PERFORMANCE OF COMPOST TUMBLER IN THE

TREATMENT OF TENORM (OIL SLUDGE)

by

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ABSTRACT

In recent years, the petroleum industry in Malaysia has developed rapidly and it has produced a vast amount of wastewater and petroleum wastes, which has the potential to contaminate the natural environment. Nowadays, there are various technological solutions that has been practised by the petroleum industry to treat oil sludge and among that is landfarming. In order to address the downsides of the landfarming treatment method, a closed composting system is to be studied for its feasibility in terms of odour control and hydrocarbons biodegradability. Various physical and chemical parameters are going to be monitored to evaluate their influence on the biodegradability of these petroleum hydrocarbons.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In the oil and gas industry, significant quantities of oily sludge are produced during oil production and processing activities. As stated by Oudenhoven et al., it has been estimated that one ton of oil sludge waste is generated for every 500 tons crude oil processed (Roldán-Carrillo et al., 2012). Petroleum waste treatments ranging from cheap to expensive are being used worldwide. A wide selection of physical, physicochemical and biological processes are available to treat oil sludges, such as landfilling; incineration; co-processing in clinkerization furnaces; microwave liquefaction; centrifugation; destructive distillations; low-temperature conversion; thermal plasma; incorporation in ceramic materials; development of impermeabilization materials; encapsulation; biodegradation in landfarming; biopiles and bioreactors. Before a method of treatment is being selected, the analysis and characterization of the oil sludge, the amounts produced and the availability of equipment are the important variables that should be identified (da Silva, Alves, & de França, 2012). In Malaysia, this oil sludge is known as Technologically-Enhanced Naturally Occuring Radioactive Material (TENORM) after it is being exposed to human activities such as mining and it is usually found in scales and sludge from the oil and gas industries.

One of the widely used treatment method of oil sludge is landfarming. Landfarming process involves the controlled application of waste on a soil surface in order to biodegrade the carbonaceous constituents by utilising the microorganisms that are naturally present in the soil and it usually takes place in an aerobic condition (Dando, 2003). Although landfarming has reported to be a cost-effective and simple method in the treatment of petroleum waste, it also comes with a few operational and environmental drawbacks. In order to carry out the landfarming process, a large land needs to be acquired and there is a possibility for contaminant movement from the treatment site to a previously undisturbed site. Another shortcoming of this method is the volatile contaminants must be pre-treated because they would volatilize into the atmosphere and cause air pollution (Khan, Husain, & Hejazi, 2004).

The problem with this method is it posed odour problem. Odours have been rated to be one of the most important concerns of the public relative to the implementation of sludge treatment facilities and with regard to this issue, it is appropriate to consider the effect they produce. It is very important to have the odour at low concentrations because in the human terms, they may produced psychological stress rather than harm to the body. Such examples are poor appetite for food, lowered water consumption, impaired respiration, nausea and vomiting, and mental perturbation (Tchobanoglous, Burton, & Stensel, 2004). The alternative method of treatment which can provide control and elimination of odour is by closed composting system with odour treatment.

1.2 Problem Statement

In the search to find an applicable treatment method for petroleum refinery sludge with a functional and cost-effective engineering design, a closed composting system is being developed in a laboratory-scale study. Although not many had done such study, previous researches had shown that it is plausible given that the right environment is provided for the treatment process to be carried out.

It is worthwhile to note that the existing treatment solutions of oil sludge are subjected to a few drawbacks. The problem that is going to be rectified in this study is to tackle the disadvantages of the widely used landfarming treatment method which is the unpleasant odour that it produces.

In order to carry out this treatment, it must be done in an open area to provide sufficient oxygen for the biodegradation of the oil sludge on the soil. The odour produced during the process which resulted from the production of hydrogen sulphide from sludge and volatile organics will be released into the air. This will cause discomfort to the people of the surrounding area.

To minimize or annihilate this problem, the biodegradation process of oil sludge will be carried out in a closed system whereby it will be called as the closed composting system. This is to control the release of odour from the mixture of oil sludge and the medium. Therefore, the present research is aimed to tackle the abovementioned limitation of the existing treatment method.

1.3 Significance of Study

This project is relevant to human, health and environment implementation. By producing an optimum result for closed composting method, the effective yet economical technique will be able to be use to overcome the problem. Eventually, this will minimize or annihilate the odour problem. Apart from treating the oil sludge waste from the oil and gas industry, this study is also aimed to:

- Determine the biodegradation rate TENORM
- Provide a proper treatment and management of oil sludge are both essential to promote the sustainable management of the profitable extraction of natural resources in the oil and gas industries

This study is developed with the aim to provide an innovative treatment method which is beneficial to the industry in terms of waste management and is particularly applicable to be practised in Malaysia especially in the oil and gas industry.

1.4 Objectives of the Study

The objectives of this study are as follows:

- To treat TENORM in a closed composting system
- To study the biodegradation rate of TENORM in a closed composting system

1.5 Scope of Study

In order to achieve the objectives mentioned in Section 1.4, the scopes of study are stated as follows:

a) Literature survey

A comprehensive desk study and patent search of the latest research done on the biodegradation technology of oil sludge is to be undertaken.

b) Enhancement of the biodegradation application for oil sludge treatment

Additional features are introduced to the existing composting treatment method so as to enhance the overall composting performance. The variables and materials are to be ascertained.

c) Selection of materials for composting treatment of oil sludge

Agricultural materials such as palm fronds and chicken manure are proposed to be used in providing necessary nutrition for biodegradation process. A plastic drum is to be designed into a composter so as to provide arbitrary closed environment. The composter will be thermally insulated to maintain the internal temperature

d) Fabrication of the composter

The composter is to be fabricated according to appropriate scale. Required equipments such as air compressor and gas flow meter will be connected to the composter at appropriate location.

e) Laboratory set-up for experiment conduct

All test apparatus and equipment are to be calibrated with care so as to prevent systematic error during measurements. These measurement equipments include gas chromatograph and gas flow meter.

f) Analysis and interpretation of the experimental results

The experimental data are to be processed by presenting it in a graphical method. These results are to be subsequently interpreted by proper engineering tool and judgment. The parameters that significantly affecting the biodegradation process of oil sludge are identified and subsequently considered as design parameters in the predictive models.

g) Comparison of result

Efficiency of the closed composting method will be assessed by comparing the test results with those of the other existing oil sludge treatment.

h) Publication/ Report writing

CHAPTER 2

LITERATURE REVIEW

This chapter outlines the fundamental concepts on oil sludge management and treatments. It reports on the previous studies done by other researcher on this aspect of the study. This information will be the benchmark for the evaluation of the biodegradation rate of oil sludge for this study.

2.1 Oil Sludge

The various activities done in the petroleum industry, such as drilling, production, transport, processing and distribution, create considerable amounts of hazardous waste. The disposal of these waste materials into the environment can cause serious environmental problems and for this reason, the search for solutions that are able to minimize the effects is highly important. Significant quantities of oily sludge is produced during oil production and processing activities (Lazar et al., 1999). The residual crude oil in storage tanks usually leads to build up of oily sludge at the bottom of the tank which should be disposed of as solid waste properly in an environmentally safe manner (Koolivand et al., 2013). The sludge is also an environmental pollution source and it occupies big spaces in storage tanks. Heidarzadeh et al. stated that oily sludge is a pasty, semisolid material made of sand which is contaminated by oil, the water produced and the chemicals used in petroleum processing is the most abundant oil waste generated in refineries (Da Silva et al., 2012). Sugiura et al. stated that, petroleum contains hundreds of significant compounds, which are generally grouped into four parts, according to their differential solubility in organic solvents: saturates, aromatics, resins and asphaltenes (Capelli, Busalmen, & Sã, 2001). Overcash and Pal also stated that petroleum-based oil wastes consist of alkanes or paraffins with 1-40 carbon atoms per molecule but in certain crudes, a substantial amount of cycloaklanes may also be present (Kirchmann & Ewnetu, 1998).

An advance analyses done by Marks et al. showed that waste oil is composed of 40–52wt% alkanes, 28–31wt% aromatics, 7–22.4wt% resins, and 8–10wt% asphaltenes (Chen & Kan, 2013). Researchers Shie et al. stated that benzene, toluene, ethyl/benzene, xylene (BTEX), phenols and polycyclic aromatic hydrocarbons (PAHs) are normally found among the aromatic compounds and Xie et al. stated they are partially responsible for the flammability of petroleum sludge and its consequent classification as a hazardous waste (da Silva et al., 2012). This is also supported by Johnson et al. and Ohura et al., in which they agreed that Polycyclic aromatic hydrocarbons (PAHs) make up an important group among the diverse pollutants that are introduced to the environment either by natural or anthropogenic sources. This is primarily because of their composition of fused aromatic rings and their specific physical properties such as low aqueous solubility and high solid–water distribution ratios stand against their microbial utilization and promote their accumulation in the solid phases of the terrestrial environment (Sayara, Sarrà, & Sánchez, 2010).

