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Research paper



Oil removal from oily sludge using surfactant technology

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Abstract

Surfactant technology is identified as one of the treatment methods that can be used for oil recovery from oily sludge. In this study, sodium lauryl ether sulfate (SLES) was used as the surfactant and its effectiveness was investigated. Several parameters involved in the study were SLES-to-oil sludge wastewater (OSW) volume ratio ranging from 0.17:1 to 1:1 and reaction time of 10 to 30 minutes. Results shows that the best condition for the percentage of loss of oil content (LOC) using SLES obtained was 59.87% at reaction time of 20 minutes and SLES/OSW ratio of 0.25. The experimental data were plotted using multilinear regression via Excel software. The value of R^2 and adjusted R^2 obtained for percentage of loss of moisture content (LMC) were 0.29 and 0.20, respectively which indicate the data are not well fitted. However, good data fitted was observed for percentage of LOC where R^2 and adjusted R^2 obtained were 0.973 and 0.1893, respectively. The ANOVA analysis shows that significance F and probability value for obtained all variables are less than 0.05 which proved the mathematical expression of LOC can be used to predict the loss of oil content from oily sludge.

Keywords: *Moisture content; oil recovery; oily sludge; surfactant; surfactant enhanced oil recovery.*

1. Introduction

Petrochemical and oleochemical industries usually generate a large volume of oily sludge during the drilling process, production, transportation, storage as well as the refining processes to obtain crude oil products. Oily sludge is usually obtained either from upstream or downstream process operations [1]. Oily sludge is a solid waste material that is considered a hazardous solid waste and requires effective further treatment before being disposed.

The industrial oily sludge wastes from the petrochemical processes received more concern due to the hazardous contaminants in the oily sludge. The compositions and physical-chemical characterization of oily sludge are very complex as it consists of oil-in-water emulsion, water-in-oil emulsion, suspended solid and other chemical components such as Boron, Zinc and Arsenic [2]. The presence of oil in sludge also reduce the performance of dewatering during sludge thickening process [3].

Generally, the oily sludge usually contains 10-11% of oil along with fine particulates and water. The suspended solid contains in the oily sludge contains iron (Fe), calcium (Ca), magnesium (Mg) as well as toxic metal such as lead (Pb), Manganese (Mn), Copper (Cu), chromium (Cr), vanadium (V), zinc (Zn), cadmium (Cd), stannum (Sn), aluminium (Al) and Nickel (Ni). The oil in the oily sludge contains 41-56% asphaltenes and maltenes along with other components. The maltenes component is composed of 49% aliphatic, 42% aromatic and 4% of polar fraction components [4-8].

Nowadays, researchers investigated various technologies or methods to increase the effectiveness of the treatment of the oily sludge such as surfactant technology, incineration, ultrasonic treatment, chemical treatment, biodegradation and solidification/stabilization [1]. Each treatment method shows different performance depending on the characterization of the oily sludge itself. Some of these methods also help to reduce or eliminate hazardous materials found in oily sludge.

At present, chemical and petroleum industries explored the use surfactant technology for the treatment of oily sludge. The use of surfactants in the petroleum industries is usually for demulsification process [1], corrosion inhibition [9], transportation [10], cleaning, water-flooding, act as chemical for foaming process, drilling process and acidization process [11]. Surfactants help to increase the process performance as well as enhance the total recovery of petroleum.

Solvent extraction is a method used for oil recovery of oily sludge by using surfactants as their cleaning agents[1]. Zubaidy and Abouelnasr [12] used synthetic surfactants such as methyl ethyl ketone (MEK) and liquefied Petroleum Gas (LPG) condensate for oily sludge treatment. They found that MEK has higher oil recovery rate (almost 40%) as compared to LPG condensate (about 30%). The optimum sludge-to-solvent ratio achieved is 4:1.

This study will thoroughly examine the potential of anionic surfactant as solvent in oil removal from oily sludge. The objective of the study is to evaluate the efficiency of the oil removal method by using anionic surfactant approach for oily sludge treatment. Several factors are considered in this research including the effect of surfactant-to-sludge volume ratio and reaction time on the loss of oil and moisture content from oily sludge. The results would provide a basis for developing economically competitive methods for the treatment of industrial oily sludge.

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2. Materials and Methods

2.1. Materials

The oily sludge was generated from a wastewater treatment plant of oil and gas refinery industry in Malaysia. The oily sludge was collected at the primary treatment of the wastewater treatment plant and it originated from the gas treatment process area. The sample was collected along with wastewater to avoid the oily sludge degrading process. Sodium lauryl ether sulfate (SLES) at concentration of 0.95 mM was used as anionic surfactant for the oily sludge treatment process. The chemical structure of SLES is shown in Fig. 1.

