

Fenton Oxidation of Leachate Effluents

by

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

JANUARY 2009

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CERTIFICATION OF APPROVAL

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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,

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2009

ABSTRACT

The objective of the project is to determine the removal efficiency of Chemical Oxygen Demand (COD) and the heavy metals by using Advanced Oxidation Process (AOP). The current methods of treating leachate are very high in cost. The simultaneous use of Fenton reagent for the treatment of leachate wastewaters generated during a hydrogen peroxide bleaching process is investigated. The experimental conditions tested during this study provide the simultaneous occurrence of Fenton reaction. The batch experimental results are assessed in terms of chemical oxygen demand (COD) reduction. Other pollution related features of the initial effluent like colour was also measured. A set of experiments was conducted under different reagent concentration with the aim to ensure the stable COD came at the end of experiments the combination of Fenton reaction has been proved to be highly effective for the treatment of such a type of wastewater and several advantages for the technique application arise from the study. Leachate from Pulau Burung Sanitary Landfill located in Pulau Pinang, non-hazardous landfill (pH 8.6; COD= 2600 mg 1-¹)was laboratory tested in different operative conditions, i.e., initial pH, Fe2+/H2O2 ratio, concentrations and reaction time. In this experiment, author change the weight of ferum (II) sulphate from 325.8 mg to 651.6 mg to see how the combination of three variables namely ferum (II) sulphate, pH adjustment and hydrogen peroxide react among them to treat to leachate sample. For the first part, the author used hydrogen peroxide without any combination with ferum (II) sulphate. However, it did not come out with good results because the result encountered with the purpose of project because COD value for all of samples increased immediately. The author believed that hydrogen peroxide acted as a stimulator in leachate sample. Maybe there are organic matters stimulated by hydrogen peroxide. As a result, the COD value rise beyond the original reading. The experiments' results have shown that low or high pH level, the possibility of COD removal efficiency is high. At the end of research and development, the author succeeded to achieve the highest total COD removal which is 37% of total COD removal

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.

HAZIM BIN HAJI HANIPA

TABLE OF CONTENTS

ABSTRACT		• •				•		•		i
CHAPTER 1	: INTR	ODUCTI	ON.							1
	1.1	Backgrou	ind of St	udy.						1
	1.2	Problem	Statemer	nt.						1
	1.3	Objective	s.	•						3
	1.4	Scope of	Study	ins after i	•	•	•	•		3
CHAPTER 2	: LITE	RATURE	REVIE	EW.						4
	2.1	Advanced	d Oxidat	ion Proce	ss .					4
	2.2	Ion Exch	ange .							5
	2.3	Chemical	Oxidati	on						5
	2.4	Advance	d Oxidat	ion Proce	ss of L	andfill l	Leachat	e.		6
	2.4	Treatmen	nt of Lan	dfill Leac	hate by	Sequer	ncing B	atch Re	actor	7
CHADTED 2	. MET		NCV.							
CHAI IEK S	2.1	Deservet	GY.	•	÷	•	•	•	•	14
	5.1 2.2	Preparatio	on of Le	achate Sa	mples	•	•	·	•	9
	3.2	Measurer	nent of (Chemical	Oxyge	n Dema	nd (CO	D).	•	10
	3.3	Fenton O	xidation	Process.	·	•	•	•	•	11
	3.4	Health, S	afety, an	d Enviror	nment A	Aspects	•	•	•	14
CHAPTER 4	: RESI	JLTS ANI	D DISC	USSION						15
	4.1	Character	rization							15
	4.2	The Fento	on Oxida	ation Labo	oratory	Test Re	sult			16
	4.3	pH Adjus	tment							18
false 3.3	100	e nemie da								
CHAPTER 5	: CON	CLUSION	AND F	RECOMN	AEND.	ATION	•	•	•	21
REFERENC	ES		00.0	10000						23
APPENDICE	S									24

LIST OF FIGURES

Figure 3.1	Raw Leachate	9
Figure 3.2	Filtered Leachate	9
Figure 3.3	Spectrophotometer include a control of the	10
Figure 3.4	Methodology of project	12
Figure 3.5	Effect of pH adjustment in mixing of leachate	12
Figure 3.6	Effect of Fenton Oxidation in leachate sample solution	13
Figure 3.7	Clean correctly apparatus after use	14
Figure 4.1	COD vs. pH	17
Figure 4.2	Flocculator machine	18
Figure 4.3	Leachate samples of 50 ml	19
Figure 4.4	COD value vs. time (pH 5)	20
Figure 6.1	Hydrogen peroxide and Iron (II) Sulphate	28
Figure 6.2	Six-1L jars is ready to placed at floc tester	28
Figure 6.3	COD Test Tube	29
Figure 6.4	Apparatus and material of COD test	29
Figure 6.5	pH metre	30
Figure 6.6	Pipette rack	30
Figure 6.7	Rapid mixing	31
Figure 6.8	DRB 200	31
Figure 6.9	The brownish leachate sample	32
Figure 6.10	Taken the COD's readings	32