2.2 Existing Technological Solutions

Over the years, a wide range of technological solutions has been used in managing the petroleum wastes. According to Da Silva et al. (2012), there are many physical, physicochemical and biological processes are available to treat oily sludges, such as landfilling; incineration; co-processing in clinkerization furnaces; microwave liquefication; centrifugation; destructive distillations; low-temperature conversion; thermal plasma; incorporation in ceramic materials; development of impermeabilization materials; encapsulation; biodegradation in landfarming; biopiles and bioreactor. Physical treatment of remediation has shown that even though the soil unchanged or unmodified by these treatments, the costs are high thus it is not applicable on a large scale (Chandra, Sharma, Singh, & Sharma, 2012).

2.3 Landfarming

Of all the existing technological solutions around the world, landfarming is b.eing used extensively. Being a cost-effective and easy-to-implement method of treatment, the oil and gas industry is using it as an in-house treatment for their oil sludge. It has been practised worldwide for over a century and by the petroleum industry for more than 25 years (Khan et al., 2004). Da Silva et al. (2012) stated that, landfarming is a bioremediation technique upon which oily sludges are scattered and mixed into the reactive soil layer in a controlled manner for the microbiota in the ground to act as a degrading agent and this is applied to a large areas because biodegradation occurs in the upper soil layer, where aerobiosis is guaranteed. The process involves the controlled application of waste on the surface in order to biodegrade the carbonaceous constituents by utilising the microorganisms that are naturally present in the soil and this technique has been effectively used for years in the management of disposal of oily sludge, other petroleum refinery wastes and other waste types (refer Table 1) (Dando, 2003).

Table 1 Landfarming waste applications

Waste Sources	Municipal
Municipal sludges	Benzene, toluene, ethylbenzene, and xylene
Chemical plant residues	Fuels of gasoline, diesel and oil
Creosote sludges	Pentachlorophenol
Food processing sludges	Polychlorinated biphenyls
Petroleum refinery sludges	Polynuclear aromatic hydrocarbons
Petroleum hazardous wastes	Pesticides
Textile mill sludges	

Landfarming is designed to optimize degradation by application of an aerobic biological process while using the soil to support biological growth and the biodegradation process is also optimized by aerating the soil with addition of nutrients by agricultural tilling technique. The biodegradation process that occurs in landfarming is aerobic respiration. Aerobic process is a biological treatment that occurs in the presence of oxygen (Tchobanoglous, Burton, & Stensel, 2004).

Figure 1 Aeration at a landfarming field

Despite the fact that landfarming is relatively inexpensive compared to other method of treatments, there are a few downsides to this method which should be taken into consideration being it is being used. As stated by (Khan et al., 2004), listed below are the disadvantages of landfarming:

- A large amount of land is required.
- Volatile contaminants must be pre-treated because they would volatilize into the atmosphere and cause air pollution.
- It is not efficient in degrading the heavy components of petroleum.
- There is a possibility for contaminant movement from the treatment site to a previously undisturbed site.
- Concentration reductions greater than 95% and constituent concentrations less than 0.1 ppm are difficult to achieve.
- It may not be effective for sites of high constituent concentrations of greater than 50,000 ppm TPH.
- Due to reduced microbial growth and metabolic rates biodegradation tends to decline with a decline in temperature. The optimum temperature range is 25–40^{o}C.
- The optimum moisture content for the highest degradation rate, for landfarming is 18%. At 33% moisture (too wet) and 12% moisture (too dry), degradation rates tend to be low.
- Nutrients, especially nitrogen, within the soil zone allow biological processes to proceed efficiently. The most rapid biodegradation of refinery sludge occurs when added nitrogen reduces the C:N ratio to 9:1.

- Maintaining the soil pH within the 6.5–7.5 range provides optimum conditions for biodegradation.

One of the main concerns in landfarming is the release of unpleasant odour from the landfarming field which comes from the oil sludge.

2.4 Composting

Previous subchapters had shown that biodegradation of petroleum hydrocarbons can be used for oil sludge bioremediation and composting as a bioremediation method is now considered as one of the best methods for decontamination of oil pollution due to its advantages including relatively low cost and simple design (Koolivand et al., 2013). PAHs is lacking. Composting can be defined basically as biological process occurring in favourable conditions (good aeration, moisture, etc.) and allowed to convert the raw initial material probably contaminated or with phytotoxic properties to stable and mature end product (Amir, Hafidi, Merlina, Hamdi, & Revel, 2005). The fact that landfarming often requires a large surface area, other bioremediation methods such as composting of petroleum wastes has therefore received increased attention as a potential sub- stitute technology for landfarmingIt has been proven that composting is effective in biodegrading PAHs, chlorophenols, polychlorinated biphenyls (PCBs), explosives and petroleum hydrocarbons, especially diesel fuel at both the laboratory and field scales (Blanca Antizar-Ladislao, Lopez-Real, & Beck, 2005). Also, a number of researchers agreed that composting appears to particularly useful in the bioremediation of petroleum hydrocarbons, especially the PAHs fractions (Sayara et al., 2010).

2.5 Biodegradation

The various parameters that influence the biodegradation process of hydrocarbons in landfarming and composting include moisture content, pH, temperature and microbial density and composition. These parameter can be grouped into three categories namely sludge composition, soil characteristics and temperature of the soil environment. Although the important parameters are the same for all biodegradation of hydrocarbons, its optimum condition may differ. For instance, previous studies had reported variations in the optimum temperature of the biodegradation process which ranges from 18^{o}C to 40^{o}C and this is likely to reflect the optimal temperature for the microorganisms to react under which oil sludge is biodegraded. Also, Kretschek and Krupka reported that the rate that at which a compound of hydrocarbon is biologically being broken down may increase or decrease depending on the presence of functional group in the hydrocarbons chain or the aromatic ring (Aramco, Arabia, & Science, 2004).

2.5.1 Sludge Composition

Kretschek and Krupka stated that the composition of sludge and the loading rate are important factors that affect the degradation process because the rate at which the compound is biologically broken down may increase or decrease depending on the presence of functional groups in the hydrocarbon chain or the aromatic ring (Aramco et al., 2004). The sludge from a different refinery plants varies in composition but they typically contains 10-30% hydrocarbons, 5-20% solids and 50-85% water. It is also widely accepted that the presence of polycyclic aromatic hydrocarbons (PAHs), which are organic micro-pollutant (xenobiotics) compounds, persistent with toxic and carcinogenic-mutagenic characteristics causes the harmful characteristics of the oil sludge (Pakpahan, 2011).

2.5.2 Soil Characteristics

The major factor of hydrocarbons biodegradability is the availability of growth nutrients in the soil since hydrocarbons are only able to provide carbon and hydrogen. Carbon is one basic element of all living material and it forms the skeletons upon which most compounds found in cells are built. Also, the design of a successful bioremediation project considers the availability of carbon, nitrogen and phosphorus whereby the latter can naturally be found in soil and groundwater (Cookson, 1995). As said by J. J. Cooney, nutrients are very vital in the process of biodegradation of hydrocarbons especially nitrogen, phosphorus and in some cases, iron (Fallon, 1998). The microorganisms require inorganic nutrients such as phosphorus and nitrogen to cell growth and sustain biodegradation processes. Although they are the major nutrients needed for biodegradation, it may happen that only a few will become the limiting factor. Atlas had given an example of which, when a major spill occurred in marine and freshwater environment, the supply of carbon will sufficiently increased and the availability of nitrogen and phosphorus will automatically become the limiting factor in this scenario (Das & Chandran, 2011). When there is an absence of nitrogen, a dispersed growth will be observed and when the supply of nitrogen increases, a filamentous growth will be observed. Although nitrogen, phosphorus and potassium (NPK) show a significant contribution to the biodegradation of hydrocarbons, Oudot et al. reported that a number of researchers claimed that high level of NPK will cause negative effects on the biodegradation of hydrocarbons (Chandra et al., 2012). Therefore, a suitable proportion of the nutrients needed for microbial activity must be supplied in order to achieve a balance to the amount of carbon in the waste to be treated. Consequently, characterization of the residue (sludge, soil, sediment) and an assessment of the bioavailability of the nutrients should be taken into consideration. Also, as reported by Rojas-Avelizapa et al., the most adequate C/N and C/P ratios for the degradation of these pollutants must be determined (Roldán-Carrillo et al., 2012).

