The Use of Plant-Based Surfactant in Removal of Oil from Oily Sludge via Thermochemical Cleaning Method

Puasa S.W, Ismail K.N, Daud S.N.S, Musman M.Z.A, Sulong, N.A

Abstract*: The conventional physical treatment technologies is difficult to dewater most of water content in oily sludge during sludge dewatering process. Oily sludge removal by using surfactant via thermochemical cleaning method is recognized as one of potential method used to enhance the performance of sludge dewatering process. This study was designed to investigate the performance of anionic and cationic plant-based surfactant in removal of oil and enhance the dewatering of oily sludge. The characterization study of raw oily sludge, PBE and SLSA and those treated with PBE and SLSA surfactants were performed via TGA and FTIR. The effect of surfactant concentration was investigated based on percentage of oil removal. FTIR spectra confirms the loss of transmission peak at 1636.11 cm^{-1} for treated oily sludge due to the loss of oil via solubilization of oil from oily sludge into surfactant solution. Results shows that the best condition for the percentage of oil removal when using PBE and SLSA surfactants was 84.3% and 67.6%, respectively at PBE and SLSA concentration of 50 mg/L and 100 mg/L. It was observed that SLSA and PBE surfactants has potential to remove oil from oily sludge and subsequently contributed to enhance the oily sludge dewatering process.

Keywords*: Oily sludge, cationic surfactant, anionic surfactant, thermochemical cleaning, surfactant-enhanced oil recovery.

I. INTRODUCTION

The refined petroleum industries is recognized as Malaysia's top export economy in the world [1]. The high demand of the production capacity directly leads to the large amount of wastewater generated during the process. Typically, the volume of discharged wastewater was almost 0.4 to 1.6 times than the refined oil [2]. The wastewater is subjected to treatment since it consists of complicated dissolved recalcitrant compounds and high concentration of polar organic molecules which are characterized as chemical oxygen demand (COD), phenol and phenolic derivatives [2], [3]. Industrial wastewater is treated via Industrial Effluent Treatment System (IETS). Generally, the oily sludge is produced at Dissolved Air Flotation (DAF) unit [4] and goes through secondary clarifier after biological treatment. The industrial oily sludge waste is an environmental concern due to its hazardous contaminants. Several researchers reported that the oily sludge may consists of magnesium (Mg), iron (Fe), calcium (Ca), as well as toxic metal such as stannum (Sn), lead (Pb), manganese (Mn), cadmium (Cd), copper (Cu), chromium (Cr), vanadium (V), aluminium (Al) zinc (Zn), and nickel (Ni). Meanwhile, the oil in the oily sludge consists of 41-56% asphaltenes and maltenes (49% aliphatic, 42% aromatic and 4% of polar fraction components) along with other components [5].

The characteristic of semi-solid oily sludge is mainly consists of water (90-99 wt%), waste crude oil (0.5-3 wt%), mineral particles (0.2-2 wt%) [4], [6] and presence of heavy metals; depending on the nature of wastewater produced at production unit. The semi-solid oily sludge needs to be dewatered and treated via treatment including bioremediation, incineration and composting [6], [7] before it can be disposed.

Sludge dewatering is an essential process to reduce the sludge volume, weight and disposal cost [8]. Common physical treatment including rotary vacuum filters, belt and filter press are used for dewatering process [7]. However, the presence of significant concentration of oil hindrance the efficiency of these equipment, hence, reduce the performance of sludge dewatering process [6], [7].

Surfactant technology is found as one of the promising methods in enhancing the sludge dewatering process. Surfactant is defined as amphiphilic compound which consists of hydrophilic polar head group and hydrophobic tail of non-polar hydrocarbon chain [9]. The hydrophobic tail of surfactant is functioned to attract oil from oily sludge into the solution. As the surfactant was added into solution containing oily sludge, the hydrophilic head will facilitate the surfactant to dissolve in water phase and increase the solubility of polycyclic aromatic hydrocarbons (PAHs) via hydrophobic interaction between organic PAHs and hydrophobic tail of surfactant. In addition, the hydrophobic tail accumulates at interface; hence decreasing the surface tension and accelerates the mobility of PAHs [10].