LIST OF TABLES

Table 1.1	The oxidizing power of hydroxyl radicals versus other oxidants	4
Table 3.1	Total needed dosage	11
Table 4.1	The COD value for raw & filtered leachate	15
Table 4.2	Percentage of COD removal	17

CHAPTER 1

INTRODUCTION

1.1 Background Studies

Municipal landfill is designed to collect, operate and manage solid waste that produced mainly from household, industrial solid-waste, factories, and construction and demolition debris. It helps to protect human population and environment from being exposed to polluted surroundings that can be dangerous to human health. However, municipal landfill also produces a highly-polluted liquid which is also known as landfill leachate.

Leachate is formed when water passes through waste at landfill area and is one of the most contaminants and environmental hazards. It usually contains both dissolved and suspended material since many organic and inorganic compounds are transported in when the water flow through the waste. The contents of leachate basically depend on the waste at the landfill. Usually, leachate consists of dissolved organic matter, suspended solids and heavy metals like lead (Pb), copper (Cu), zink (Zn) and cadmium (Cd). This liquid moves at the base of landfill and need to be collected before it penetrates into the ground.

According to Noor Ida Amalina, 2006, an ideal leachate treatment should have the ability to treat a wide range of chemical constituents, inexpensive to construct, and easy to maintain with low energy and personnel requirements. The most conducted system in treating leachate is by using aerobic treatment systems which operated based on the activated sludge process. It ranges from simple aerated lagoons to complex process plant. Based on the research done by Byung-Uk Bae et al., 1998, it was proven when the raw leachate was treated by the activated sludge process, the small organic fraction was

removed and the large organic component remaining was broken down after Electron-Beam radiation. However, this method is very high in cost.

Therefore, in recent years, constructed wetland systems or anaerobic systems was considered as the alternative ways to treat leachate. As a chemical-free technology, it is aesthetically pleasing and less expensive to operate and maintain. Various treatment of leachate by wetlands includes microbial mediated transformation, plant uptake, and precipitation and adsorption reactions.

1.2 Problem Statement

The rapid population growth, rising urbanization and industrialization in most municipalities has resulted in increasing amount of waste and refuse from year to year in Malaysia. The amount of solid waste generated in Peninsular Malaysia went up from 16,200 tons per day in 2001 to 19,100 tons in 2005, an average of 0.8 kilogram per capita per day. Forecasts have shown that this number will increase further in coming years.

According to Razman et al., 1993, this increment of waste generation will obviously increase the volume of leachate generated per day. Since leachate characteristic was similar to toxic waste due to content of heavy metals such as lead and cadmium, treatment of leachate is obligatory. The danger that can be caused by leachate is if it enters any watercourse, it can lower the dissolved oxygen (DO) content. The high concentrations of dissolved nutrients contains in leachate will be the source of food for aerobic micro-organisms. These organisms grow rapidly and will consume large amount of oxygen from the water around them. Besides, the methane and other toxic gaseous produced from the degradation of organic materials at landfill can dissolved easily in leachate. Hence, the aquatic life will be affected by the toxin accumulation and the shortage of oxygen.

The current methods of treating leachate are very high in cost. In Pulau Burung Landfill Site, Powdered Activated Carbon (PAC) is used as the medium to treat leachate.

1.3 Objective of Study

The purpose of this project is to conduct a further study on landfill leachate treatment and investigate the effectiveness of pH level. The objective of the project is to determine the removal efficiency of Chemical Oxygen Demand (COD) and the heavy metals by using Advanced Oxidation Process (AOP).

1.4 Scope of Study

The sample of landfill leachate was collected from the Pulau Burung Sanitary Landfill, Pulau Pinang. The influent and effluent from the research will be taken into consideration in doing the research. The study concentrate on sample of sanitary landfill leachate and there is no comparison with other leachate sources.

CHAPTER 2

LITERATURE REVIEW

2.1 Advanced oxidation processes

Advanced oxidation processes (AOP) combine ozone (O_3), ultraviolet (UV), hydrogen peroxide (H_2O_2) and/or catalyst to offer a powerful water treatment solution for the reduction (removal) of residual organic compounds as measured by COD, BOD or TOC. All AOP are designed to produce hydroxyl radicals. It is the hydroxyl radicals that act with high efficiency to destroy organic compounds.

The table below shows the oxidizing power of hydroxyl radicals versus other oxidants [2].

Oxidizing Agent	EOP (mV)	EOP vs. Cl ₂
Hydroxyl Radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.3
Hypochlorite	1.49	1.1
Chlorine	1.36	1
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.9

Table 1: the oxidizing power of hydroxyl radicals versus other oxidants

The advanced oxidation process (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. The term advanced oxidation processes refers specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals. AOPs usually refer to a specific subset of processes that involve O_3 , H_2O_2 , and/or UV light [2].