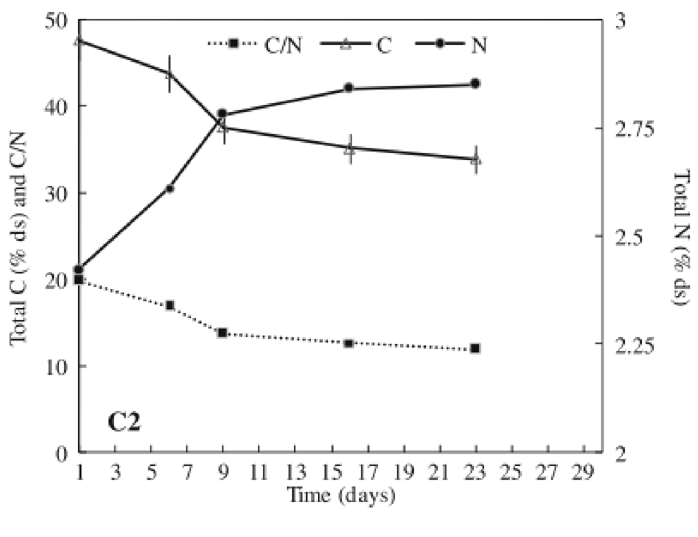

Figure 2 Changes in total C, total N and C/N ratio during biodegradation

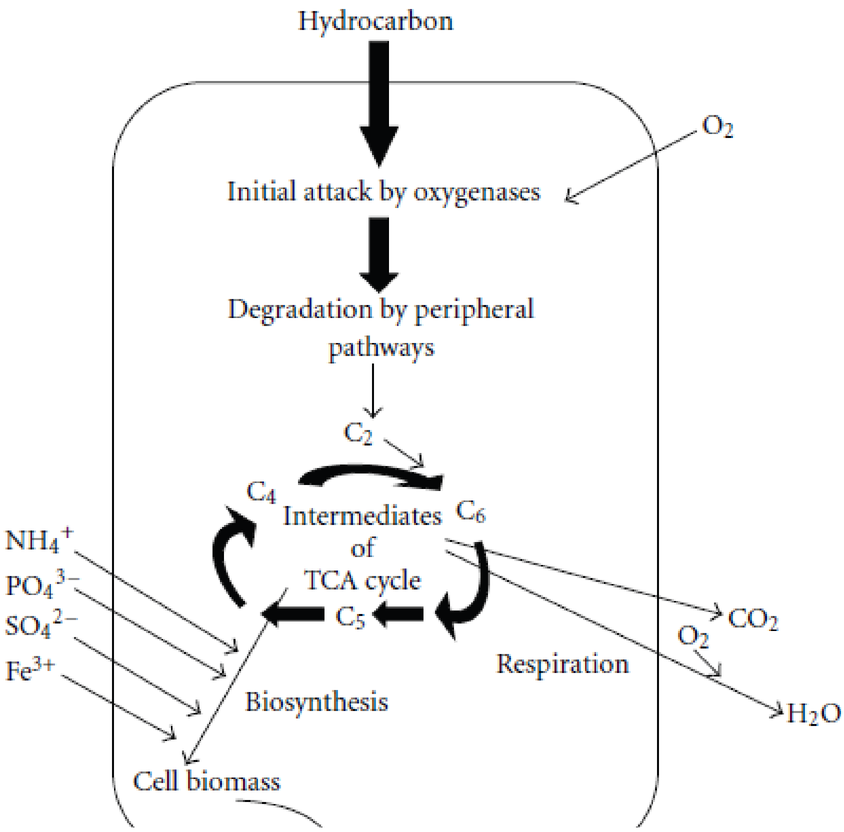

Figure 2 Main principle of aerobic biodegradation of hydrocarbons by microorganisms in the soil

Another important limiting factor of biodegradation is temperature. Temperature plays a vital role in biodegradation of hydrocarbons by directly affecting the chemistry of the pollutants as well as affecting the physiology and diversity of the microbial flora. Figure 4 shows the hydrocarbon degradation rate in different types of environments. Even though the biodegradation of hydrocarbons can take place at a wide range of temperature, the rate of biodegradation generally decreases with a decrease in temperature (Das & Chandran, 2011). Atlas discovered that the viscosity of oil increased at low temperatures, while the toxicity of the low molecular weight hydrocarbons decreases causing a slower biodegradation rate (Chandra et al., 2012). Other than that, temperature not only affects the physiological reactions rates and population dynamics of microbes, but also the physico-chemical characteristics of the environment and therefore, it is highly agreeable that temperature is an important environmental variable in composting environment (Blanca Antizar-Ladislao et al., 2005). Figure 4 also shows the optimum range of temperature for biodegradation in different types of environment.

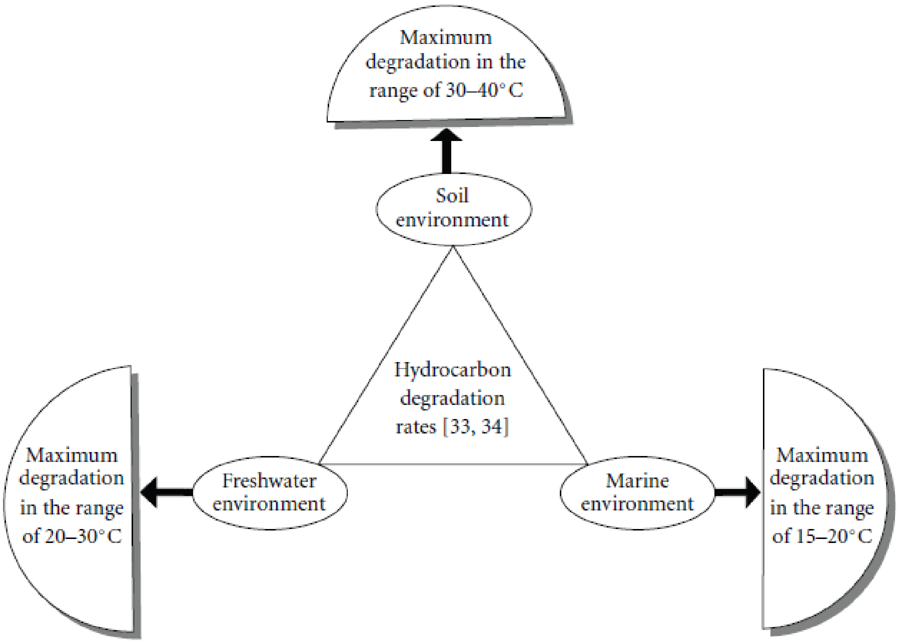

Figure 3 Hydrocarbon degradation rate in different type of environment

In order for the aerobic respiration in the biodegradation process to occur, electron acceptor needs to be present and sufficient for the microbial activity. Being highly reduced substrates, hydrocarbons require an electron acceptor and molecular oxygen is the most common choice. A research done using an abiotic reactor which is vertically set up and equipped with continuous air flow had been done in order to avoid oxygen limitation to the biodegradation process (Koolivand et al., 2013). The growth rate increases depending on the availability of oxygen and yield of aerobic organisms. Mono-oxygenases and dioxygenases aerobes are two uniquely effective enzymes in the oxidation of hydrocarbons. The presence of oxygen, however, can suppress anaerobic processes, such as the degradation of halogenated pollutants, through the inhibition of reductive dehalogenation but as reported by Donald and Freeman, oxygen is rapidly depleted at heavily contaminated sites, in the case of biodegradation of hydrocarbons, thus resulting in anaerobic conditions (B. Antizar-Ladislao, 2010). It is important to maintain the biodegradation of oil sludge in aerobic respiration because in the absence of oxygen, the microbes will take sulfate ions (SO_4^{2-}) that is abundant in water as their source of oxygen for respiration and this will lead to the production of hydrogen sulphide (H_2S) which has a low solubility in the wastewater and a strong, offensive, rotten-egg odour (Zhang, Yan, Tyagi, & Surampalli, 2013). The unwanted production of hydrogen sulphide gas can be controlled by providing adequate oxygen supply to the biodegradation environment. Therefore, the presence of electron receptor is important in order to carry out the respiration in biodegradation process.

Previous researches also reported that the moisture content has a significant impact on the biodegradation rate, and indirectly affects the hydrocarbons contents in the sludge sample and other parameters as well. For instance, excessive amount of moisture can hinder the supply of oxygen and as a result will decrease the rate of biodegradation of oil sludge (Ho & Rashid, 2008). Air would usually be injected into or extracted from the vadose zone or soil with or without addition of nutrients to stimulate indigenous bacteria to biodegrade petroleum hydrocarbons in aerobic bioremediation treatment (Davis, Laslett, Patterson, & Johnston, 2013). Moisture content was also proven to have significant impact in regulating the temperature and air permeability of the biodegradation environment. According to Gajalakshmi and Abbasi, moisture content should be in between 45-60% in weight for an ideal biodegradation process because lots of moisture will be lost through evaporation and with the decrease in water content, the rate of biodegradation will decrease (Muktadirul Bari Chowdhury, Akratos, Vayenas, & Pavlou, 2013). However, according to Ho & Rashid (2008), the optimum range of moisture content is in between 30% to 40%. This is probably valid assuming that there is no lost of moisture content. As for the relationship between moisture content and air permeability, Druilhe et al., Poulsen and Moldrup, and Richard et al. found out that there was an increase in air permeability when moisture content increased because when moisture content increases, water is dragged into the small pores of the matrix, thus creating larger aggregates which in turn lead to larger inter-aggregate pores and which results in an increased air permeability (Huet, Druilhe, Trémier, Benoist, & Debenest, 2012). The aforementioned facts proven that moisture content of the medium of biodegradation plays an important role in ensuring an optimum condition for the biodegradation environment.

