Waste Mud in Oil and Gas CEPU PPSDM Using Bioremediation

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Abstract. Bioremediation is one method of treating hazardous waste environmentally friendly. This method of waste treatment Utilizes a microbial activity to treat hazardous waste. Oil sludge from the processing of petroleum in PPSDM Migas Cepu is one of the dangerous wastes, so it must be processed first before being discharged into the environment. The bioremediation process of oxygen and nutrients is needed by microbes to decompose harmful compounds in the oil sludge so that the addition of a bulking agent in the form of rice husk and sawdust is needed. Bacteria that help the bioremediation process are heterophilic bacteria, heterophilic bacteria used in this study are aeruginous Pseudomonas, Bacillus cereus and Bacillus spheres. This study aims to determine the effect of the addition of bulking agents on bioremediation and Determine the performance of heterophilic petroleum degrading bacteria in waste. The results of this study indicate the addition of a bulking agent Gives a fairly good result in bioremediation in the reduction in TPH and TCLP values Compared to bioremediation reactors without the addition of a bulking agent. Petrophilic Also bacteria play an important role in the bioremediation process as evidenced in the decline in TPH and TCLP values. The addition of a bulking agent, in a variable one (25; 75) there was a decrease in the value of% TPH namely 56.22%, variable 2 (40:60) there was a decline in the value of% TPH 55.95 and in variable 3 there was a decrease in the value of% TPH by 49. 73%. During the bioremediation process, the increase is in the pH value from 3. 6 to 6.5 indicates the presence of bacterial activity in degrading oil sludge waste. Percent of Percent Nitrogen and Carbon in bioremediation Decreased by 80 and 56%. The success of the bioremediation process was demonstrated by the results of FT-IR analysis, with peaks of 3418.39 cm-1, 2924.65 cm-1, and 1746.22 cm-1.

Keywords: Bioremediation, oil sludge, bacteria heterophilic

1. Introduction
Center for Human Resource Development of Oil and Gas (PPSDM Gas) produce products such as parasol, diesel, and residue. The results of processing these products produce waste in the form of oil sludge. Waste oil sludge is a waste from oil mining. Oil sludge interpreted also as oil sludge which is a heavy metal compound with characteristics that are difficult to remove by water so that it can threaten the health of the environment in the coastal areas.
and coral reefs. Based on Government Regulation (PP) 101 2014, sludge included in the category of B3 waste (hazardous and toxic) (Munawar et al, 2015).

The negative impact caused by waste oil sludge is waste hydrocarbon contaminated soil would be dangerous because hydrocarbons are toxic and carcinogenic (Zam, 2011). One of the petroleum processing techniques to reduce the negative impact of living beings and the environment is to use a method of bioremediation. Bioremediation can be used in the processing of petroleum sludge and environmentally friendly due to the bacteria used for bioremediation can bind unhealthy ingredients contained in petroleum residual sludge bulking processing is processing waste bioremediation method with additional ingredients used in the bioremediation process to improve the rate of biodegradation in the soil remediation process.

2. Methodology

The research method that will be used that is surveys and experiments in laboratory scale and implemented in PHP Laboratory of Human Resource Development Center for Oil and Gas (PPSDM Migas). The method consists of sampling survey in the field. An experimental method to test heterophilic bacteria to degrade the waste oil sludge.

2.1. Material

Materials used in this research that the oil sludge obtained from the exploration, production to landfill. The bulking agent used is rice husk and sawdust with the same size. The bacteria used in bioremediation as Bacillus spheres, Bacillus cereus, and Pseudomonas aeruginous. Media used in this study is derived from the contaminated soil in PPSDM Migas Cepu.

2.2. Tools

The tools used in this research is spectrophotometry IR, FT-IR instrument, pumpkin Kjeldahl, and a screening tool.

2.3. Start-up Bioremediation

Oil sludge as much as 100 grams placed in containers. The addition of a bulking agent with the variable bulking agent is added to the (25; 75, 40:60 and without an added bulking agent). Addition heterophilic bacteria used in bioremediation, namely with the same concentration.

2.4. Parameter Observation

Soil physical parameters measured were the temperature is measured using a thermometer, water content by gravimetric method (ASTM D2216), the specific gravity and bulk density particles according to the method of immersion in the pycnometer and gravimetric (Black and Hartge 1986). Soil chemical parameters were observed pH is measured using electrometry method (ASTM D4972-01), organic C according to ASTM D 2974-87, N-total by the Kjeldahl method (USEPA Method351.3), and TPH by gravimetric methods (USEPA Method 1664).