AOP can act on organic compounds in water in several ways: convert one compound into another (conversion), conversion with a reduction in toxicity and mineralization (breaking the organic down to CO_2 and inorganic salts). In some cases, discharge permits simply require conversion from a compound of interest to another compound that is not covered by the permit. For example, some permits require taking phenol to a fraction of a ppm. In other cases, permitting authorities require the toxicity of the compound/wastewater to be reduced prior to discharge. In some cases, mineralization is needed as measured by a reduction of TOC [2].

2.2 Ion exchange

Ion exchange is well suited for general and selective removal of heavy metals and toxic anions from dilute aqueous waste streams. the process involves the interchange of ions between an aqueous solution and a solid material (the ion "exchanger" or "resin bed").after removal of undesirable ions from the solution and exhaustion of the bed, the regeneration cycle is achieved by exposure to a second aqueous solution of different composition which removes the ions picked up by the exchanger. The process is most frequently carried out by pumping the waste stream through one or more fixed beds of exchanger.

Full-scale operations include cleanup of dilute solutions from electroplating and other metal-finishing operations, recovery of effluents from fertilizer manufacturing, and industrial deionization. Promising applications include removal of cyanides from mixed streams, and use of newer exchangers for selective removal f heavy metals. The dilute purified product stream is dischargeable to the environment. The regenerant stream requires further treatment for recovery or disposal [3].

2.3 Chemical Oxidation

Chemical oxidation is used for the destruction of cyanides, phenols and other organics, and precipitation of some metals. The treatment technologies for its large-scale industrial applications are well established. The oxidation-reduction or Redox reactions are those in which the oxidation state of at least one reactant is raised while that of another is lowered. Chemical oxidation should be considered for dilute aqueous streams containing hazardous substances, or for removing residual traces of contaminants after treatment. Chemical oxidation should be considered as a first treatment step when it contains constituents not amenable to other treatment methods or as a final step to remove traces of contaminants after other treatment.

The process train for the chemical oxidation process includes adjustment of pH of the solution. The oxidizing agent is added gradually and mixed thoroughly. The oxidizing agent may be in the form of a gas (e.g., ozone, chlorine), a liquid (e.g., hydrogen peroxide), or a solid (e.g., potassium permanganate).application to industrial wastes is well developed for oxidation of organics and inorganics in dilute waste streams. In addition to the already established applications for removal of hazardous substances, chemical oxidation may be used to remove chlorinated hydrocarbons and pesticides from dilute streams. Laboratory and pilot studies have demonstrated the potential for chemical oxidation for treatment of hazardous waste streams [3].

2.4 Advanced Oxidation Process of landfills leachate

The use of more expensive sorbents such as activated carbon, adsorbent resins is possible with related economic implications. Alternatively, landfill leachate may be evaporated, incinerated or, in arid-semiarid areas, it may be re-circulated on the waste thus taking advantage of the evaporation favoured by the dry climatic conditions. An odour emission is however the main limit of the operation [4]. Application of conventional biological treatment to reference liquors is limited by the presence of toxics (e.g., heavy metals) and/or recalcitrant organics (pharmaceuticals, polyphenols, endocrine disrupters) [5]. More than the generalised bio-toxicity, the technological problem is related to biorefractory nature of the organic matter due to the presence of high molecular weight substrates. Possibly, the autotrophic biomasses mediating

hydrolysis of organic macromolecules are more sensitive to the mentioned toxicity and generalised non-viable conditions for biomass proliferation in the biological reactors. Growing interest is lately focussed on the Advanced Oxidation Process (AOP) of landfills leachate with a multipurpose goal associated with: a) abatement of refractory COD load, with related enhancement of biodegradation after rising of the BOD₅/COD ratio; b) simultaneous removal of toxic contaminants by sorption-co precipitation [6]. AOP are based on the formation of hydroxyl radicals (OH•), an extremely strong oxidant

resulting from several reactions such as the synergistic action of two oxidants: $O_3+H_2O_2$; a catalyst and an oxidant: $Fe_2++H_2O_2$ (the Fenton's reagent); a photocatalyst and an oxidant: $TiO_2+H_2O_2$; irradiation plus oxidation: $UV+O_3/H_2O_2$); etc.[7,8]. Generally speaking, full scale application of the Fenton's reagent does not require supplementary operative costs beyond chemicals strictly needed for the oxidation reaction. In acidic media hydroxyl radicals are very efficiently formed for technical purposes. Chemicals are cheap, process layouts simple.