The importance of the aforementioned parameters had been proven to affect the biodegradation of oil sludge. In composting treatment, bulking agent is usually added to the mixture of oil sludge and soil in order to optimize the biodegradation process. Haug stated the difference between composting and other ex situ soil treatments is the addition of bulking agent to the compost mixture to increase porosity and serve as sources of easily assimilated carbon for biomass growth (Blanca Antizar-Ladislao et al., 2005). A research has been done whereby the addition of a carbon-rich bulking agent (wood shavings) is used to improve oxygen diffusion and to create suitable aerobic conditions within the composting piles (Marín, Moreno, Hernández, & García, 2006). It has also been proven that optimal porosity of 30–35% can be achieved by using inexpensive bulking agents, such as wood chips, sawdust, peat or bark and the addition of these organic matters has been found to boost the degradation of PAHs during bioremediation of contaminated soils (Kriipsalu, Marques, Nammari, & Hogland, 2007). This is also supported by the study done by Marı´n et al., whereby the most successful composting treatment was the one in which the bulking agent was added, where the initial hydrocarbon content was reduced by 60% in 3 months as compared with the 32% reduction achieved without the addition of bulking agent (Juwarkar, Singh, & Mudhoo, 2010).

CHAPTER 3

METHODOLOGY

The focus of this chapter is to discuss on the equipments that are to be used in the testing of the test model. The experiments conducted in this study were done at Building 13 at Universiti Teknologi PETRONAS (UTP). Since the major area of the study in dealing with the biodegradation of oil sludge, more concern is focused on the parameters such as the nutrients, optimum temperature, sufficient moisture content and adequate oxygen. This chapter also discusses on the process in conducting the study and the planned Gantt chart for the overall study.

3.1 Fabrication of the Composter

A compost tumbler with a certain design criteria was designed with the aim of having a compost tumbler which is effective in providing a suitable environment for the biodegradation process of TENORM (Oil sludge). The design that was introduced for this study is a modification of landfarming and garden compost tumbler which has been practised in the industry and by the public respectively. The design of the composting system will enhance the ability of the existing treatment method which is landfarming by addressing its primary downsides. This expected to eliminate the impact of TENORM towards the environment and also the people.

3.1.1 Composting Equipment & Materials

Experimental apparatus consisting of a compost tumbler made of plastic drum with a capacity of 10 litres was used in this study, in which half of it was filled with compost mixture. The temperature in the composter was kept warm by thermally insulating the compost tumbler in order to provide optimum temperature for the biodegradation process of oil sludge. This was done with the means of covering the tumbler with a dark or black cover around it whenever no samplings are done. Attached to the compost tumbler is an air compressor which provided oxygen to the compost mix on a daily basis.

Two types of oil sludge samples were acquired from PETRONAS Penapisan Melaka Sdn Bhd, namely the sweet crude and sour crude (4 litres each). In order to provide a proper environment for the biodegradation process to occur, a few other materials were obtained to provide to give sufficient nutrients for the process. Meshed coconut husks was used as the source of nitrogen and also acted as the bulking agent in the compost mix, whereas nitrogen and phosphorus was added by mixing with chicken manure.

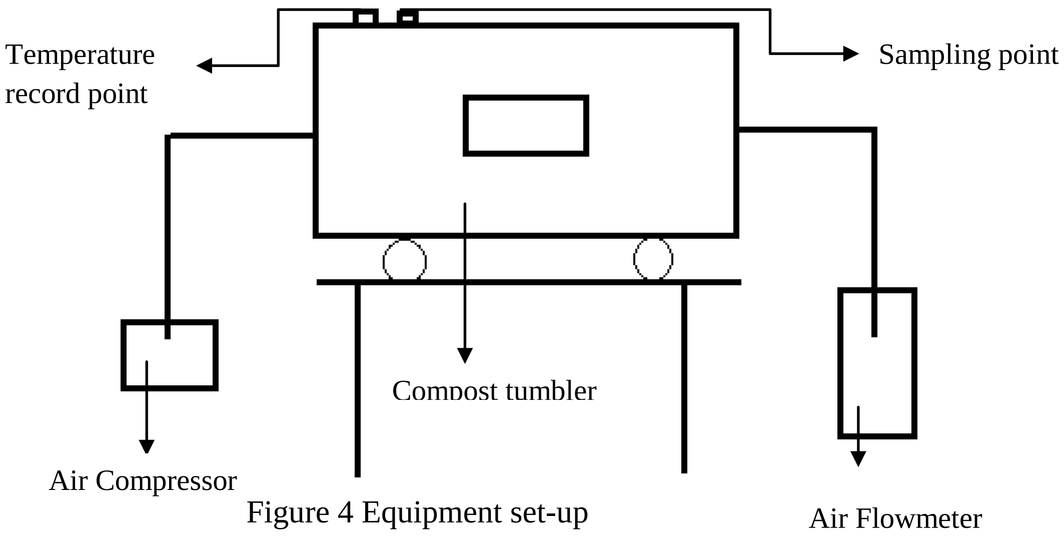

Figure 4 Equipment set-up

Figure 5 Equipment set-up

Figure 6 Experimental Set Up at the laboratory; The red circle shows the gas outlet

3.2 Total Petroleum Hydrocarbon (TPH) Analyzer – Analysis of TPH content

Samples of oil sludge were collected directly and weighed (to the nearest 0.1 gram) EPA/VOA 40 ml vial. The sample should be about ¾ of the volume of the vial. The sample was weighed to the nearest 0.1 gram, subtracting the tare weight of the vial. 5 grams of sodium sulphate was added because the sample was wet and clumpy. Spatula was used to break up the clumps. The same amount of solvent (Hexane) as the weight of the sample in grams (weight of sodium sulphate is not included) was added. This will give a 1:1 extraction ratio. The vial was capped with the Teflon side of the liner toward the sample. The sample was then shaken vigorously for 2 minutes. A filter paper was placed in a filter funnel and approximately 1 teaspoon of silica gel is added. The sample was poured from the vial through the silica gel into a clean container. 50 microlitres of the sample was extracted using a pipette onto the centre of the HATR-T2 plate and the analysis is run. Results of analysis are as shown below. The readings were taken in triplicate to ensure accurate data.

Table 2 TPH content in the oil sludge sample

1	2	3	Average (g/kg)
467	468	465	466.7

3.3 Phosphorus Test

The samples were preheated for 30 minutes using a DRB200 reactor which has been preheated at 150^{o}C. A spectrophotometer was used to determine the phosphorus content in the sample and materials. The samples were mixed with Potassium Persulfate Powder Pillow for Phosphonate before heating begun. Sodium Hydroxide Standard Solution and PhosVer 3 Powder Pillow were added to the vial and readings were taken after 2 minutes to allow reaction of the mixtures.

3.4 CHNS Analyzer – Determination of Carbon and Nitrogen content in materials and samples

The total content of Carbon and Nitrogen in the oil sludge, coir and poultry manure were determined using CHNS Elemental Analyzer. This equipment provided a mean of determination of carbon, hydrogen, nitrogen and sulphur in organic matrices or other materials. In the combustion process, carbon was converted to carbon dioxide, while nitrogen is converted to nitrogen gas at a temperature of 1000^{o}C. Carbon and nitrogen content were determined in order to calculate the C:N:P ratio for the compost mix.

Figure 7 CHNS Analyzer used to analyzed the carbon and nitrogen content of the poultry manure, oil sludge, palm fronds and coir

3.5 Biodegradation Assay

Meshed palm fronds were added into oil sludge to have the initial concentration expressed as total of nitrogen and carbon using the CHNS analyzer. The initial and final Total Petroleum Hydrocarbons (TPHs) was measured using TPH Analyzer. This indicated the susceptibility of the biodegradation process. Following that, the compost mixture will be prepared according to the ratio shown.