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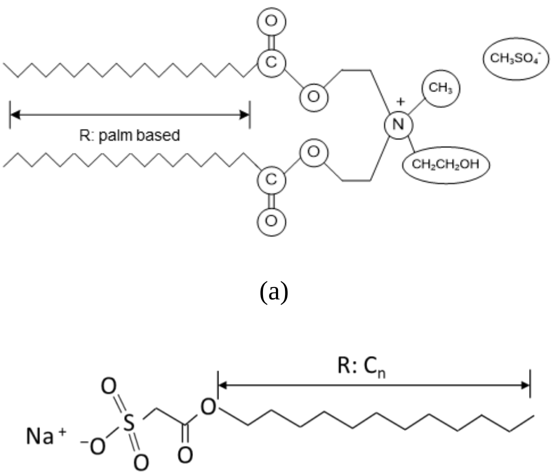
Generally, thermochemical method is described as washing of oily sludge and reclaiming oil. This method involves dilution of oily sludge in water at selected temperature followed by addition of surfactant to enhance the separation of oil from oily sludge [11]. Researchers explored the application of this method to recover oil from oily sludge and enhanced the sludge dewatering process [11]-[13]. However, the use of chemical surfactant in sludge dewatering is not environmental friendly due to its toxicity and resist to biodegradation. The rhamnolipid biosurfactant shows its potential in enhancing the sludge dewatering process [4]. However, the use of biosurfactant is costly [14]. Therefore, there is a need to investigate the potential of biodegradable plant-based surfactant in enhancing the sludge dewatering process via thermochemical method to ensure this method is safe and environmental friendly.

This study examined the potential of plant-based surfactants in enhancing the oily sludge dewatering process. A cationic Palm-based esterquat (PBE) surfactant and anionic Sodium Lauryl Sulfoacetate (SLSA) surfactant were used in this study and their performance were investigated. The characterization study of raw oily sludge, PBE and SLSA and those treated with PBE and SLSA surfactants were performed via TGA and FTIR. The study on the effect of surfactant concentration was discussed based on the percentage of oil removal.

II. MATERIALS AND METHOD

A. Materials

The concentrated oily sludge (COS) was generated from Industrial Effluent Treatment System (IETS) of petrochemical industry in Malaysia. It is collected at dewatering equipment. The cationic PBE surfactant and SLSA surfactant were obtained from local supplier. The chemical structure of PBE and SLSA is presented in Fig. 1.



(a)

(b)

Fig. 1. Chemical structure of (a) PBE surfactant, and (b) SLSA surfactant

B. Thermochemical treatment

The mass of COS was kept constant at 10 g. The anionic SLSA concentration was varied from 50 mg/L to 400 mg/L while the cationic PBE surfactant concentration was varied from 50 mg/L to 250 mg/L. The COS was dissolved in 200 mL of surfactant solution. The mixture of COS and surfactant were mixed at 80 rpm for 20 minutes at ambient temperature. Then, the mixture was allowed to settle down for an hour. The sample was then filtered by using vacuum filter. The treated sludge obtained from filtration was dried in oven at 105°C for 5 minutes to remove moisture from the sludge [12].

C. Analysis

The proximate analysis of raw COS was conducted via Thermogravimetric Analysis (TGA) (Mettler Toledo). The functional group of raw COS, PBE surfactant, SLSA surfactant and treated dry oily sludge were analyzed using Fourier-Transform Infrared Spectroscopy (FTIR) (Perkin-Elmer Spectrum 2000). The absorbance of PAHs at FTIR's selected wavelength was determined as [15]:

$$A = 2 - \log_{10}(\%T) \quad (1)$$

where A is absorbance and T is transmittance, respectively.

The percentage of oil removal (OR) of oily sludge was calculated as follows:

$$\%OR = \left(\frac{A_{raw} - A_{treated}}{A_{raw}} \right) \times 100\% \quad (2)$$

where A_{raw} is absorbance of COS and $A_{treated}$ is absorbance of treated oily sludge, respectively.

III. RESULTS AND DISCUSSION

A. Characterization study via TGA analysis

Table I presents the proximate analysis of raw concentrated oily sludge (COS). The loss of moisture content due to the presence of bound water in COS is about 21.4 wt%. There was 7.8 wt% of volatile matter contains in COS. The total weight loss obtained was 30.95%.