2.5 Treatment of landfill leachate by sequencing batch reactor

Leachate production is the results of rain precipitation, infiltration etc., phenomena which cause infiltration of water into the landfill waste and, after saturation, generation of wastewater [8] .The flow rate and composition of leachate vary from site to site, seasonally at each site and depending on the age of the landfill. Young leachate normally contains high amounts of volatile fatty acids. These readily degradable volatile acids account for the bulk of the chemical oxygen demand (COD) of young leachate, so the ratio of biological oxygen demand (BOD) to COD is relatively high. As the waste ages, the biodegradable fraction of organic pollutant in leachate decreases, as a result of the anaerobic decomposition taking place in landfill site [9], High COD and ammonium content, high COD/BOD ratio and the presence of heavy metal ions present unique difficulties in biological treatment of landfill leachate [10].

Biological treatment is mostly the first stage in a combination with additional chemical physical process. Those treatment methods used for leachate treatment are mainly aerobic, anaerobic and anoxic processes which are used in combination [11] .The main task of the leachate biological process is the reduction of the organic biodegradable compounds and nitrogen in order to minimize secondary treatment cost. The most popular biological treatment of landfill leachate is the sequencing batch reactor (SBR) method. The SBR process strategy is characterized by a controlled periodic change of process conditions such as concentration of oxygen, and availability other biological reactants. These environmental conditions are controlled using fill and draw operations at distinct time intervals [12].

Cavitations occur above a certain intensity threshold, when gas bubbles are created which first grow in size before violently collapsing within a few microseconds. The violent collapse produces very powerful hydromechanical shear forces in [13]. Cavitations are accomplished by high pressure gradients and extreme increase of the temperature inside the bubble. These extreme conditions can lead to the thermal destruction of compounds present in the cavitations bubbles and to the generation of very reactive hydroxyl radicals. The effects that can be observed when cavitations are generated in aqueous solution can be summarized as:

- High mechanical shear stress.
- Radical reactions: creation of OH and H radicals; chemical transformation of substances.
- Thermal breakdown of volatile substances.

In this study the effect of ultrasound pre-treatment on leachate degradability was investigated using ultrasound at a frequency of 20 kHz and high acoustic intensities. Leachate needed to be diluted with synthetic wastewater in order to reach biomass-non inhibiting concentration. The aim of the research was to evaluate the maximum percentage of leachate that can be biologically treated without any inhibition of microbiological activity and examine the effect of leachate ultrasound disintegration on the efficiency of the aerobic digestion process [13].

CHAPTER 3

METHODOLOGY

3.1 Preparation of Leachate Samples

Leachate sample was collected from Pulau Burung Sanitary Landfill located in Pulau Pinang, Malaysia on the 7th April 2008. It was stored in refrigerator with temperature of 4°C before being tested in laboratory works. This step was taken to minimize the biodegradation of any compounds amenable to biological assimilation and or oxidation. 1500mL samples of leachate was taken and placed into beaker labelled "Raw Samples". Meanwhile, another 1500mL samples of leachate was taken and placed into beaker and filtered before it was stored into beaker labelled "Soluble Samples". The filtration process was done by filtering the leachate samples using filter paper pore sized 0.45µm. Both samples were thoroughly agitated for re-suspension of possible settling solids before conducting the test. Figure 3.1 and Figure 3.2 have shown the apparatus during the filtration works.



Figure 3.1: Raw Leachate



Figure 3.2: Filtered Leachate

3.2 Measurement of Chemical Oxygen Demand (COD)

The COD measurement is to determine the amount of chemical oxygen demand in the leachate sample before and after being treated. The test was conducted by adding 2 mL of supernatant of the sample into a vial. Three vials were prepared for each sample. The blank sample was prepared by pipetting the distilled water into the vial. All the vials were shaken properly on the rotator. The samples later were heated at temperature of 150 °C for 2 hours in the heater. After 2 hours, COD reading was taken using the spectrophotometer.



Figure 3.3: Spectrophotometer

3.2.1 Procedure

The preparation of material and equipment are the first stage before conducting the experiments. The solution of Hydrogen Peroxide, H_2O_2 , and the powder of FeSO₄.7H₂O and leachate sample are the main items that should be ready to use. First of all, the pH of the leachate is measured by pH machine. The value of pH is fixed to the pH 3.the magnetic bar is used to let the leachate continuously stirring. The leachate sample is filled in one 1-L jar with 500mL of the leachate sample. The jar is placed under the paddle of the leachate sample. Rapid mix at 200 rpm will be started. It speed continuously in same rate from the beginning the end of the test.

Using the picagary, the first 50mL sample after 15 minutes will be taken. The next sample will be taken after every 30 minutes. Sodium hydroxide in high concentration is dropped to every 50mL beaker. The COD test will be run after 10 hours

later to let the sediment settling very well. After that, we Measure COD value versus retention time. The data are recorded to the table.