3. Results Discussion

In this study, wastewater treatment PPSDM Migas Cepu oil sludge using bioremediation methods. Bioremediation process requires the help of a bulking agent as a bulking agent in the contaminated soil and as additional nutrients for bacteria to degrade the hydrocarbon chain heterophilic. This method has not been done in PPSDM Migas Cepu.

From the physical properties of waste which is processed using bioremediate wastes which originally shaped mud and smelled unpleasant after bioremediation has a shape like normal soil and smell almost like soil. The first variable (25:75) the waste has a crumbly texture compared to other variables. That is because a bulking agent that serves as a bulking agent has a ratio of more than the others. For variable (40:60) outcome is still a waste
bioremediation clot because it is saturated by ground and has a stronger odor than the variable one. The smell is caused by the comparison bulking agent less than a variable one.

3.1. Effect of pH before and after bioremediation

According to Hapsari (2014), the optimum pH value is used in the bioremediation method that is 6.7 to 9, while according to Sharma (2012), the optimum pH for growth of bacteria that is 6.5-8. To reduce the amount of nitrogen lost pH should not be more than 8.5. When composting the waste nearly perfect then the pH will be close to 7 in this case because the microbial activity that causes the pH value close to normal (Hapsari, 2014).

![Figure 1. Graph pH Before and After Bioremediation; Description: a = Variable 1 (25; 75), b = Variable 2 (40; 60), c = Variable 3 (without bulking agent)](image)

Original initial pH of 3.6 weekly rise, this happened due to microbial activity degrading conducting enzymatic reactions. pH obtained after bioremediation conforms with the quality standard that after bioremediation pH should be around 5-7, while the pH obtained an average of 6. It can be one piece of evidence that oil-degrading bacteria in waste oil sludge can work well as the pH produced by the provisions of the optimum pH for microbial degradation of petroleum hydrocarbons in which the range of pH, nutrients for microorganisms soluble and oxygenase enzyme produced by microorganisms degrade hydrocarbons can be optimized.

3.2. Water levels on Bioremediation

The test results showed that the moisture content decreased the percentage of water content. This can be caused by aeration or stirring process that is done every day during the study that led to evaporation. Physical environmental conditions such as temperature and mechanical factors such as aeration and agitation also affect the percentage of degradation. Hydrocarbons spilled in nature will be degraded naturally because of environmental factors, although the rate of degradation was slow. The degradation process includes evaporation, emulsified in water, adsorbed on the solid particles, immersed in water and biodegradable by microbes users hydrocarbons, (Piedat et al., 2008; Ojo, 2006).

For bioremediation of oil sludge process with the addition of a bulking agent affects water levels in optimizing hydrocarbon degradation process. Optimum water content bioremediation process to transfer gas ranges between 25-35%, (Cookson, 1995). In other research humidity ideal for bacterial growth at 25% -28%, while the optimal moisture to degrade hydrocarbons that is 30% -90%.
3.3. Test Results TPH (Total Petroleum Hydrocarbon)

- **Figure 3.** Test Results TPH (Total Petroleum Hydrocarbon) Bioremediation; Information: ■ = Variable 1 (25; 75), □ = Variable 2 (40; 60), △ = Variable 3 (without bulking agent)

Testing TPH (Total Petroleum Hydrocarbon) conducted to determine the decrease in hydrocarbon concentration in the reactor. The possibility is reinforced by the data that is to add compost reactor. The results obtained showed a decrease in the concentration of hydrocarbons within 3 weeks as the initial sample which showed a decrease in TPH this can be caused by several factors. These factors, among others, a bulking agent, moisture, pH and agitation (aeration). In the three variables, TPH value also decreased, but the decline is smaller than a variable one and two, it was because the oil sludge The indigenous bacteria can degrade TPH.

Variable 2 has a decreasing value of TPH is best compared to other variables it can be due to the amount of land on bioremediation reactor at most so that the probable number of bacteria that degrade hydrocarbons heterophilic more. The composition of the bulking agent on two variables also influences due to bulking provide nutrients for bacteria to degrade hydrocarbons. While the first variable has a value smaller decline compared variable TPH 2, it is caused by the comparison between the media and the bulking agent.

There are two decisive component degradation, namely the hydrocarbon component as a degradable material acts as a substrate and microbes as degradation act as enzymes in the
enzymatic reaction mechanisms. Degradation products are degradable material undergone renovation produces molecules simpler compounds. Overhaul of hydrocarbon molecules takes place continuously during degradation (enzyme) supplied with sufficient nutrients O2 and serves as an external acceptor. Hydrocarbons are degraded in a row by some enzymes, in the presence of oxygen will liberate CO2 gas, water, and simple organic molecules in the form of degradation of organic compounds are acidic, causing the pH change in the media degradation. PH change media degradation is the limiting factor hydrocarbon component degradation process. Based on research that has been done, bulking effect on the decline in value of TPH it is evidenced in the results of TPH value that has been done. Bulking agents can affect the required oxygen transfer microbes to degrade hydrocarbons (Juliani et al, 2011). TPH reduction values may continue to decrease as the time used for bioremediation longer so that microbes can with up to degrade hydrocarbons.

