Pre-Treatment of TENORM by Using Mechanical Composting Method

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Abstract

The petrochemical industry generates a series of liquid effluents as known as oil sludge during the petroleum-refining process. These effluents contains various heavy metals, solid particles and hydrocarbons which are carcinogenic to human being, hence it must be treated before it can be disposed according to the EQA 1974. Currently, there are various technologies of remediation of the oily sludge and among them is the popular landfarming treatment method which offers cost effective yet environmental friendly. But one of the drawbacks of this method is that it produces a strong unpleasant odour during the sludge processing which comes into the concern of community. This study is about the pre-treatment of the oily sludge by using a closed composting system in order to contain the odour during hydrocarbon biodegradation. Using various materials, chemicals, and physical parameters, the feasibility of this method is studied by evaluating the effect of various conditions, compositions and environments on the degradation of hydrocarbon and odour level. This paper elaborates these findings in details.

Index terms – Biodegradation, Composting, Oil sludge, TENORM, Petroleum Waste.

1. Introduction

Technologically Enhanced Natural Occurrence Material (TENORM) is defined as materials, usually industrial wastes or by-products enriched with radioactive elements found in the environment and are brought to the surface through human activities such as oil and gas exploration or mining and through natural processes. In petroleum industry it is known as oil sludge which is the end product in petroleum refinery. These effluents must be treated through depuration processes. The wastes or burning them with no previous treatment has serious environmental consequences and presents a risk to both ecosystems and human health.

Due to its content of harmful organic compounds, oil sludge has been recognized as a potentially dangerous waste product and categorized under scheduled waste under Environmental Quality Act 1984 Hence restricted to Environmental Quality Act 1974 where:

- Scheduled waste shall be disposed of at prescribed premises only
- Scheduled waste shall be rendered innocuous prior to disposal
- Scheduled waste shall be treated at prescribed premises or at on-site treatment facility only

There is a variety of oily sludge treatment methods that have been developed 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, and the most commonly used in Malaysia is ‘landfarming’ method which offers a cost-effective, energy efficient, and environmentally friendly with minimal residue disposal problems [3]. 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. One of the downside of using this method of treatment is that it creates a strong unpleasant odour originated from the hydrogen sulphide generated during the sludge processing causing the community to complaints.

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. This study is developed with the aim to provide an innovative treatment method which is related to human health, safety and environment implementation and 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.

1.1 Factors Affecting Biodegradation

The oil sludge biodegradation can be affected by a variety of factors, such as the type of microorganisms, treatment duration, temperature, nutrients, concentration, loading rate and characteristics of oily sludge (J. T. Dieble and R. Bartha, 1979). This has been supported by Kretschek and Krupka where they state that various parameters that influence the biological process of hydrocarbons degradation includes moisture content, pH, temperature and microbial density and composition. Although the important parameters are the same for all biodegradation of hydrocarbons, its optimum condition may differ. (Aramco, Arabia, & Science, 2004).

2. Materials and Method

2.1. Materials

4 litres sample of oil sludge are acquired from PETRONAS Penapisan Melaka Sdn Bhd in the form of sweet crude which is free from phosphorus content. In order to provide a proper environment for the biodegradation process to occur, a few other materials need to provide to give sufficient nutrients for the process. Dry palm fronds are being used as the source of nitrogen and also act as the bulking agent in the compost mix, whereas phosphorus will be obtained from chicken manure (artificial fertilizer).

2.1.1. Physical and Chemical Analysis of the materials

TPH Analysis

Samples of oil sludge (sweet) were collected directly and weighed EPA/VOA 40 ml vial. The sample should be about ¾ of the volume 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 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 micro litres 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.

Sample 1 (mg/g)	Sample 2 (mg/g)	Sample 3 (mg/g)	Average (mg/g)
441	445	440	442

Table 1: TPH content of the sweet crude sample

C:N:P ratio

The samples were preheated for 30 minutes using reactor at 150 ^{o}C. 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. A spectrophotometer was used to determine the phosphorus content in the sample and materials. The total content of Carbon and Nitrogen 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.