3.3 Fenton Oxidation Process

In order to conduct the test, we need to prepare some apparatus such as, six 1-L jars, six 100mL beakers, two 10mL graduated pipettes, six 50 mL pipettes and pH meter. The six 1-L jars are filled with leachate sample. Each of jars is filled with 500mL of leachate sample. The pH reading of water sample is measured. Jars are placed under the paddles of the jar test apparatus and the paddles are lowered to the same depth in each jar. Rapid mix is started for two minutes. After two minutes, speed with slow mix is continued at 30rpm for 20minutes.During the slow mixing, any flocculation in each jar is observed and recorded as good, air and poor. At the end of 20minutes the stirrer is turned off to allow settling for 20minutes.

After 20 minutes, each of samples is taken in order to read their new COD values. Before COD test is run, the six 1-jars is put back at the floc tester. The procedure is same as done before. After rapid mix is started, the jars are dosed with hydrogen peroxide, H_2O_2 as Table 3.1.

Jar	pН	Hydrogen Peroxide	Concentration of	Weight of Iron(II)
		35%, H ₂ O ₂ (mL)	Hydrogen Peroxide	Sulphate, FeSO ₄
			35%,H ₂ O ₂ (mg/L)	(mg)
1	2	1	350	0
2	3	2	700	0
3	6	10	3500	0
4	8	20	7000	0
5	10	50	17500	0
6	12	100	35000	0

Table 3.1: Total needed dosage

Step for taken COD value is described here. 2ml of leachate sample was measured and poured into a test tube containing potassium dichromate. The test tube is then shaken properly. Heat was produced, indicating an exothermic process. All the test tubes

together with a blank as indicator were then put into the rotator and left for 2 hours. Three readings are taken down and the average of those readings is calculated.



Figure 3.4: Methodology of project



Figure 3.5: Flowchart of experiment of Effect of pH adjustment in mixing of leachate

The author has undergone various studies to make this project successful. Figure 3.5 shows the simple flow of project. At the first stage, The COD is taken in the leachate sample before and after being treated. The color and pH tests also conducted to identify it in detail.second stage taken part to identify the suitable chemical in order to make sense in the experiment. After checking the suitability of the chemical, the last stage which the leachate treatment process that author want to study.



Figure 3.6: Flowchart of experiment of Effect of Fenton Oxidation in leachate sample solution

3.4 Health, Safety, and Environment Aspects

3.4.1 Personal Protective Equipment

It is the laboratory supervisor's responsibility, with assistance from the University Safety Coordinator, as needed, to specify all necessary personal protective clothing for lab staff and students. The University is responsible for providing basic safety equipment such as First Aid Kits and fire extinguishers.

3.4.2 Laboratory Safety Guidelines

In order to ensure the safety at laboratory, there are some points that we should highlight. The first one is about consultation. Discuss our safety concerns with our supervisor or seek advice from the technician which meets regularly to discuss problems and seek solutions.

Sometimes, we have incident at lab. All accidents or near misses must be reported to technician and supervisor. Job safety Analysis (JSA) should be applied during lab works. Work for specific hazards should be evaluated and for minimizing the risk of injury. A periodic laboratory inspection is conducted to identify and correct hazardous conditions and unsafe practices.

In order to make sure all equipment in good conditions and lab look good, a good housekeeping must be practiced in all working areas. All chemicals are labelled to show nature and degree of hazard (sample concentration). Opportunity to discuss the results of inspections and aspects of laboratory safety with friends, technician and supervisor should be taken.



Figure 3.5: Clean correctly apparatus after use

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization

Before the COD test is ran, the preparation of samples taken carefully. During the lab works, the largest sample practical and the largest glassware are used and that is in keeping with good laboratory practice. We also Use the volumetric flasks and volumetric pipettes with a large bore. We're aware that the sample has the sediment at the bottom of volumetric pipettes. From the data obtained in Table 4.1, the average of COD value for raw and filtered leachate sample can be calculated. The Colour and pH test was investigated and characterized to examine pH and colour values. Result indicated that the colour of leachate turned from black to light brown at lower and at higher pH values. The results for the raw and filtered leachate are shown in Table 4.2 and Table 4.3:

Table 4.1: The COD value for raw & filtered leachat

Type of Sample	Average COD reading (mg/L)	Unit (Ptco)	рН
Raw Leachate	3200	50	8.107
Filtered Leachate	3100	31	8.085

4.4 Discussion on The Fenton Oxidation Laboratory Test Result

The COD value taken due to The COD value is much higher than the Biochemical Oxygen Demand (BOD) because the COD value is the amount of oxygen required to oxidize an organic compound (biodegradable and unbiodegradable) under the influence of a strong oxidant ($K_2Cr_2O_7$) in an acid environment (silver nitrate used as a catalyst) while BOD value is the amount of oxygen required to oxidize biodegradable organic matter only.