Table 3 Mixture of materials for Batch 1

Samples	Oil Sludge (kg)	Coir (kg)	Processed Poultry Manure (kg)
Experiment 1 (Sour crude)	1	0.5	3

Table 4 Mixture of materials for Batch 2

Samples	Oil Sludge (kg)	Palm Fronds (kg)	Raw Poultry Manure (kg)
Experiment 2 (Sour Crude)	1	0.5	3

Table 5 C:N:P ratio for both Batch 1 and Batch 2

	C	**N**	**P**
Experiment 1 (Sour crude)	100	16.0	0.2
Experiment 2 (Sour crude)	100	20.0	5.0

Finally, the components of the composting mixture were mixed manually according to the aforementioned ratios which will occupy approximately a quarter of the compost tumbler. The compost mixture was aerated with air from the air compressor on a daily basis and turning of the compost tumbler was done to ensure that the air is supplied homogenously to the compost mixture.

3.5.1 Content of Compost Mixture

For the first batch of experiment, the compost mix consists of 1 kg sour crude oil sludge, 0.5 kg of coir and 3 kg of processed poultry manure. In order to provide microorganisms and bacteria to the compost mix, 1.5 kg of soil is added. On the other hand, for the second batch of compost mix, it consists of 1 kg sour crude oil sludge; 0.5 kg dried and meshed palm fronds, and 2 kg of raw poultry manure. The raw poultry used in the second batch of experiment contains natural bacteria and microorganisms, therefore no addition of soils are needed.

Figure 8 Dried palm fronds

3.6 Sampling

During the composting period, the performance of the compost was monitored by taking samples daily (2g) to measure the level of TPH using the TPH Analyzer and also to record the moisture content. The temperature of the compost mix was taken daily to monitor the performance of the compost tumbler experiment. The samples were also tested for the amount of moisture content to make sure that the level was within the optimum which has been set earlier. The moisture content was calculated using the formula below.

$$C = \frac{A - B}{A} \; x \; 100$$

Where, A = the initial weight of the sample before being dried, g;

B = the final weight of the sample after being dried, g;

C = the total moisture content of the sample, %.

Since pH is also one of the most important factors in ensuring a good biodegradation environment, the pH of the compost mix will also be monitored daily.

3.7 Gantt Chart

In the second half of the study, the focus was more on the set-up of equipment, preliminary experiments and finally the biodegradation experiments. Thus, it was important to have a Gantt chart in which helped in keeping track of the progress and proceed accordingly. The Gantt chart gave a clear indication on the tasks that will be done and to ensure the feasibility of the study as it is initially planned in the beginning of the study. The Gantt chart for the progress of the second half of the final year project is given in Figure 6.

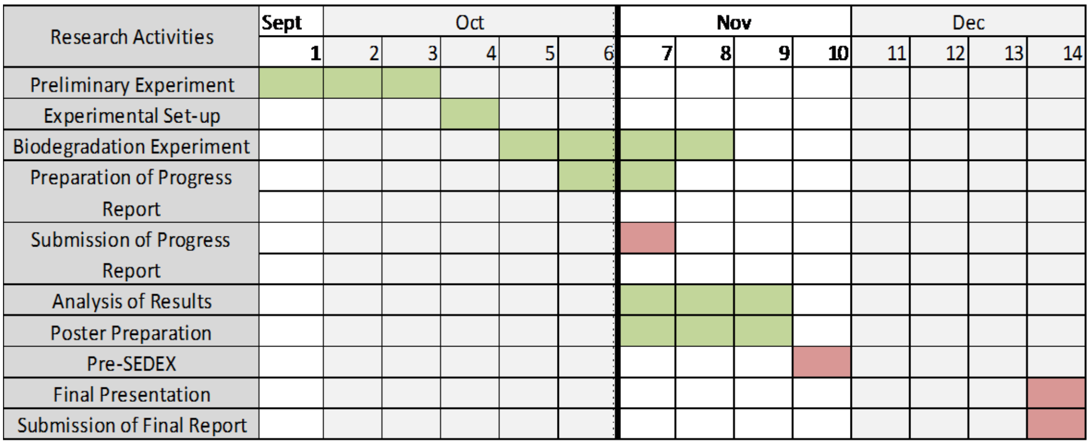

Figure 9 Gantt Chart for FYP 2

CHAPTER 4

RESULTS AND ANALYSIS

The parameters listed in previous chapter affects the rate of biodegradability of petroleum hydrocarbons which can also be used to identify the optimum condition to treat oil sludge. Above all, the content of oil sludge was the upmost important thing to ensure the success of the biodegradation process. For this research, two batches of biodegradation assays were prepared. For each sampling occasion, the sample was analyzed for its temperature, moisture content, total gas production and TPH content. The aims of these experiments are to determine the extent of rate of hydrocarbon biodegradation and to compare the effects of different C:N:P ratios to the biodegradation process.

Figure 10 A sample taken from the compost reactor which consists of oil sludge, coir and poultry manure

Figure 11 The compost mixture in the compost reactor

4.1 Temperature

For Batch 1 and Batch 2, the temperature profile of the substrate is measured on a regular time intervals throughout the composting duration. The substrate was mixed thoroughly before the temperature was measured. In the beginning of the experiment, the temperature for both mixtures had slightly increased above the ambient, which indicated that biodegradation process was currently taking place. The ambient temperature of both of the composting environments was almost the same, whereby they ranged from 26^{o}C to 29^{o}C. It had been fluctuating in between the range which was probably because of the moisture content in the mixture. However, the temperature was never too low at which it will have the potential to stop the biodegradation process because the low temperature will give an unsuitable environment for the biodegradation of hydrocarbons.

Ho & Rashid (2008) reported that the optimum temperature for biodegradation is 35^{o}C and it is also proven in their study on oil sludge composting. After a week, the compost mixture had not yet to coincide with the optimum temperature for biodegradation of hydrocarbon which is 35^{o}C. A few factors such as the materials used will be taken into consideration. The next figure shows the progress in terms of temperature of the composting environment in both mixtures.