Table I: Proximate analysis of concentrated oily sludge

Analysis	Moisture content	Volatile matter content	Ash content	Fixed carbon
Percentage of weight (wt%)	21.4	7.8	69.05	1.75

B. Characterization study via FTIR analysis

Fig. 2(a) and Fig. 2(b) present the comparison of FTIR spectra between raw COS with PBE and raw COS with SLSA surfactant, respectively. Both PBE and SLSA surfactants show strong absorption peak at 2922.67 cm^{-1} and 2918.52 cm^{-1}, respectively as compared to raw COS (2923.74 cm^{-1}) which is assigned to alkanes C-H stretch. These findings evident COS consists mostly the PAHs rather than alkanes long chain hydrocarbon as PBE and SLSA. There are also distinguish peak observed between COS with PBE and SLSA. The FTIR spectra of COS shows visible peak at 3337.96 cm^{-1} and 1636.11 cm^{-1} indicates the OH and aromatic C=C stretch, respectively; which are recognized as typical functional group presents in oily sludge [16].

For both PBE and SLSA surfactants, the strong absorption peaks noticeable at 1741.06 cm^{-1} and 1731.19 cm^{-1} signify the presence of C=O stretch. Fig. 2(b) shows the distinguish strong absorption peak of SLSA as compared to PBE and raw COS presence at 1197 cm^{-1} and 1050.40 cm^{-1} which indicates the functional group of S=O and S–O, respectively.

