OIL AND WATER REMOVAL FROM OILY SLUDGE USING CATIONIC PLANT BASED-SURFACTANT VIA SURFACTANT ENHANCED OIL RECOVERY

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Abstract— Oil refinery is a significant industry that we have in Malaysia. Many wastes can be produced in this industry for example is oily sludge. One of the source of oily sludge produced from wastewater treatment plant. This oily sludge can be considered as a hazardous material to the environment and human health. Oily sludge contains many types of heavy metal, petroleum hydrocarbons, water and solid particles. Since the oily sludge contains heavy metal and oil and it can be classified as scheduled waste. Many types of method and technologies has been applied for treatment of oily sludge. This treatment purpose is to reduce the poisonous of the oily sludge, so these oily sludges can go through the landfilling process. One of the method is surfactant enhanced oil recovery. This type of treatment use surfactant to remove the oil and water from the oily sludge. It is a more cheap and efficient process and this method can treat more pollutants. However, usage of chemical surfactant can produce problems to our environment and human health. Therefore, usage of plant-based surfactant is preferable because it is an environment friendly substance. In this study, parameter that has been used is the concentration of the surfactant. The surfactant was mixed with the oily sludge for 20 minutes and then was heated for 1 hour to obtain the moisture lost. The concentration that can remove higher percentage of moisture and oil is at 100 ppm concentration of surfactant. From the study, the plant-based surfactants can remove 70% to 80% of the water and oil in the oily sludge. Based on this study, it shows that this plant-based surfactant can be used in industrial oily sludge treatment.

Keywords—oil recovery, oily sludge, Surfactant Enhamced Oil Recovery

I. INTRODUCTION

In the world nowadays, there rapid expansion of petroleum and allied industries that can produce the waste. Oily sludge is a very common solid waste produced in the oil refinery industry. Oily sludge is a substance that contain long hydrocarbon chain and it has hydrophobic component in it. It can be considered as a hazardous to human health and environments because of the presence of a lot amount of petroleum hydrocarbons (Hu, Li, & Zeng, 2013). These oily sludges contain too much water and oil that can make conventional sludge treatment process to be slow, unproductive and consume too much cost.

Oily sludge treatment has been developed every year to obtain the great and environmental friendly treatment. There is a research, ("SCADA system for oil refinery control," 2014) and experiment has been done to get better and great result for the oily sludge waste treatment. Basically, there are three types of oily sludge waste management plan that must be used. The three types of strategy are using technologies to decrease the amount of oily sludge manufacture from oil refinery industry, recovering and regaining valued fuel from present oily sludge and dumping of the remains oily sludge itself if neither of the first and second strategy is cannot be done (Hu et al. 2013).

In the end of the oil recovery process from the oily sludge, there will some residue and waste will form, and several actions must be taken on that waste. There several technologies that can be used for the disposal methods such as incineration, stabilization/solidification, oxidation, and bioremediation.

For Surfactant Enhanced Oil Recovery, it is a method that use surfactant to remove organic contaminants from solid matrices and it is a more cheap and efficient process and this method can treat a more pollutants. There are several surfactants that are preferable to increase the contains of Petroleum Hydrocarbons in aqueous phase such as sodium dodecyl sulphate (Mukhopadhyay, Hashim, Sahu, Yusoff, & Gupta, 2013), Corexit 9527, Triton X-100, Tween 80 and Afonic 1412-7. Research has been done and shown that 80% of water can be removed from the oily sludge using surfactant based demulsified mixture to break down petroleum sludge emulsion (Hu et al. 2013).

Nevertheless, there several problems can occur for example environmental toxicity and resistance to biodegradation when these chemical surfactants been used. Besides, bio-surfactant also can be used for this oil recovery and shows better environmental compatibility, higher diversity, better surface activity, lower poisonousness, more emulsification capability, more selectivity and more biodegradability.

This bio-surfactant can be formed from bacterial or yeast from various substrates including sugars, oils, alkanes, and wastes. There are five categories of bio-surfactants, including glycolipids, lipopeptides, phospholipids, fatty acids, and neutral lipids, polymetric bio-surfactant and particulate bio-surfactant. Cationic bio-surfactants is the one that contain amine groups meanwhile the other bio-surfactants are either anionic or neutral. It has structures including amphiphilic molecules with a hydrophobic moiety such as fatty acids and a hydrophilic moiety for example alcohol, phosphate, amino acid, carboxylic acid, cyclic peptide or carbohydrate. Moreover, many field-scale and laboratory studies have been performed to use bio-surfactants in the treatment of oily sludge. Some of the results for the studies shown that if bio-surfactant is used for recovery of oil from oily sludge, it can recover almost 91.5% of the oil (Mukhopadhyay, Hashim, Sahu, Yusoff, & Gupta, 2013).