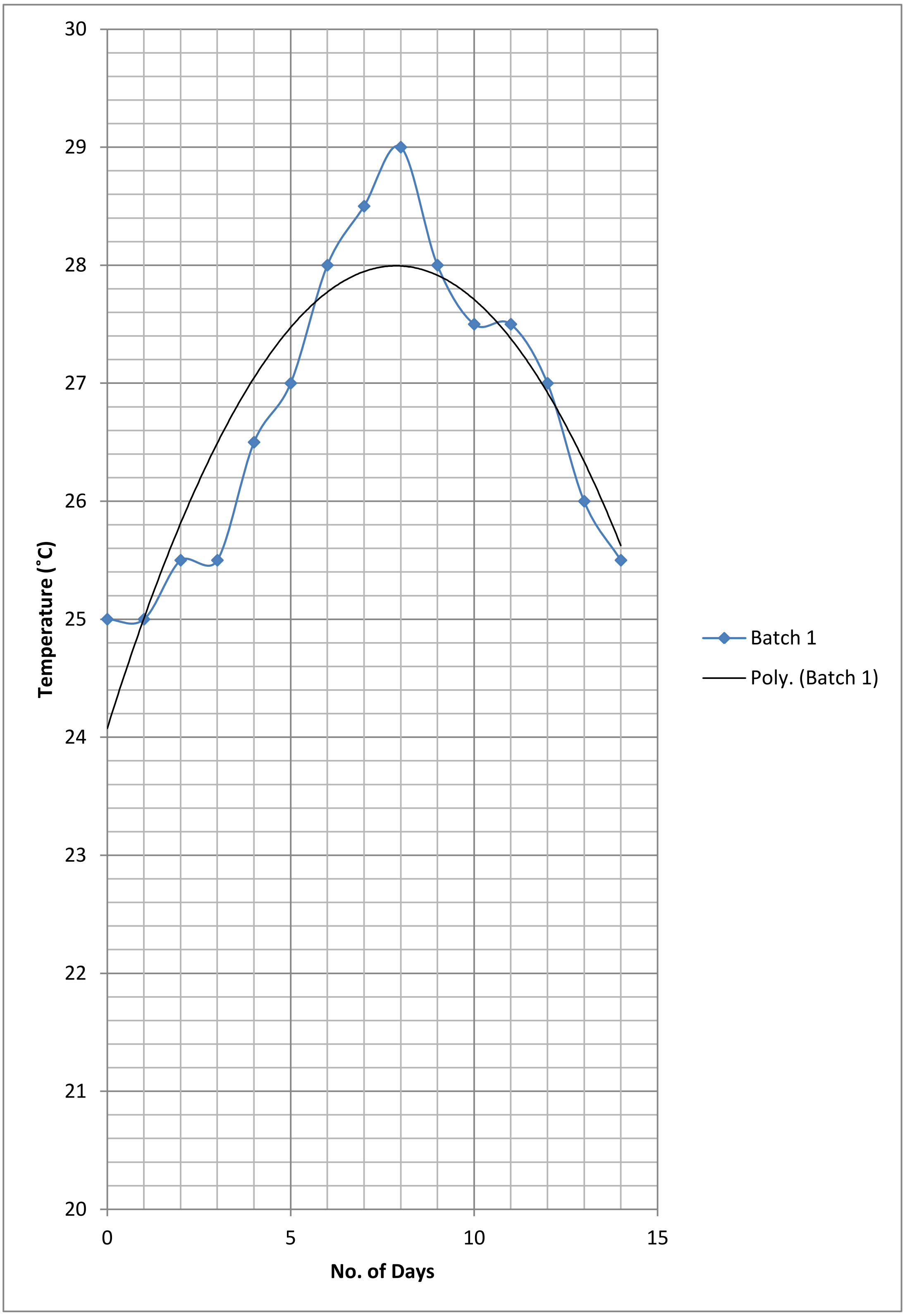

Figure 12 Temperature profile for Batch 1 against time

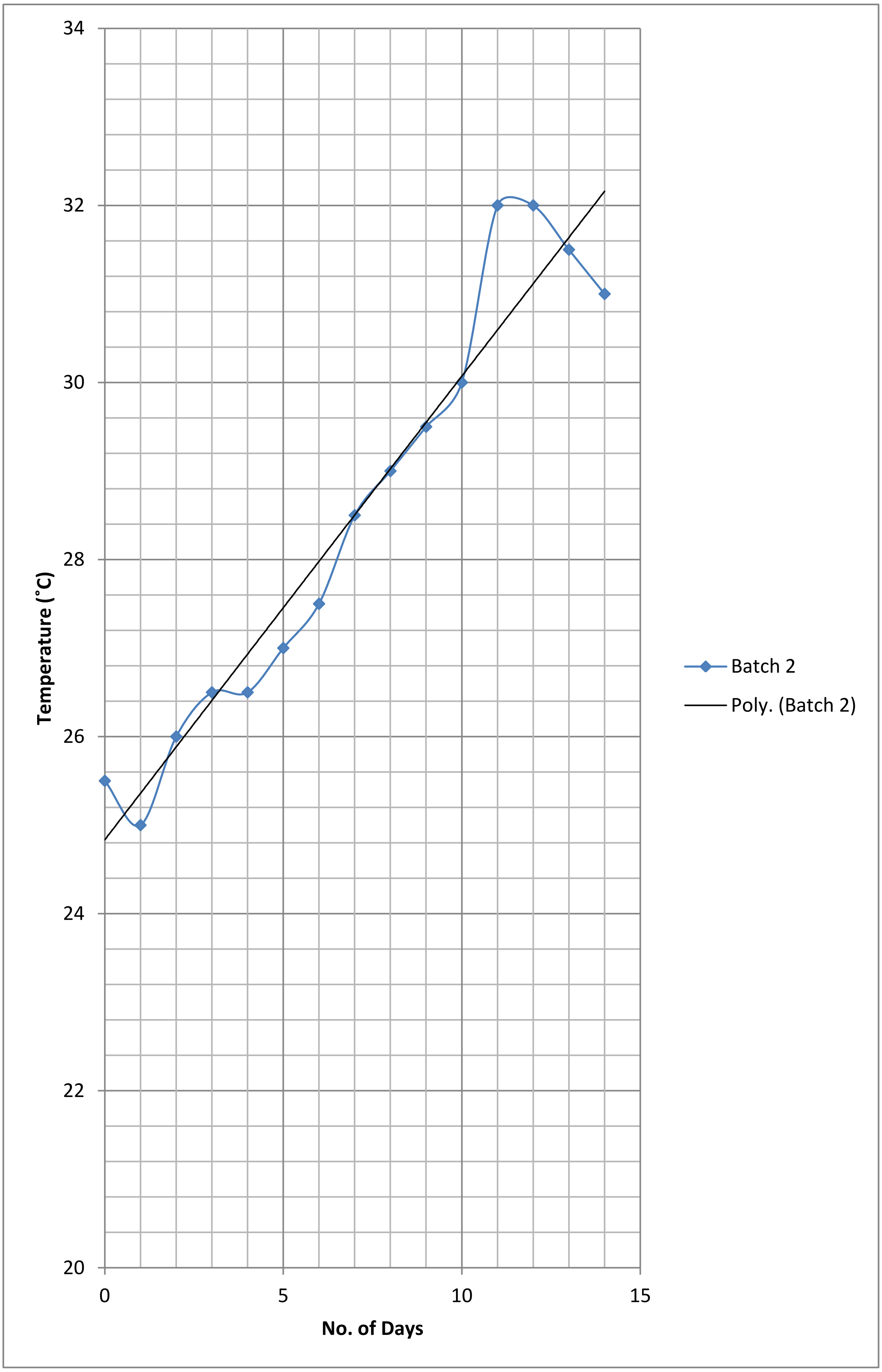

Figure 13 Temperature profile for Batch 2 against time

As expected, the temperature for the compost mixture in both Batch 1 and Batch 2 increased after a few days of composting. However, the temperature never reached the thermophilic range (>45^{o}C) or in other word, both experimental mixes were always in mesophilic range. Even though the biodegradation of hydrocarbons can take place at a wide range of temperature, the rate of biodegradation generally decreases with a decrease in temperature (Das & Chandran, 2011).

4.2 Moisture Content

Moisture content is one of the most important parameter in the success of biodegradation process of hydrocarbons. Therefore, it is important to make sure that the level of moisture content is kept constant at all times. According to Ho & Rashid (2008), the biodegradation process will not be interrupted as long as the moisture content is kept above the minimum, although however the biodegradation process may become halted if there is excessive moisture content which reduces the available oxygen level. This leads to insufficient supply of oxygen to the microorganisms and bacteria. The initial moisture content of both Batch 1 and Batch 2 were above the optimum moisture content which were 59% and 57% respectively. In order to lower down the moisture content to be in the range of 30% to 40%, dried soil with 5% moisture content was added to the composting mixture.

Figure 14 Oven-dried soil with 5% moisture content

Figure 15 The moisture content of the compost mixture is measured using moisture analyzer operated at 105^{o}C

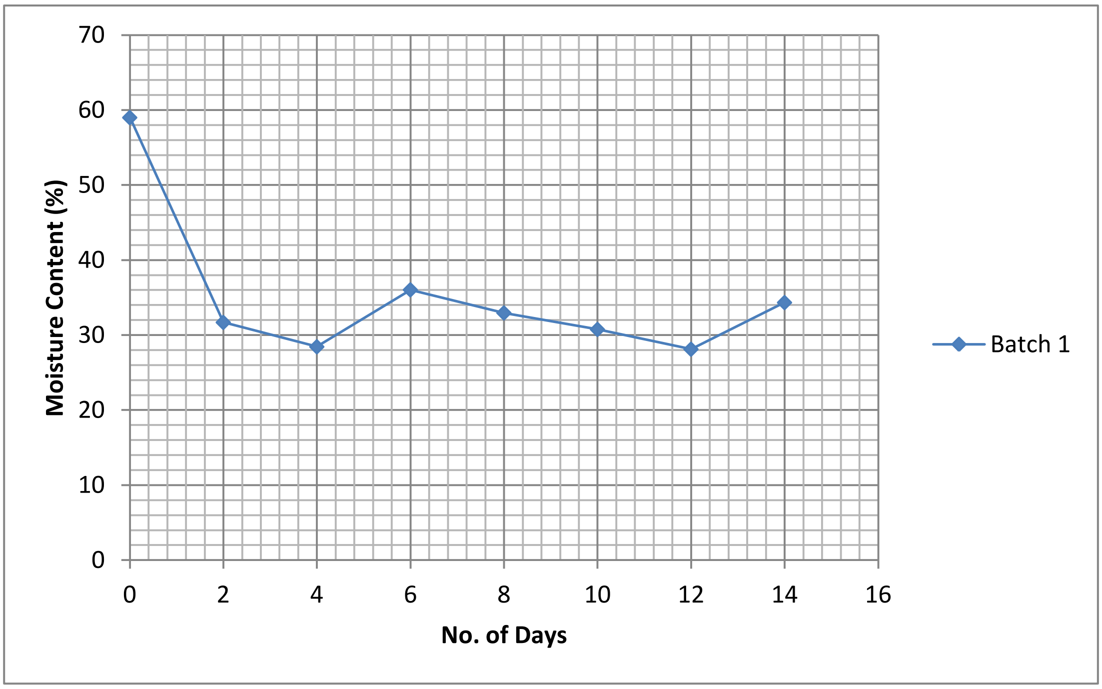

Figure 9 Moisture content of Compost Mixture in Batch 1 over the experiment period