Material	C:N:P Ratio
Oil Sludge	100 : 0.72 : 0.508
Soil	100 : 1.38 : 0.016
Manure	100 : 2.66 : 0.9
Palm Fronds	100 : 107.5 : 6.03

Table 2: C:N:P ratio of the material

Moisture Content

The moisture content of the compost mixture is measured using Moisture Analyser XM 60 operated at 105^{o}C.

Material	Moisture Content, %
Oil Sludge	71.4
Soil	66.3
Manure	48.75
Palm Fronds	9

Table 3: Moisture content of the material

2.2. Mixing and Composting

The sample will be tested with different composition of soils with different C:N:P ratio. According to the data collected from the literature research, optimum biodegradation happens in C:N:P ratio range of 100:20:5 and 100:4:0.6 . The study will have four different samples with different ratio within the optimum C:N:P ratio to determine the most optimum ratio for the oil sludge to biodegrade. The samples are then left in the composter for two weeks while the parameters are being watched on a regular basis.

Sample	Oil Sludge (g)	Soil (g)	Poultry Manure (g)	Palm Frond (g)
1	600	100	250	50
2	600	250	100	50
3	900	500	500	100
4	900	1000	750	100

Table 4: Loading rate of the sample material

Sample	C:N:P ratio
1	100 : 6.5 : 0.7
2	100 : 4.2 : 0.9
3	100 : 15 : 0.5
4	100 : 17.5 : 2.1

Table 5: C:N:P ratio of the sample

The compost mixture will then be aerated with air from the air compressor on a daily basis and turning of the compost tumbler will be done to ensure that the air is supplied homogenously to the compost mixture.

2.3. Sampling

During the composting period, the performance of the compost will be monitored by taking 20 grams of sample daily to measure the level of TPH using the TPH Analyzer and also to record the moisture content. The temperature of the compost mix will be taken daily to monitor the performance of the compost tumbler experiment.

3. Result and Analysis

To observe the performance of the compost tumbler, three parameters has been monitored regularly to be analysed which are the temperature, gas production and also TPH content of the samples.

3.1. Temperature

The temperature for the compost mixture in all samples increased after a few days of composting. However, the temperature never reached the thermophilic range (>45oC) or in other word, both experimental mixes were always in mesophilic range. One of the factor that might contribute to this is because of low loading rate where the compost only occupy ¼ of the volume of the composter. Besides, the experiments have been conducted in a room temperature with air-conditioner at 28°C.

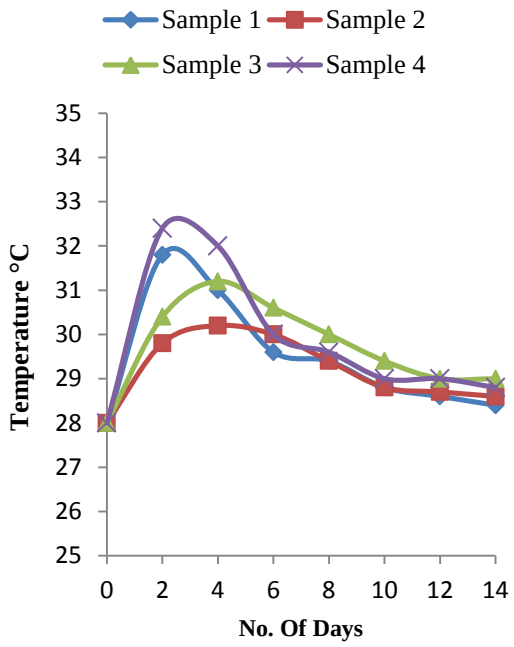

Figure 1: The temperature profile of the experiments over the period of 14 days

The temperature rises rapidly during the first 6 days of the composting and gradually decreases after the following days. The sudden rocket rise of the temperature might be because of the optimum condition for the microbial to degrade and after few days the nutrients are depleted and the microorganism's activity are decreased. Other than that, the temperature recorded shows that it was almost impossible for the petroleum hydrocarbons to be volatilized under such condition.

3.2 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.

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

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.