For analysis of total petroleum hydrocarbons decrease supporter, FT-IR analysis to determine the functional groups contained in the oil sludge.

![Figure 4. The results of FT-IR Sludge](image)

The results of FT-IR analysis sludge who has done the most content that is shown in the peak Phenol 3418.39 cm⁻¹ CH aliphatic alkanes that at peak 2920.79 cm⁻¹, C = C peak alkenes at 1645.93 cm⁻¹, CH alkanes in the peak 1462.70 cm⁻¹ and CF alkyl halide 1036.47 cm⁻¹.

![Figure 5. The results of FT-IR Variable 1](image)
The results of FT-IR analysis of sludge that has done the most phenol content shown on peak 3418.39 cm\(^{-1}\) is CH aliphatic alkanes that at peak 2920.79 cm\(^{-1}\), CF alkyl halides in peak 1036.47 cm\(^{-1}\), CH alkanes in the peak 1462.70 cm\(^{-1}\) and C = C alkenes at peak 1644 cm\(^{-1}\).

![Figure 6. The results of FT-IR Variable 2](image)

The results of two variables on an FT-IR analysis of the highest hydrocarbon content in oil sludge contained in the peak 2924.65 cm\(^{-1}\), which is the functional group of aliphatic alkane CH, CH alkanes in the peak 1460.78 cm\(^{-1}\) and 1377.84 cm\(^{-1}\). The third most functional groups are ketones shown in peak 1707.65 cm\(^{-1}\) and the last most functional groups are aldehyde shown at peak 1740.43 cm\(^{-1}\).

![Figure 7. The results of FT-IR Variable 3](image)

FT-IR results of which have been performed on three variables, namely the highest functional groups aliphatic CH alkane, alkane CH, C-Cl Akil halide and alkyl ketones methylene shown in peak 2924.65 cm\(^{-1}\), 1464.63 cm\(^{-1}\), 812.74 cm\(^{-1}\), 1746.22 cm\(^{-1}\) and 722.09 cm\(^{-1}\). Based on the theory of the largest hydrocarbon compounds contained in crude oil are alkanes are saturated aliphatic hydrocarbons so that the research results with the
same theory that supported their all alkane compounds contained in the sludge, one variable, two variables, and three variables.

3.4. C / N ratio

Analysis of nitrogen in the reactor was conducted by Kjeldahl bioremediation. Samples were analyzed, namely early and sample soil after the bioremediation. Graph of analysis% N on bioremediation show a decline, it based on research shows that bacteria heterophilic the process of degradation of hydrocarbons in sludge refinery gases PPSDM Migas Cepu (Zam, 2011). Decreased% nitrogen also showed that the bacteria heterophilic need nutrients such as nitrogen in the process of bioremediation to degrade hydrocarbons.

![Figure 8. Graph% Nitrogen Bioremediation; Information: ■=% Nitrogen](image)

In addition to nitrogen, carbon heterophilic also required for bacteria to degrade hydrocarbons. Thus, in figure 3.4% carbon reduction also indicates that a process of degradation of hydrocarbons by bacteria heterophilic. Carbon is used as a nutrient heterophilic bacteria. Analysis of carbon content was also analyzed soil samples beginning and end after bioremediation using Walkley & Black titration method.

3.5. Biodegradation Mechanism on Oil Waste
Hydrocarbon components in a material such as petroleum sludge are generally divided into 2 groups, ie, aliphatic and aromatic compounds. Degradation of aliphatic components (alkanes) in contrast to the degradation of aromatic components. The reaction mechanism of aliphatic compounds (alkanes) involves the formation of alcohols, aldehydes, and fatty acids. Fatty acids are broken down, the CO2 is released and form a new fatty acid which is a 2-carbon unit shorter than the parent molecule, a process known as beta (β) oxidation. (Nugroho, 2009; Nababan, 2008).

The following is a reaction mechanism of aerobic degradation of alkanes by a microbe using alkane monooxygenases enzyme to convert hydrocarbons into alcohol:

\[
\text{Enzymes involved in the degradation process of hydrocarbons are oxygenase enzyme}
\]

The hydrocarbon decomposition process can be accelerated by Pseudomonas aeruginous the required enzyme lactase. The mechanism by adding the enzyme lactase, then the bonding strength of the polymer will be reduced thereby aeruginous Pseudomonas bacteria were able to digest the hydrocarbon component faster (Xuanzhen Li et al., 2012; Acevedo et al., 2011).