In this study, I used plant-based surfactant to remove the oil and water from the oily sludge. Basically, plant-based surfactant can be divided into three types which are anionic, cationic ad non-ionic surfactant. Plant-based surfactant is economical, easy to produce, and possess high inhibition efficiency and low toxicity (Mobin et al., 2017). Besides, a plant-based surfactant also biodegradability low toxicity, possibility of reuse, and easy isolation from plants. In previous research, they have used this surfactant for recovery of heavy metals from contaminated soils (Song, Zhu, & Zhou, 2008) and as effective corrosion inhibitor for mild steel (Chami, 2015).

This study will be done on order to investigate the applicability of cationic plant-based surfactant in removal of oil and water from oily sludge. The main objectives for this research is to evaluate the effect of concentration of cationic plant-based surfactant in oil removal. The result from this study should provide a process of oily sludge treatment which is an environmental friendly and an economical friendly.

II. METHODOLOGY

A. Materials

Oily sludge was collected from wastewater treatment of petroleum refinery. The oily sludge sample seemed to be black, viscous and in the form of semi-solid cake at ambient temperature (Yan et al., 2012).

B. Oily Sludge Characterization

These oily sludges were characterized using Fourier Transform Infra-Red (Banjare et al.) spectroscopy equipped with an Attenuated Total Reflectance (ATR) Crystal Accessory. From the Fourier Transform Infra-Red (FTIR) spectroscopy we can obtain the functional group that present in the oily sludge (Abdel Azim, Abdul-Raheim, Kamel, & Abdel-Raouf, 2011; Yan et al., 2012). The oily sludge also had been characterize using thermogravimetric analyser (TGA) to obtain the amount of oil and water in the oily sludge.

C. Plant-Based Surfactant Characterization

The chemical structure and components of the crude plant-based surfactant sample were determined using the Fourier Transform Infra-Red (FTIR) spectroscopy equipped with an Attenuated Total Reflectance (ATR) Crystal Accessory. The IR scan was performed over 400-4000 cm-1 with a resolution of 2 cm-1 (Banjare et al., 2017).

I. Critical Micelle Concentration

This critical micelle concentration can be determine using two methods.

1. Simplified Colorimetric Method

This experiment must carry out at room temperature which is 25^{o}c. 1 mL of 0.1 wt% R016 solution (dye) added into 50 mL of PBE surfactant. Then, the mixture is mixed for 10 minutes at 300 rpm using MR Hel-Tech hotplate stirrer. After 10 minutes, filtrate the precipitate form with Whatmann filter paper. The filtrate solution then analysed using Lambda UV-Vis Spectrophotometer.

2. Conductivity Method

This experiment must carry out at room temperature which is 26oc. 50 mL of PBE surfactant was added into a beaker. Then, successive injection of deionized water is added to the surfactant. The mixture then stirred using using MR Hei-Tech Digital Hotplate stirrer and use EKT Hei-Con Temperature Control to maintain the surfactant temperature. The conductivity value measured after 5 minutes.

D. The Effect of Operating Parameter in Oil Removal

10 g of the sludge sample was placed in 600 ml beaker. After that, the plant-based surfactant with 250 ppm concentration is added into the oily sludge. Then, the oily sludge will be stirred for 20 min by a mechanical stirrer at 80 rpm. After the stirring process, the mixture will be let to settle down for 1 hour. Then, the mixture will undergo the vacuum filter to filtrate the precipitate form with Whatmann filter paper. The results will be recorded. The quantity of separated aqueous phase was measured, and the sediment was weighed (Abdel Azim et al., 2011). Then, the sediment was characterize using the Fourier Transform Infra-Red (FTIR) spectroscopy equipped with an Attenuated Total Reflectance (ATR) Crystal Accessory. The filtrate solution then analysed using Lambda UV-Vis Spectrophotometer. Repeat the experiment using different concentration of surfactant which are 200ppm, 150ppm, 100ppm and 50ppm.