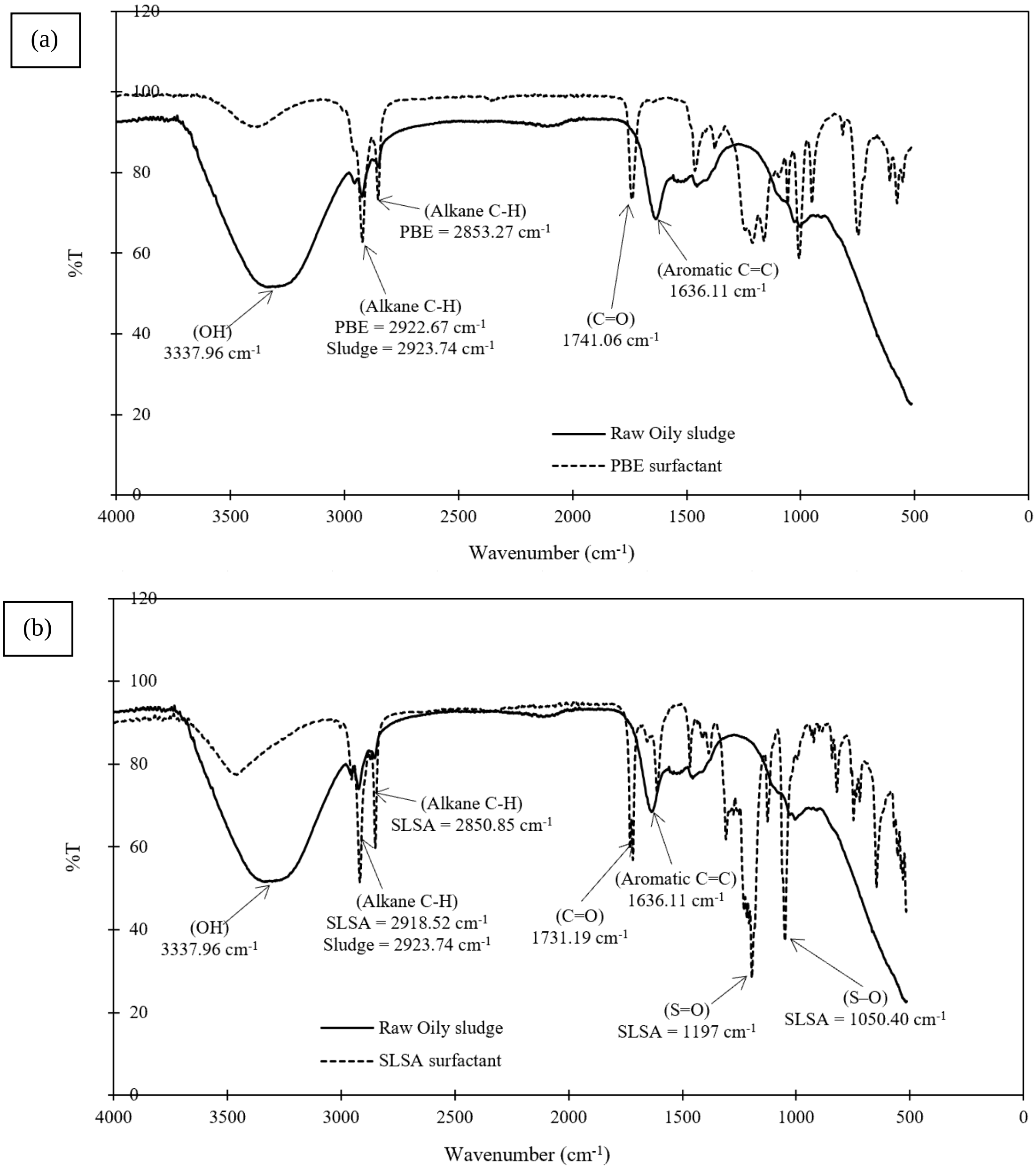


Fig. 2. Comparison of FTIR spectra for (a) Raw COS and PBE surfactant, and (b) Raw COS and SLSA surfactant.

C. Thermochemical cleaning using PBE and SLSA surfactant

The transmittance data at wavenumber of 1636.11 cm^{-1} (aromatic C=C) was used to determine the absorbance of PAHs (Equation (1)); hence used to calculate the percentage of oil removal (Equation (2)). The percentage of oil removal (OR) from oily sludge treated with PBE and SLSA surfactants via thermochemical cleaning method is shown in Fig. 3.

From Fig. 3, it is observed that the percentage of OR obtained was 84.34% using PBE concentration of 50 mg/L. This finding indicates the hydrophobic tail of PBE surfactant monomer interact with most of oil containing PAHs via hydrophobic interaction; hence enhance the solubility of oil into PBE surfactant solution during mixing process. The similar observation was reported by Zhang, Li, Thring, Hu and Song [17]. However, the percentage of OR decreased from 83.75% to 63.95% as the PBE concentration increased from 100 mg/L to 250 mg/L. This may due to the formation of aggregate micelles at PBE concentration exceeds its critical micelle concentration (CMC). It is reported that the CMC of PBE surfactant was in range between 90 mg/L to 100 mg/L [18], [19]. At CMC, hydrophobic interaction occurs between hydrophobic tail of PBE monomers whereby it will bind together to produce aggregates or micelles [20]. As a result, less amount of PBE monomer presence in the solution; hence, reduce the tendency of oil to be extracted from sludge.

This finding evidenced that the solubilization of oil is well performed at PBE surfactant state in monomer phase. Several researchers reported that the presence of micelles would enhance the oil removal whereby the extracted oil from sludge will solubilize into the palisade layer of hydrophobic core micelles [21]. Therefore, the nature of oily sludge may contribute to the selection of surfactant concentration used to extract oil from oily sludge via thermochemical cleaning method.

