water Science and Technology 35 : 4 : 321-327

16. Melike, Y. K., Kadir, K., Taner, Y. (2007). "Landfill Leachate Treatment by the Combination of Physicochemical Methods with Adsorption Process." Journal of Biological Environment Science 1: 1 : 37-43

17. Mofidi, A. A., Min, J. H., Palencia, L. S., Coffey, B. M., Liang, S., Green, J. F. (2002). "Advanced Oxidation Processes and UV Photolysis for Treatment of Drinking Water." California Energy Commission Mid Year Report

18. Montgomery, D. C. (2005). "Design and Analysis of Experiments : Response Surface Method and Designs." John Wiley and Sons, Inc., New Jersey

19. Munter, R. (2001). "Advanced Oxidation Process – Current Status and Prospects". Proceedings of Estonian Academic Science Chemistry 50 : 2 : 59-80

20. Myers, R. H., Montgomery, D. C. (1995). "Response Surface Methodology : Process and Product Optimization Using Designed Experiment." Wiley-Interscience Publication, New York

21. Ozturk, I., Altinbas, M., Koyuncu, I., Arikan, O., Gomec-Yangin, C. (2003). "Advanced Physico-chemical Treatment Experiences on Young Municipal Landfill Leachates." Waste Management 23 : 441-446

22. Pignatello, J., Oliveros, E., MacKay, A. (2006). "Advanced Oxidation Processes for Organic Contaminant Destruction Based On The Fenton Reaction and Related Chemistry." Critical Reviews in Environmental Science and Technology 36 : 1-84

23. Primo, O., Rivero, M. J., Ortiz, I. (2007). "Photo-Fenton Process as an Efficient Alternative to The Treatment of Landfill Leachates." Journal of Hazardous Materials 153 : 834-842

24. Sarasa, J., Llabres, T., Ormad, P., Mosteo, R., Ovelleiro, J. L. (2006). "Characterization and photo-Fenton Treatment of Used Tires Leachate." Journal of Hazardous Materials B136 : 874-881

25. Steensen, M. (1997). "Oxidation Technologies for Water and Wastewater Treatment." Water Science and Technology 35 : 4 : 249-256.

26. Sun, Y., Pignatello, J. J. (1993). "Photochemical Reactions Involved in the Total Mineralization of 2,4-D by $Fe^{3+}/H_2O_2/UV$". Environmental Science and Technology 27 : 304-310.

27. Tatsi, A. A., Zouboulis, A. I., Matis, K. A., Samaras, P. (2003). "Coagulation-Flocculation Pretreatment of Sanitary Landfill Leachates." Chemosphere 53 : 7 : 737-744.

28. Tchobanoglous, G., Theisen, H., Vigil, S. (1993). "Integrated Solid Waste Management: Engineering Principles and Management Issues." McGraw-Hill, Boston, Mass.

29. Uygur, A., Kargi, F. (2004). "Biological Nutrient Removal from Pre-Treated Landfill Leachate in a Sequencing Batch Reactor." Journal of Environmental Management 71: 1 : 9-14. Elsevier.

30. Wiszniowski, J., Robert, D., Surmacz-Gorska, J., Miksch, K., Weber J.V. (2006) "Landfill Leachate Treatment Methods : A review." Springer Berlin/Heidelberg 4: 1 : 51-61