III. RESULTS AND DISCUSSION

A. Oily Sludge Characterization

I) Fourier Transform Infra-Red spectroscopy

These oily sludges will be characterize using Fourier Transform Infra-Red spectroscopy equipped with an Attenuated Total Reflectance (ATR) Crystal Accessory. From the Fourier Transform Infra-Red (FTIR) spectroscopy we can obtain the functional group that present in the oily sludge.

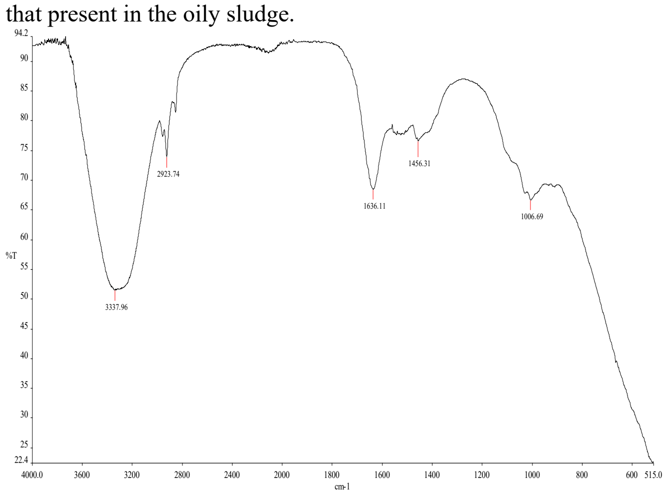

Figure 1 FT-IR spectra of Oily Sludge

From figure 1 shows the Fourier Transform Infra-Red spectroscopy result. It shows content that the oily sludge has. The first peak that appears which is 3337.96 cm-1 can indicate as OH group. It has very distinct strong and broad shape and elongated "U" shape around this region. For the second peak, it indicates carbon and hydrogen bond (C-H) in range between 2960 - 2850 cm-1. The peak 1636.11 cm-1 indicates the present of alkene in the oily sludge. Besides, for 1456.31 cm-1 indicates the benzene in the oily sludge meanwhile the last peak which is 1006.69 indicates the carbon and hydrogen bond (C-H).

Based on study by Zubaidy and Abouelnasr (2010), the oily sludge has high level of carbon residue and asphaltenes, which indicates the large amount of high molecular weight hydrocarbons. Therefore, the exact composition of the hydrocarbon in the oily sludge cannot be determine by using FTIR only because the function of FTIR just analyse the functional group of the oily sludge instead of composition.

II) Thermogravimetric Analyser (TGA)

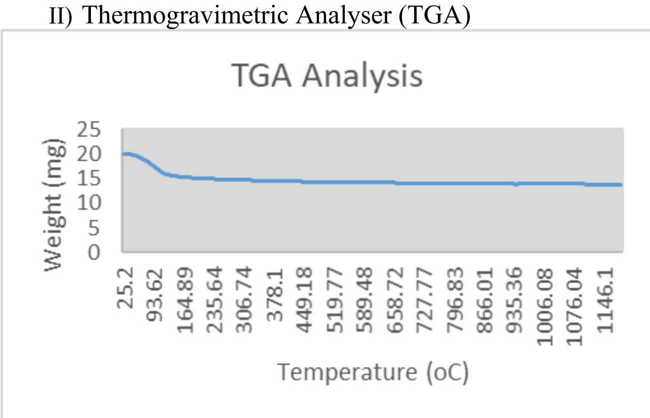

Figure 2 Thermogravimetric Analyser (TGA) result of Oily Sludge

From figure 2, the moisture content in the initial slope until temperature at 93.62^{o}c which is 22.88%. Meanwhile, for the volatile matter is in the middle of the slope which is 6.88%. lastly the positive value that is obtain in the slope which is 9.64% indicates the ash. The balance of the oily sludge which is 60.40% indicates the fixed carbon that contain in the oily sludge. The moisture content has been approved by heating 5mg of oily sludge for 5 minutes to have only moisture lost. If heating has been done more than 5 minutes, maybe there were more content lost than moisture of the oily sludge.

Heating Time	Weight of Sludge (g)	Weight of Dried Sludge (g)	Weight of Moisture lost (g)	Percentage of Moisture Lost (%)
5min	5	3.995	1.005	20.10

Table 1 Result for Moisture Lost

B. Plant-Based Surfactant Characterization

The surfactant has been analyse using Fourier Transform Infra-Red spectroscopy equipped with an Attenuated Total Reflectance (ATR) Crystal Accessory.