Oxygen plays an important role in the metabolism by microbes, oxygen required by microbes to cut hydrocarbon group aliphatic (long-chain) through metabolic processes of hydrocarbons. Petrofilik metabolic processes in bacteria occur oxidation of primary alcohols methyl become. Petrofilik bacterial metabolism also requires dehydrogenase enzyme that functions as oxidizing primary alcohols to aldehydes and henceforth into fatty acids. Hydrocarbons which has to be fatty acids, then digested by bacteria heterophilic through the beta-oxidation process to get the final result of H2O and ATP.

A decisive factor for the degradation process is the contact time (interaction) bacteria with hydrocarbon component. Overview biochemical oxygenase enzyme that is active for the adequacy of nutrient and oxygen supply would improve the performance of the bacteria. Production of the enzyme has a high correlation with the ability to break down hydrocarbons. Overview of organic chemicals from the aspects of the reaction mechanism, ie, aliphatic components undergo oxidation reactions produce alcohol in the presence of oxygen, wherein the carbon atom oxidation number of -3 becomes -1, and if further oxidized will produce aldehyde compounds (oxidation number of carbon atoms changed from -1 to +1) and partly to ketones (carbon atom oxidation number of -1 to +2). Aldehyde product may undergo further oxidation reaction produces a carboxylic acid (carbon atom oxidation number of +1 to +3), then the resulting carboxylic included in the β-oxidation cycle, so that the compound decomposes producing energy and CO2. Increasing the number of bacterial inoculum is known to raise the level of degradation and cause
degradation of aliphatic compounds, or aromatic compounds. The other thing is because the enzyme produced more varied in type and degree of decomposition as well as the amount of enzyme that is more than a single culture so that decomposition is faster (Nababan, 2008). Increasing the number of bacterial inoculum is known to raise the level of degradation and cause degradation of aliphatic compounds, or aromatic compounds. The other thing is because the enzyme produced more varied in type and degree of decomposition as well as the amount of enzyme that is more than a single culture so that decomposition is faster (Nababan, 2008). Increasing the number of bacterial inoculum is known to raise the level of degradation and cause degradation of aliphatic compounds, or aromatic compounds. The other thing is because the enzyme produced more varied in type and degree of decomposition as well as the amount of enzyme that is more than a single culture so that decomposition is faster (Nababan, 2008). The hydrocarbon decomposition process can be accelerated by Pseudomonas aeruginous the required enzyme lactase.

3.6. TCLP Test Results (Toxicity Characteristic Leaching Procedure)

| Variables | Cu  | Fe  | Pb  |
|-----------|-----|-----|-----|
| sludge    | 33.12 | 168.29 | 24.54 |
| 1         | 17.12 | 133.53 | 14.57 |
| 2         | 19.83 | 108.39 | 18.1 |
| 3         | 29.19 | 138.11 | 19.57 |

TCLP analysis is done by using the AAS method is based on Table 3.1 shows the TCLP analysis also decreased from its initial samples of sludge that has not undergone the bioremediation process, but the results are still far above the TCLP analysis of the quality standards set in this case because the time used for bioremediation less long and nutrients that are used for fewer bacteria. In the analysis of the variables Cu 3 has the greatest level of 29.19 is compared variable 1 and 2 it is due to the variable 3 there is an additional bulking agent so that bacteria heterophilic less nourishment to react with heavy metals and toxic compounds.

Fe and Pb analysis on three variables also have the highest levels of variable 1 and 2, it is also due to variable 3 not given a bulking agent that serves as additional nutrients in bioremediation so that bacterial bioremediation heterophilic at less than the maximum.

4. Conclusion
1. Impairment% TPH in bioremediation process in the variable 1 (25:75) ie 56.22%, variable 2 (40:60) 55.92% and a variable 3 (without bulking agent) 49.73
2. Performance heterophilic bacteria in degrading hydrocarbons in oil sludge can reduce the pH value, TPH, and TCLP. The final pH value is 6 appropriate quality standards. The decline in the value of TPH reached 40% and decreased levels of heavy metals Fe by 60%, Cu 16% and 10% Pb.

5. Suggestions
1. Bioremediation process needs to be done with a longer time, about 60 days
2. It takes the addition of nitrogen as a nutrient for bacteria in the bioremediation process
3. Indigen bacterial isolation needs to be done from the ground mining before bioremediation, and perform treatment according to the characteristics of bacteria used in bioremediation

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