4.4.1 Experimental Procedure Part 1

From the data obtained, the average COD value for the sample of pH 2 is 3498 mg/L. Theoretically, the value is supposed to be in the range of 2700 mg/L to 3200 mg/L. This is because there was a mistake during did the experiment. Therefore, the sample has been chemically reacted by the acid sulfuric. Thus, the COD value is high. The average COD value for the sample of pH 3 is 3765 mg/L. the average COD value for the last sample before the stirring namely sample of pH 6 is 4035 mg/L. These three samples showed the increasing if the sample have high pH.

4.4.2 Experimental Procedure Part 2

The COD value for the sample taken after the stirring is higher than before. The value is high due to stirring cause acid spread out in solution very well. It found that the COD value make sense with stirring even there is no chemical added into solution.

4.4.3 Experimental Procedure Part 3

The selection of a specific advanced oxidation process is application dependent. The author evaluates the suitability of wastewater to see which Advanced Oxidation Process (AOP) fits best based on the type of compounds to be removed, treatment objectives, concentrations and budget. In order to get the best result, the author already done a lot of tests to make sure the accuracy of results.

In Fenton Oxidation process, the author use chemical such as hydrogen peroxide, Iron (II) sulphate and pH adjustment. The results obtained are as shown in Table. From the data obtained in Table 4.4, the graph is plotted in figure 4.1 in order to obviously see the difference after conducted the test.



Figure 4.1: COD vs. pH

In Figure 4.1, there is increasing in COD value which is worse than the original COD. This occurred due to existing of hydrogen peroxide into the samples. From the data obtained in Table 4.4, the percentage removal of COD for leachate sample can be calculated (see in Appendix). Value for raw leachate is 3200 mg/L as shown earlier in Table 4.1. Percentage COD removal are shown Table 4.5.

Table 4.5:	Percentage	of COD	removal
------------	------------	--------	---------

Process	pН	COD Removal (%)	Total COD Removal (mg/L)
Effect of pH	2	-39	-1253
adjustment &	3	-41	-1325
hydrogen peroxide,	6	-46	-1472
H ₂ O ₂	8	-45	-1454
to leachate sample	10	-43	-1365
	12	-36	-1165

4.3 pH Adjustment

The preparation of pH 3 for the leachate sample is prepared by added some drops sulphuric acid; H_2SO_4 in high concentration in to lower the original pH of leachate sample. The original pH for the sample is about pH 8. The pH metre is used to control the reduction of pH. The pH metre must be calibrated to make the reading on pH metre accurate. During the pH reduction, precaution must be taken. The pipette is used to drop the sulphuric acid; H_2SO_4 carefully. The pH reduction is easily to drop during H_2SO_4 usage. It is slightly different with acid hydrochloride, HCL in low concentration.

At the preliminary stage, the acid hydrochloride, HCL is used but it has to use in a lot of quantities before it really reduce the pH. The iron (II) sulphate weighted in the scale metre. The weight of iron (II) sulphate very small in quantity. The mistakes during weighted can affect the conducted experiment. The hydrogen peroxide, H_2O_2 is taken by using the pipette calibration.



Figure 4.2: Flocculator Machine

The figure 4.2 shown the set of flocculator machine. The Jar is set well so that the paddle is really at the centre of the jar. The speed is fixed to the 100 rpm



Figure 4.3: Leachate samples of 50 ml

The figure 4.3 shown the sample during the experiment. Five samples are taken to each jar so that we get the COD reading at different time started from 15 minutes until 120 minutes.

4.3.1 Results and discussion of sample test

Based on the result that has been obtained, some of the result might need further elaboration to clear the question that might arise. In this part, the result of the experiment will be discussed in detail based on the rest of respective laboratory test. Based on the result that is shown in Table 4.6 (see in appendix), a graph is plotted and is shown in Figure 4.3 and Figure 4.4.



Figure 4.3: COD value vs. time (pH 3)



Figure 4.4: COD value vs. time (pH 5)

Figure 4.3 shows the COD value of pH 3 with respect to time in two hours of mixing while figure 4.4 shows the COD value of pH 5 with respect to time in two hours of mixing. The COD removal efficiency in Figure 4.3 is better than The COD removal efficiency in Figure 4.4.it shows that lower pH level, a better progress produced. From the data obtained in Table 4.7 (see in appendix) the percentage removal of COD for leachate sample can be calculated (see in Appendix). Value for raw leachate is 3200 mg/L as shown earlier in Table 4.1. Percentages COD removals are shown in Table 4.7 (see in appendix) the author manipulate the weight of the Iron (II) sulphate as the variable. In these experiments, author makes pH level as a constant.

In this experiment, author change the weight of Iron (II) sulphate from 325.8 mg to 651.6 mg to see how the combination of three variables namely Iron (II) sulphate, pH level and hydrogen peroxide react among them to treat to leachate sample. For the first part, the author used hydrogen peroxide without any combination with Iron (II) sulphate. However, it did not come out with good results because the result encountered with the purpose of project because COD value for all of samples increased immediately. The author believed that hydrogen peroxide acted as a stimulator in leachate sample. Maybe there are organic matters stimulated by hydrogen peroxide. As a result, the COD value rise beyond the original reading.