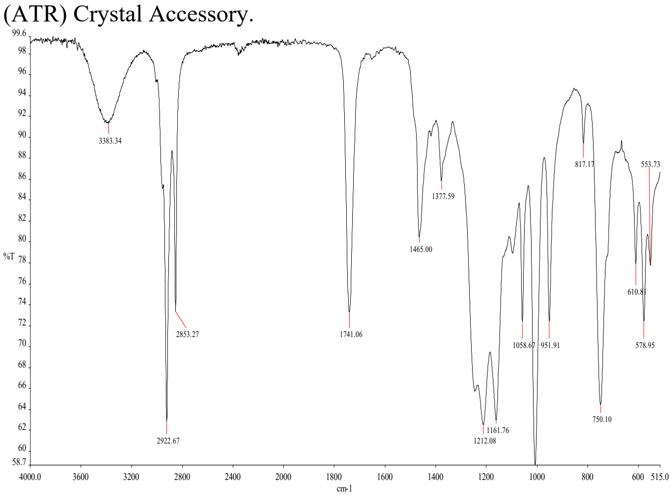

Figure 3 FT-IR spectra of Cationic Plant Based Surfactant

From figure 3, the spectra show that functional group that appears are almost the same with oily sludge. The functional groups are alcohols, sp3 carbon and hydrogen bond (C-H), alkene, benzene and carbon and hydrogen bond (C-H). However, both of oily sludge and surfactant have different FTIR value that indicates the absorption of infrared light. These values different is obtained because of signal intensities which frequently differentiate with weak, medium, strong and variable signal.

I) Critical Micelle Concentration

1. Simplified Colorimetric Method

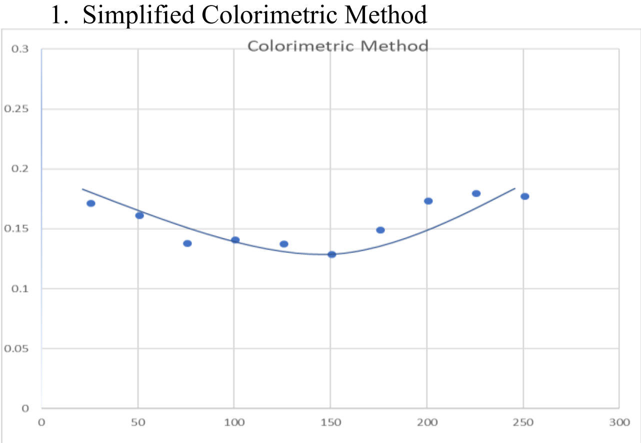

Figure 4 Uv-vis analysis of Cationic Plant Based Surfactant with RB4 solution (dye)

This figure 4 shows the result for Uv-vis analysis of Cationic Plant Based Surfactant with RB4 solution (dye). The value of the point in every concentration was obtained from abs value at 595nm at every concentration. Based on the figure 4, the peak of the graph, the Critical Micelle Concentration (CMC) is at 149 ppm. This result must be compared to the result that obtained in Conductivity Method experiment.

2. Conductivity Method

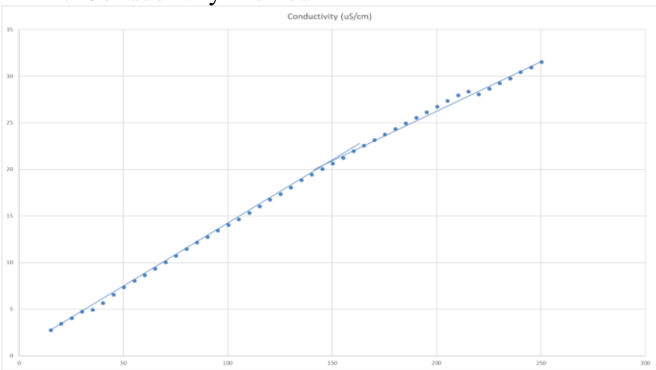

Figure 5 2. Conductivity Method analysis of Cationic Plant Based Surfactant

Critical Micelle Concentration (CMC) can be explained as the concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles. The surface tension changes strongly with the concentration of the surfactant before reaching the CMC. However, the surface tension remains moderately constant or changes with a minor slope after reaching the CMC. This was shows in the figure 5. Therefore, the CMC that I obtained from this experiment is at 149 ppm concentration.