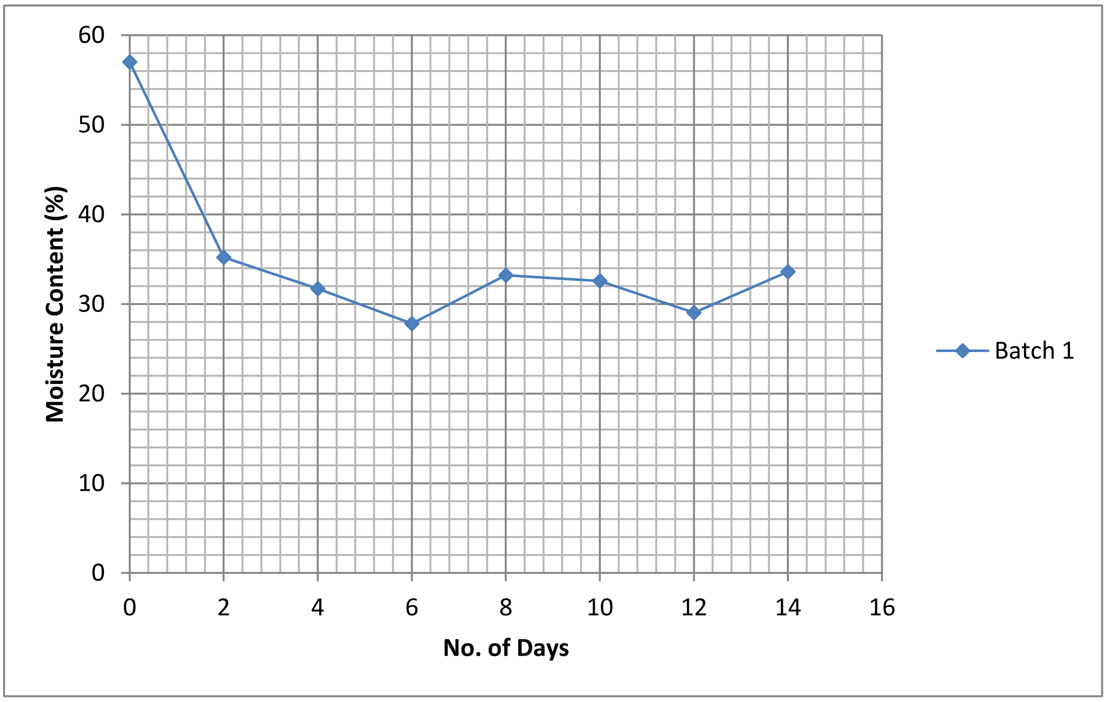

Figure 10 Moisture content of Compost Mixture in Batch 2 over the experiment period

The compost mixture moisture content was measured on an alternate basis to ensure that it was maintained between 30% and 40%. Water was added accordingly if the moisture content was below 30%. This was probably due to evaporation when the biodegradation experiment was being carried out and also during the aeration process.

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$$

4.3 Gas Production

Biodegradation products include carbon dioxide, water and other compounds. In order to ensure that there was biodegradation process that was taking place inside the composting reactors, the level of gas produced was measured by connecting an outlet to the compost reactors.

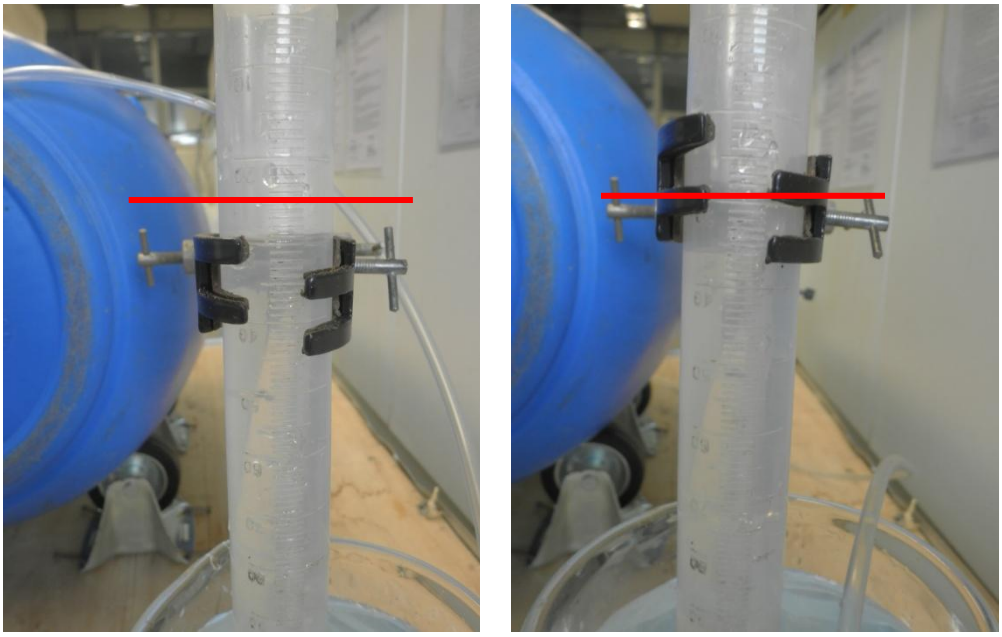

Figure 18 The initial reading on the measuring cylinder and the reading after 2 days of composting

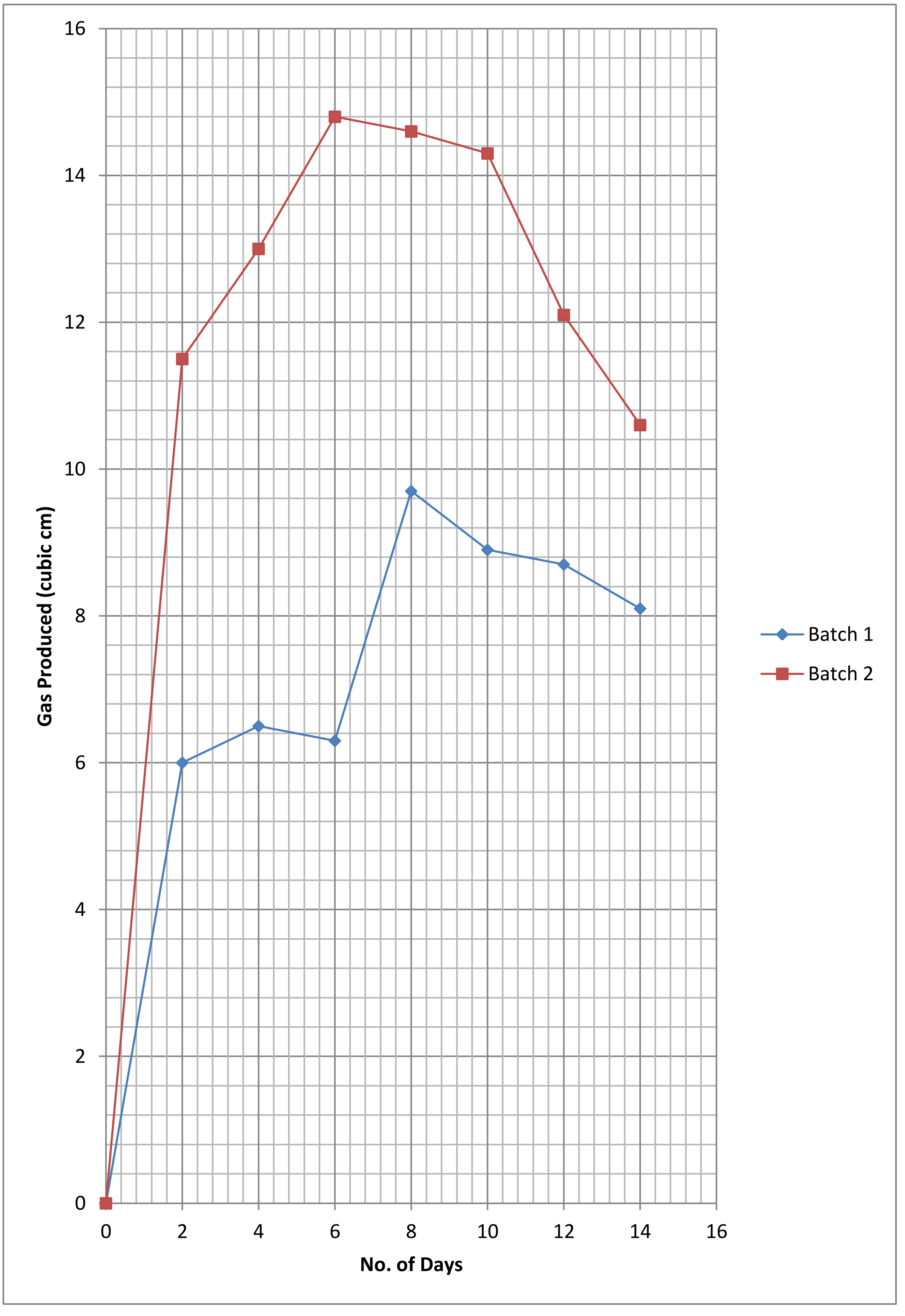

Figure 19 The gas production of Batch 1 and Batch 2

The product of biodegradation process includes energy (heat) and carbon dioxide. However, the composition of the gas produced in this experiment may be consisting of carbon dioxide and also the volatilized compounds from the compost mixture. The percentage of volatilized compounds in the total gas production is probably of a small amount. As reported by Sayara, Sarra and Sanchez (2010), the total amount of volatilized hydrocarbons could not be determined because the amount of it volatilized into gas is very small. Other than that, the temperature recorded for Batch 1 and Batch 2 experiment shows that it was almost impossible for the petroleum hydrocarbons to be volatilized under such condition. Since carbon dioxide is one of the biodegradation product, the amount of carbon dioxide produced should increase when rate of TPH decrement increases.