CHAPTER 5

CONCLUSIONS

Based on results, author found the Fenton oxidation process is the ideal way to treat the leachate. It proved that the combination of hydrogen, Iron (II) sulphate and pH level produced the positive results. The three variables which is the main target are successful manipulated.

After doing the studies and laboratory test, the author has concluded that this project has potential to practise at municipal landfill or any place. In order to commercialize it, there are a lot of studies must be done because only the laboratory tests going to prove the project either it work or not. During the author experienced the lab activities, this project can be concluded that combination of hydrogen peroxide and Iron (II) sulphate in certain pH level can reduce the COD in leachate's contain. There is no reductions occur if only hydrogen peroxide is mixed with leachate sample. in author 's point of view , the reduction of COD only happen when hydrogen peroxide combine with Iron (II) sulphate.

The optimum pH is three. The pH 3 is suitable for treatment because it is in acidic condition. Based on the acid's characteristic, the author succeeded manipulating the pH level to provide the optimum pH to sample. Absolutely, the good medium for the sample mixing is at pH 3.

Optimum H_2O_2 can be achieved by provided every 15 minute continuously till two hours. the frequent observation is the good reason why every 15 minutes the author taken the sample.15 minutes interval per reading is the reasonable COD value reading.

The optimum H_2O_2 :FeSO₄ ratio is recorded in pH 5 after 120 minutes of mixing. More time taken contribute to more reaction. But it doesn't mean the short time taken is not efficient. The long time is practical way because it saves the total of catalyst and other variables usage.

RECOMMENDATIONS

So far from author's observation, there are few recommendations that can be made to ensure a better outcome towards this project, such as conduct as lot as possible tests involve of three main variables that author already mentioned in discussion chapter.

This experiment can be improved by collecting the COD readings for every ten minutes so that the COD removal is closely observed. In order to get the good result, it prefers if we have continuously during conducting the experiments.

Although the six 1-L jars are prepared simultaneously can less time consuming. But it is not really a good idea. During conducted the test, the possibility not taking care all of jars are high. It's better if run the three 1-L jars at one time. This idea can make the tests more accurate and efficient.

Leachate treatment through the advanced oxidation process is more effective because it can be the off-site treatment. As everyone knows there are some benefits when leachate treatment applies in the landfill areas. One of benefits such as the leachate treatment can make least amount of on-site infrastructure. When we apply least amount of on-site infrastructure, automatically we can cut the capital cost. Absolutely, the lowest capital cost will be produced. Best option for initial years, once the quantity and quality of leachate become stable and well characterized, long-term treatment may be re-evaluated

If author can't produce a lot of data based on test, the author also thinks how to apply a new leachate treatment method which is not very time consuming. The author always learns from mistakes. This attitude encourage author eagerly learn something without afraid of doing mistake. It is a recommendation to all researchers and scientist to have it. It all about how they want to improve themselves. As a human being, errors in test is the obvious thing that author can't escape while ran the test. But it can't make the reason or taking advantage for it. try the best in practice is the spiritual word that make sense to person to make their project successfully. If these recommendations are taken into consideration and applied into the leachate treatment, it would definitely help to reduce the COD in leachate sample.

REFERENCE

- [1] Syed R. Qasim & Walter Chiang, 1996, Generation, Control and Treatment, Sanitary Landfill Leachate
- [2] Spartan Environmental Technologies, Retrieved August 10, 2008, from <<u>http://www.spartanwatertreatment.com</u>>
- [3] Syed R. Qasim & Walter Chiang, 1996, Generation, Control and Treatment, Sanitary Landfill Leachate
- [4] Blight G.E., 1989, Generation of leachate from landfills in water deficient areas, Sardinia.
- [5] Birkett J.W., Lester J.N., 2003, Endocrine Disrupters in Wastewater and Sludge Treatment Process, Lewis Pub.Co., CRC Press, Boca Raton, FL, USA.
- [6] Bertanza G., Collivignarelli C., Pedrazzani R., Collivignarelli M.C., Zanaboni S,2003,L'ossidazione chimica nel trattamento di acque di scarico e rifiuti liquidi; Esperienze e prospettive di ricerca, Ingegneria Ambientale.
- [7] Kang S., Chang H., 2000, Effect of reaction conditions on the oxidation efficiency in the Fenton process, Wat. Res., 34, 2786-2790.
- [8] Kim S., Geissen S., Volgepohl A., 1997, Landfill leachate treatment of by a photoassisted Fenton reaction, Wat.Sci.Technol., 35, 239-248.
- [10] J.M. Lema, R. Mendez and R. Blazquez, 1998, Characteristics of landfill leachates and alternatives for their treatment.
- [11] I. Kruempelbeck and H. Ehrig, in: T.H. Christensen, R. Cossu, R. Stegmann, eds., Long term behaviour of municipal solid waste landfills in Germany.
- [12] S. Park, K.S. Choi, K.S. Joe, W.H. Kim and H.S. Kim, 2001, Variations of landfill leachate properties in conjunction with the treatment process Environ. Technol..
- [13] Noor Ida Amalina, 2006, Leachate Treatment using Constructed Wetland with Magnetic Field.