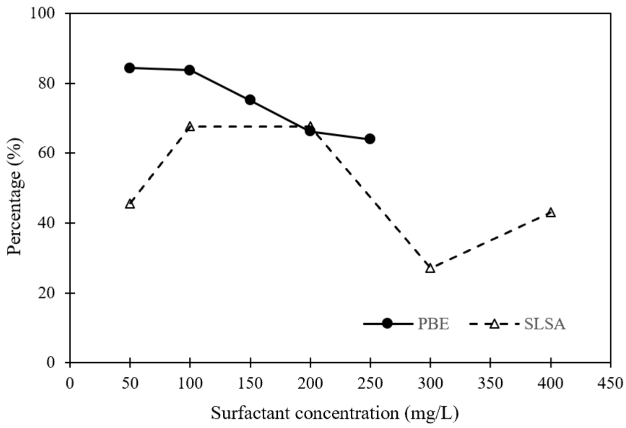


Fig. 3. Percentage of oil removal (OR) at various PBE and SLSA concentration

The percentage of oil removal (OR) increased from 45.7% to 67.6% as SLSA concentration increased from 50 mg/L to 100 mg/L. This is due to the increase of surfactant monomer concentration; hence, more oil will be extracted from sludge. The percentage of OR remain constant although the SLSA concentration increased from 100 mg/L to 200 mg/L which may due to the solubilization of oil has reached its limit. Further increase in SLSA concentration to 300 mg/L resulted in the decrease in percentage of OR to 27.1%. This finding is similar to PBE surfactant which probably due to the formation of micelles. The inconsistent trend of OR at SLSA concentration beyond 200 mg/L may contributed to the competitive hydrophobic interaction between hydrophobic tail monomers to form micelles and hydrophobic tail monomers with oil in mixing process.

From Fig. 3, it is shows that the percentage of OR for PBE surfactant is higher as compared to SLSA surfactant. This is due to the different types of surfactant's hydrophobic chain used in thermochemical cleaning process. SLSA consist of single tail while PBE consists of two tails of hydrophobic chain. Therefore, the hydrophobic interaction of PBE with oil is stronger than SLSA; hence, capable to interact with more oil which resulted in higher percentage of OR by using PBE as compared to SLSA surfactant.

Fig. 4(a) and Fig. 4(b) presents the FTIR spectra of raw COS and selected treated sludge for both PBE and SLSA surfactants. From Fig. 4(a), there was no peak observed at 1741.06 cm^{-1} (C=O) for treated sludge using PBE concentration of 50 mg/L and 100 mg/L which indicates least PBE surfactant deposited or attached onto treated sludge. This finding indicates that most of oil containing PAHs interact with PBE surfactant via hydrophobic interaction; hence, enhance the solubility of oil into PBE surfactant solution during mixing process. In addition, the tendency of oil to interact with hydrophobic tail of PBE monomer is stronger than the tendency of hydrophobic tail of PBE monomer to attach onto sludge via hydrophobic interaction. The loss of peak occurs at 1636.11 cm^{-1} and 3337.96 cm^{-1} (OH) indicates most of PAHs in oily sludge were solubilized in PBE surfactant via thermochemical cleaning method. However, the peak indicates OH and aromatic C=C were observed at 3337.96 cm^{-1} and 1636.11 cm^{-1}, respectively for treated sludge using PBE concentration of 200 mg/L. The formation of micelles beyond PBE concentration of 100 mg/L may cause the oil to solubilize into the palisade layer of hydrophobic core micelles [21]. There is tendency of these micelles to attach onto sludge via hydrophobic interaction; which indirectly allowing the oil to reattached or re-deposited onto the treated sludge.

From Fig. 4(b), it is noticeable that there was also no peak observed at 1731.19 cm^{-1} (C=O) for treated sludge using SLSA concentration of 100 mg/L and 200 mg/L. This finding is similar to PBE surfactant which indicates least SLSA surfactant deposited or attached onto treated sludge. The loss of peak at 1636.11 cm^{-1} (aromatic C=C) was observed due to the loss of oil from oily sludge into SLSA surfactant solution. However, for treated sludge using SLSA concentration of 300 mg/L, the peak indicates OH and aromatic C=C were noticeable at 3337.96 cm^{-1} and 1636.11 cm^{-1}, respectively while peak indicates S–O was noticeable at 1004 cm^{-1}. Similar to PBE surfactant, this finding may due to the solubilization of oil into micelles followed by attachment of micelles onto treated sludge via hydrophobic interaction.