Since carbon dioxide is one of the biodegradation product, the amount of carbon dioxide produced should increase when rate of TPH decrement increases.

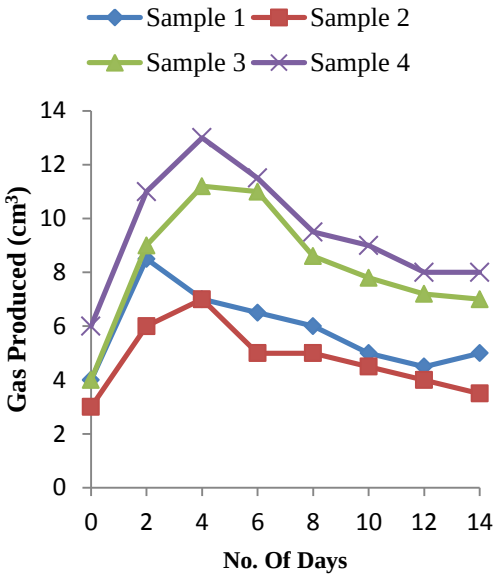

Figure 2: The gas production profile of the experiments

The gas produced up until day 4 of experiment was the highest for all samples from 3 cm3 minimum gas produced to over 12 cm3. 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. Since carbon dioxide is one of the biodegradation product, the amount of carbon dioxide produced should increase when rate of TPH decrement increases.

3.3 TPH Content

The initial TPH content of the oil sludge is measured before the biodegradation assays are being carried out and then 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. The results of TPH content over the period of 14 days are as tabulated below.

No. Of Days	Batch 1 (mg/g)	Batch 2 (mg/g)	Batch 3 (mg/g)	Batch 4 (mg/g)
0	442	442	442	442
2	413	418	408	403
4	393	398	382	376
6	388	390	362	340
8	380	387	354	333
10	373	383	349	329
12	369	382	345	324
14	365	379	339	318

Table 6: TPH content of the samples for 14 days

From the results tabulated above, it can be concluded that the compost mixture in Sample 4, which consisted of 100:17:2.1 of the C:N:P ratio, caused more decrement in the TPH content of the oil sludge. This might be because of higher C:N:P ratio and higher loading rate compared to the other samples.

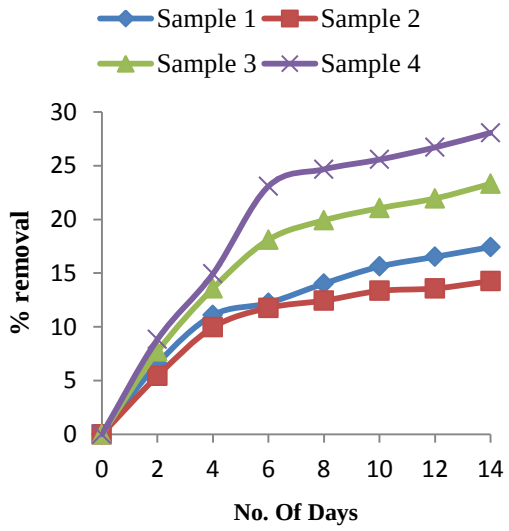

Figure 3: Comparison of percentage TPH removal between samples

The TPH content for the oil sludge for Sample 4 and Sample 3 decreased 28.05% and 23.3% followed by Sample 1 and with 17.4% and 14.3% respectively. In which Sample 4 with the highest removal of TPH and it can be derived that the C:N:P ratio in Sample 4 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.

4. Conclusion and Recommendation

4.1 Conclusion

In this paper, the closed composting treatment method which utilizes the biodegradation process has been carried out successfully with a significant result of TPH content being removed. By incorporating the concept of oil sludge biodegradation; closed composting system 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 oxygen for aerobic respiration, the level of moisture content, and 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.

4.2 Recommendation

The experiment can further be improved by measuring the odour of oil sludge with appropriate standard technique such as the Threshold Odour Number test which can quantify and prove that the odour problem has lessened. Lastly, the period of the experiment should be lengthened to get a significant result of TPH content removal.

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