APPENDICES

Condition	Sample	рН	COD	reading	(mg/L)	Average	
	Number		1	1 2		reading	
	1	2	3500	3500	3494	3498	
Before	2	3	3765	3765	3766	3765	
	3	6	4036	4035	4035	4035	
	4	8	3673	3672	3672	3672	
	5	10	3456	3456	3459	3457	
	6	12	3347	3345	3349	3347	
	1	2	3750	3755	3761	3755	
After Mix	2	3	3945	3953	3951	3950	
	3	6	4134	4132	4132	4133	
	4	8	3976	3972	3973	3974	
	5	10	3868	3861	3867	3865	
	6	12	3654	3658	3653	3655	
0	1	2	4450	4457	4451	4453	
After	2	3	4521	4528	4525	4525	
Dose the jars with H ₂ 0 ₂	3	6	4673	4671	4673	4672	
	4	8	4652	4651	4659	4654	
	5	10	4563	4567	4564	4565	
	6	12	4364	4367	4363	4365	

Table 4.4: COD reading in different pH level

		Retention	Hydrogen	Iron (II) Sulphate,	pH						
Jar	Beaker	(min)	H_2O_2 (µl)	FeSO ₄ .7H ₂ O (mg)	3	5					
			2 2 4 7		COD (mg/l)					
1	1	15	60		2342	2453					
	2	30		in the second	2320	2357					
1	3	60	5692	325.8	2367	2487					
	4	90	175	100	2310	2368					
	5	120		L STREET	2332	2321					
	1	15			2237	2420					
	2	30			2220	2410					
2	Э	60	7589	434.4	2268	2310					
	4	90			2238	2285					
	5	120			2232	2247					
	1	15		68	60	60	68	69		2206	2356
	2	30			2217	2456					
3	3	60	9487	543	2235	2230					
	4	90			2223	2106					
	5 120		2212	2100							
	1	15			2210	2247					
	2	30			2206	2210					
4	3	60	11384	651.6	2203	2168					
	4	90			2211	2078					
5	5	120			2202	2032					

Table 4.6: COD for sample in different weight of Iron (II) sulphate

Process	рН	Jar	Beaker	Retention Time (min)	COD (mg/l)	COD Removal (%)	Total COD Removal (mg/L)
			1	15	2342	27	858
	F		2	30	2320	28	880
	F	1	3	60	2367	26	833
	F		4	90	2310	28	890
	F		5	120	2332	27	868
l	t		1 1	15	2237	30	963
			2	30	2220	31	980
Effect of pH		2	3	60	2268	29	932
adjustment		-	4	90	2238	30	962
& bydrogen	3		5	120	2232	30	968
peroxide,	Ŭ		1	15	2206	31	994
H ₂ O ₂ to			2	30	2217	31	983
leachate		3	3	60	2235	31	965
sample			4	90	2223	31	977
			5	120	2212	31	988
		6. r =	1	15	2210	31	990
			2	30	2206	31	994
		4	3	60	2203	31	997
			4	90	2211	31	989
			5	120	2202	31	998
			1	15	2453	23	747
		1	2	30	2357	26	843
		1	3	60	2487	22	713
			4	90	2368	26	832
			5	120	2321	27	879
			1	15	2420	24	780
			2	30	2410	25	790
Effect of pH		2	3	60	2310	28	890
aujustment &			4	90	2285	29	915
hydrogen	5		5	120	2247	30	953
peroxide,			1	15	2356	26	844
H_2O_2 to			2	30	2456	23	744
sample	1	3	3	60	2230	30	970
sample			4	90	2106	34	1094
			5	120	2100	34	1100
			1	15	2247	30	953
			2	30	2210	31	990
		4	3	60	2168	32	1032
			4	90	2078	35	1122
			5	120	2032	37	1168

Table 4.7: Percentage COD removal in Fenton oxidation process



Figure 6.1 : Hydrogen peroxide and Iron (II) Sulphate



Figure 6.2: six-1L jars is ready to placed at floc tester



Figure 6.3: COD Test Tube



Figure 6.4: Apparatus and material of COD test



Figure 6.5: pH metre



Figure 6.6: pipette rack



Figure 6.7: Rapid mixing



Figure 6.8: DRB 200



Photo 6.9: the brownish leachate sample



Figure 6.10: taken the COD's readings