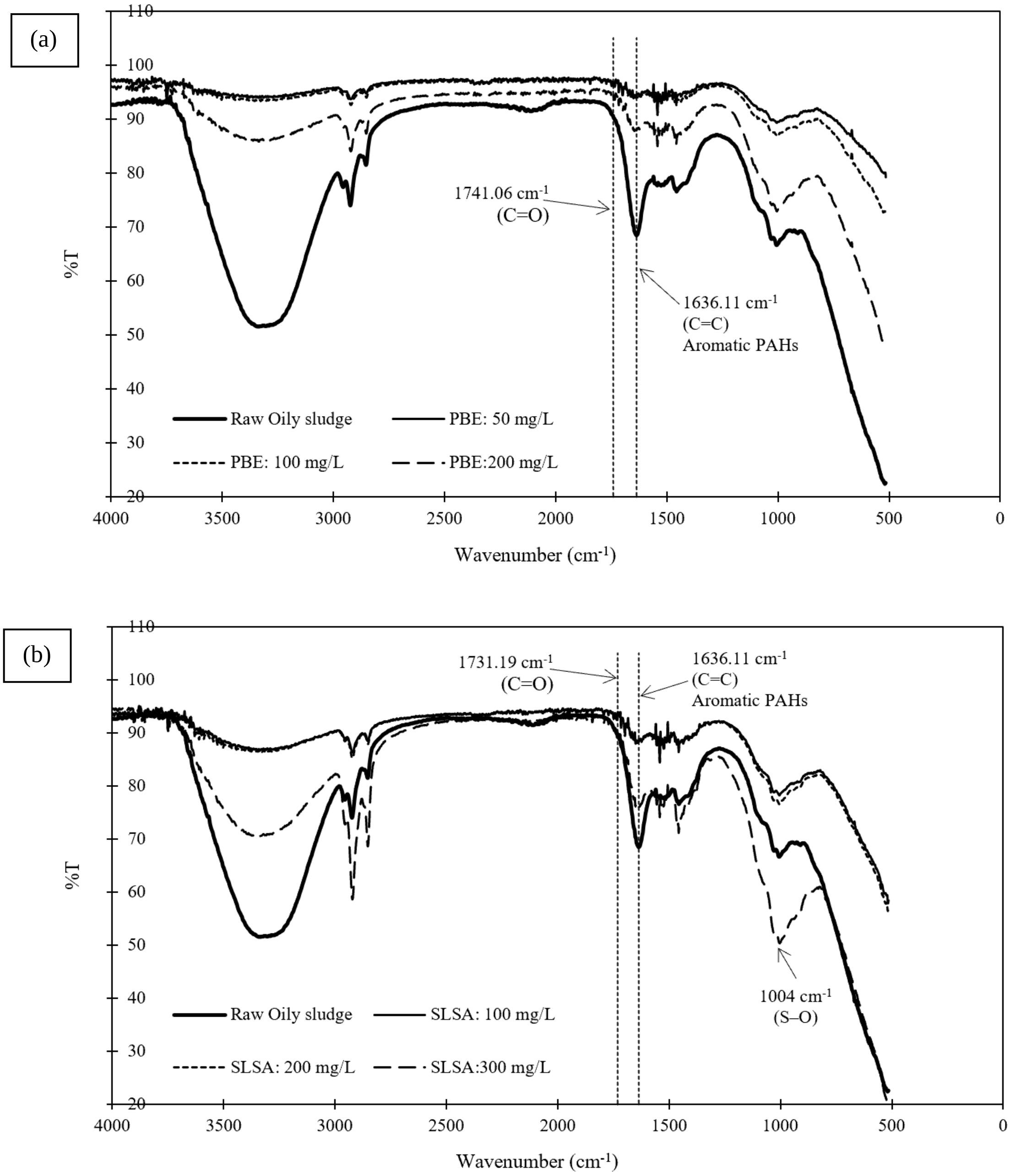


Fig. 4. FTIR spectra of raw COS and treated sludge at various (a) PBE; and (b) SLSA concentration

IV. CONCLUSION

The removal of oil from oily sludge using cationic PBE anionic SLSA plant-based surfactants via thermochemical cleaning method were investigated. The treatment COS using PBE and SLSA surfactants show significant removal of oil from COS. PBE surfactant has potential to remove about 64% to 84% of oil content from COS at concentration of PBE surfactant range from 50 mg/L to 250 mg/L. The percentage of OR removal varies from 27% to 68% at concentration of SLSA surfactant in range of 50 mg/L to 400 mg/L. The highest percentage of OR removal was 84.3% using 50 mg/L of PBE surfactant and 67.6% using 100 mg/L of SLSA surfactant, respectively whereby the FTIR spectra confirms least of PBE and SLSA surfactant attached onto treated sludge at this condition. It is evident that cationic PBE and anionic SLSA plant-based surfactants have potential to remove oil from oily sludge and subsequently enhance the oily sludge dewatering process.

V. ACKNOWLEDGEMENT

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