The Critical Micelle Concentration is a concentration where the surfactants in the bulk at which micelles start forming. In oil refinery industries, CMC is considered prior to injecting surfactant in reservoir regarding enhanced oil recovery (EOR) application. Below the CMC point, interfacial tension between oil and water phase is no longer effectively reduced. Therefore, it will not work well and need to add more surfactant. Thus, the surfactant must have higher concentration than CMC to work well.

C. The Effect of Surfactant Concentration in Oil Removal

Concentration (ppm)	Weight of Oily Sludge (g)	Weight of Oily Sludge After Treatment (g)	Weight of Moisture and Oil Lost (g)
250	10	2.6511	7.3489
200	10	2.8744	7.1256
150	10	3.0005	6.9995
100	10	1.8694	8.1306
50	10	2.4255	7.5745

Table 2 Result for Moisture and Oil Lost

From table 2, the data can be used to calculate the percentage of oil lost using the formula below:

$$\frac{Wet\ raw\ oily\ sludge\ (g) - Dry\ treated\ Oil\ Sludge\ (g)}{Wet\ raw\ oily\ sludge\ (g)} x100$$

Concentration (ppm)	Percentage of Oil and moisture Lost (%)
250	73.49
200	71.26
150	70.00

100	81.31
50	75.75

Table 3 Percentage of Oil and moisture Lost

From table 3, the loss of oil and moisture content have the highest percentage at 100ppm concentration of surfactant at 81.31%. meanwhile, for the lowest percentage is at 150ppm concentration of surfactant at 70%.

I) Fourier Transform Infra-Red spectroscopy

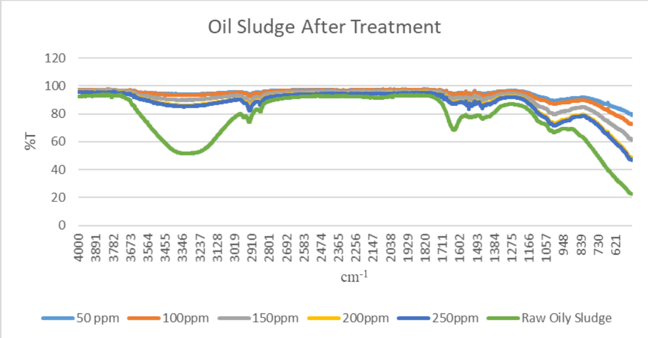

Figure 4.6 FT-IR spectra of oily sludge after treatment

In figure 6, the FTIR result shows that there are significant different between the raw oily sludge and the treated oily sludge value that indicates the method of oil recovery method from oily sludge using cationic plant-based surfactant is an effective method. The transmission percentage of raw oily sludge shows smaller value compared to the treated oily sludge. Moreover, the FTIR results also shows that the lowest concentration of cationic surfactant which is 50 ppm have the highest effectivity to remove oil and moisture from oily sludge.

IV. Conclusion

In this study required me to investigate the removal of water and oil from refinery oily sludge by using cationic plant based-surfactant via surfactant enhanced oil recovery. For this oily sludge treatment, it shows that cationic plant based-surfactant can reducing almost all amount of oil and water from the oily sludge. With different concentration used in this study, it displays that the cationic plant based-surfactant can affectively removes oil and water from the oily sludge ranging from 70% to 82%.

From this study, the optimum concentration for the cationic plant based-surfactant is 100 ppm. The oil and water removed by using 100 ppm of cationic plant based-surfactant is 81.31%. Therefore, this cationic plant based-surfactant is an effective solvent that can be used for this oily sludge treatment.

In FTIR analysis, the amount of oil present in the oily sludge has been decreased very well. Moreover, the heavy metals that contain in the oily sludge effectively decreasing after the treatment. This shows that the cationic plant based-surfactant is a great solvent that an ability to reduce the interfacial tension for better extraction process in the oily sludge.

However, this study has been done just to investigate the effectiveness of oil and water removal from oily sludge by using the concentration of cationic plant based-surfactant. There are many parameters does been used in this study such as the effect of temperature, the reaction time and the ratio between amount of surfactant and the oily sludge. The oil and moisture recovered from the oily sludge may need further treatment. The oily sludge that been treated need to have a further study before being disposed to make sure that the treated oily sludge is safe. The recovered oily sludge need to have further study in the future.

In conclusion, the removal of oil and water from oily sludge by using cationic plant based-surfactant via surfactant enhanced oil can be considered as environmental friendly and an effectively treatment process to remove oil and water from oily sludge.

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