As can be seen from the graphs, the gas produced up until day 2 of experiment was the highest for both Batch 1 and Batch 2. This was because at the beginning of the experiment, there was sufficient nutrient content in the compost mixture. Thus, it provided a suitable environment for biodegradation process to occur. However, the gas produced decreased from day 6 and day 8 for Batch 1 and Batch 2 respectively. Over time, the nutrients provided by the compost mixture were eventually used by the indigenous bacteria in order to degrade hydrocarbons. Since the nutrients were not added, the biodegradation process slowed down due to insufficient nutrients. This caused the decrement in gas production and also the rate of TPH degradation.

Although addition of nutrients may increase the biodegradation rate of hydrocarbons, it was important to know the limit of the nutrient level needed. Namkoong et al. (2002) has reported that even though the addition of organic supplements is able to increase the biodegradation rate, excessive supply would eventually inhibits the process.

4.4 Total Petroleum Hydrocarbons (TPH) content

The goal of this analysis was to quantify the rate and extent of hydrocarbons degradation under the provided biodegradation environment. In this analysis, the Total Petroleum Hydrocarbons (TPH) level is monitored on an alternate day basis in order to observe the trend in the decrement of the hydrocarbons.

The initial TPH content of the oil sludge is measured before the biodegradation assays are being carried out. The TPH content of Batch 1 and Batch 2 are being monitored on an alternate day basis to observe the trend. According to previous research, the TPH content should decreases with an increased rate when the retention time increases. This is also dependent on the parameters mentioned earlier such as temperature and moisture content. The initial TPH content of the oil sludge in Batch 1 and Batch 2 are as shown below.

Table 6 Initial TPH content of the oil sludge before compost treatment

1	**2**	**3**	**Average (g/kg)**
467	468	465	466.7

The reduction of TPH content for Batch 1 and Batch 2 after a few days of biodegradation process is as tabulated below.

Table 7 The decrement of TPH content within 14 days of composting

g/kg		
No. of Days	**Batch 1**	**Batch 2**
0	466.67	466.67
2	452.67	431.67
4	432.67	399.33
6	421.67	344.70
8	414.67	337.40
10	405.00	325.00
12	391.67	317.67
14	388.67	309.67

From the results tabulated above, it can be concluded that the compost mixture in Batch 2, which consisted of 100:20:5 of the C:N:P ratio, caused more decrement in the TPH content of the oil sludge. The combinations of natural microorganisms present in the soil and poultry manure had increased the rate of biodegradation of the hydrocarbons in Batch 2. The microorganisms in compost mixture Batch 1 is only provided by the soil because the processed poultry manure used can only supply nutrients since most of the microorganisms had been destroyed during the manufacturing process of the poultry manure.

The TPH content for the oil sludge for Batch 1 and Batch 2 decreased 16.7% and 33.6% respectively. In which Batch 2 with the highest removal of TPH and it can be derived that the C:N:P ratio in Batch 2 has increased the degradation of hydrocarbons with an increase in the nitrogen and phosphorus content in the mixture. This also concludes that the aeration, turning of compost tumbler and nutrients are enough to stimulate the microbial activity (Roldán-Carrillo et al., 2012).

Figure 20 TPH analyzer that is used to determine the TPH level in the compost mixture

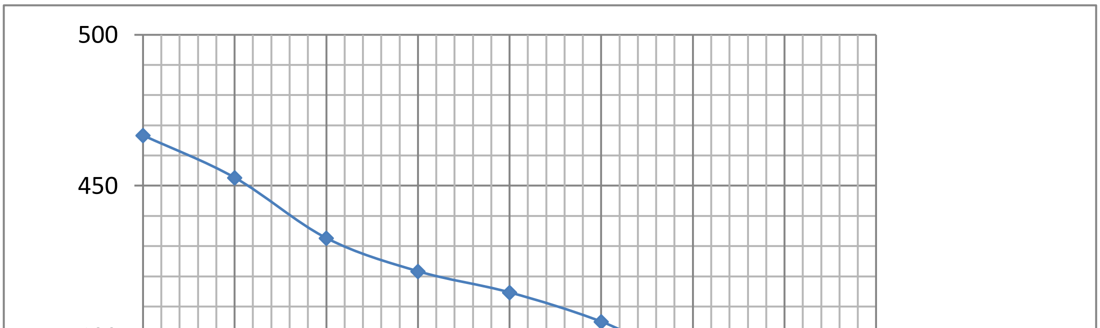

Figure 21 The decrease in TPH content in Batch 1 against time

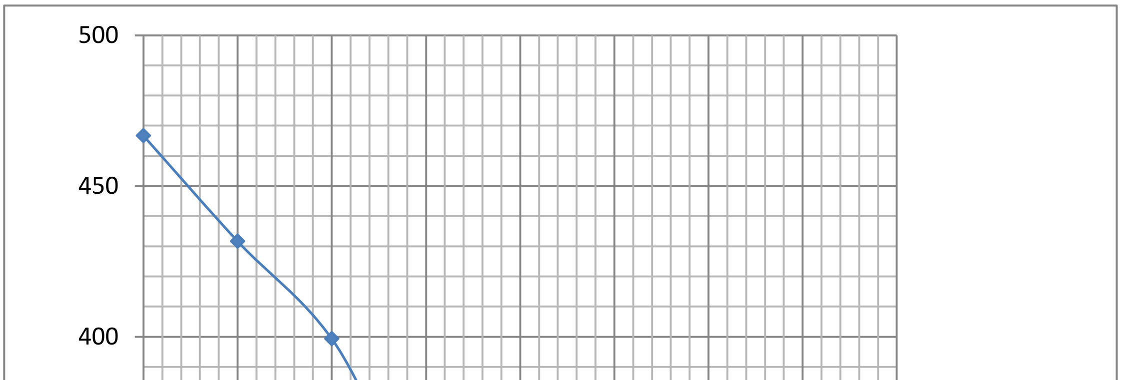

Figure 22 The decrease in TPH content in Batch 2 against time

Figure 11 Comparison of percentage removal between Batch 1 and Batch 2

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

In this paper, the closed composting treatment method which utilizes the biodegradation process is being carried out. Although composting is an old technology which had been widely used in the agricultural field, by incorporating the concept of oil sludge biodegradation; it can be used as oil waste treatment method given a suitable condition. Therefore, the important parameters of oil sludge biodegradation are being identified based on the previous researches done around the world in order to ensure the success of the lab-scale study.

The important parameters of biodegradation include:

- the availability of nutrients in the medium (soil),
- the optimum temperature of the biodegradation environment,
- the presence of electron acceptor (e.g: oxygen)
- the level of moisture content
- the usage of bulking agent

The parameters listed above affects the rate of biodegradability of petroleum hydrocarbons which can also be used to identify the optimum condition to treat oil sludge. Above all, the content of oil sludge is the upmost important thing to ensure the success of the biodegradation process. As it has been proven in this experiment, with a suitable amount of nutrients and the presence of indigenous bacteria, the biodegradation of hydrocarbons can be done at an optimized rate.

Batch 2 which had a higher C:N:P ratio as compared to Batch 1 resulted with a higher percentage of decrement in TPH content. Since no additional nutrients were added throughout both runs of experiments, the available nutrients in Batch 1 was used up at a faster rate because of the lower amount as compared to the nutrients content in Batch 2. In terms of temperature, Batch 2 experiment resulted in a higher peak temperature of 32˚C as compared to Batch 1 with only 29˚C. This is because the biodegradation rate in Batch 1 decreases at an earlier stage which then limits the temperature of Batch 1 compost mix from increasing any further compared to Batch 2.

However, the experiment can further be improved with a thorough analysis in determining the oil sludge content. This is to determine the radioactivity level of the oil sludge which is contributed by the polycyclic aromatic hydrocarbons. Also, the odour of oil sludge should be measured with appropriate standard technique such as the Threshold Odour Number test which can quantify and prove that the odour problem has lessened. Last but not least, the C:N:P ratio of the compost mix should be determined before the experiment is conducted to ensure that a sufficient amount of nutrients is provided at the early stage of experiment.

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