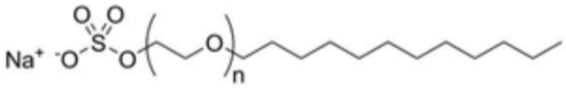


Fig. 1: Sodium Lauryl Ether Sulfate (SLES)

2.2. Methods

2.2.1. Solvent extraction

The parameters investigated in this research were surfactant (SLES) to oily sludge wastewater (OSW) volume ratio and reaction time. The experiments were conducted at SLES-to-OSW volume ratio ranging from 0.17:1 to 1:1 and reaction time varying from 10 to 30 minutes.

For each sample, 250 mL of OSW was mixed with specified SLES surfactant solution volume based on SLES/OSW volume ratio. The mixing process was performed at 150 rpm for specified reaction time at an ambient temperature [13]. The sample was then filtered by using vacuum filter. For blank study, 250 mL of OSW was also filtered using vacuum filter and the weight of raw sludge was recorded. The filtered oily sludge was collected for the drying process before being analyzed. The drying process of the oily sludge was performed at 60°C for 3 minutes for each sample. The dry oily sludge was weighed and compared with the raw sludge to identify the percentage of loss of oil and moisture content in the oily sludge. The percentage of loss of oil content (LOC) and loss of moisture content (LMC) were calculated as follows:

$$\%LOC=\left(\frac{RWS-TWS}{RWS}\right)\times 100\% \quad (1)$$

$$\%LMC=\left(\frac{TWS-TDS}{TWS}\right)\times 100\% \quad (2)$$

where RWS is weight of raw wet sludge, TWS is weight of treated wet sludge and TDS is weight of treated dry sludge, respectively. The residue of sludge and wastewater was collected for further analysis.

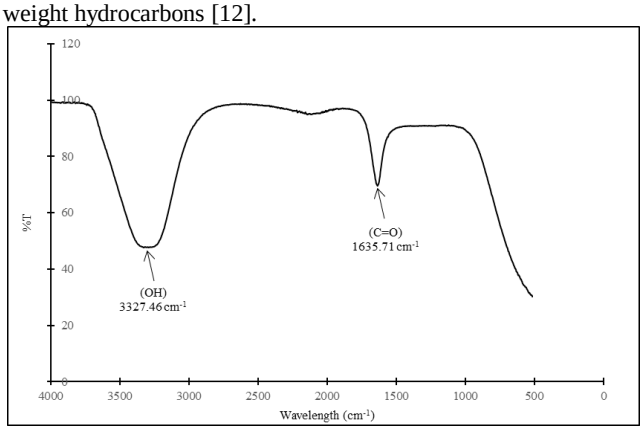
2.2.2. Analysis

The functional groups consist in raw and treated wastewater of oily sludge were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) (Perkin – Elmer Spectrum 2000).

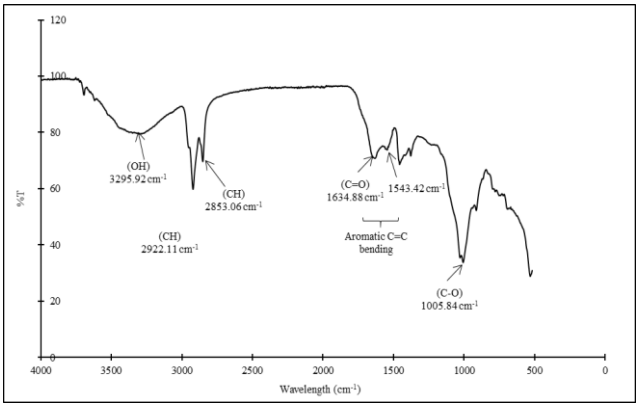
3. Results and Discussion

3.1. Characterization of oily sludge wastewater and SLES surfactant

Fig. 2(a) presents the FTIR spectra of raw wastewater. This figure shows a very strong absorption peak at 3327.46 cm^{-1}, which is assigned to alcohol and phenol O-H stretch. The peak visible at 1635.71 cm^{-1} indicates C=O stretch and aromatic C=C bending.
FTIR spectra of oily sludge is shown in Fig. 2(b). From this figure, it is clearly seen that oily sludge having similar peak with raw wastewater noticeable at 3295.92 cm^{-1} and 1634.88 cm^{-1} which indicates O-H stretch and C=O bending, respectively. In addition, strong absorption peaks were observed at 2922.11 cm^{-1} and 2853.06 cm^{-1} which are assigned to alkyl C-H stretch. The peaks visible at 1634.88 cm^{-1} to 1543.22 cm^{-1} indicates aromatic C=C bending. The oily sludge has high level of carbon residue and asphaltenes, which indicates the large amount of high molecular weight hydrocarbons [12].



(a)



(b)

Fig. 2: FTIR spectra of (a) raw wastewater (b) oily sludge

3.2. Solvent Extraction using SLES surfactant

3.2.1. Loss of oil content from oily sludge

The SLES-to-OSW volume ratio has a significant impact in the loss of oil content (LOC) from the oily sludge. Fig. 3 shows the percentage of LOC from oily sludge at SLES/OSW volume ratio range from 0.17 to 1. It is clearly shown in Fig. 3 that the percentage of LOC increases with the increase of SLES/OSW ratio until it reaches SLES/OSW ratio of 0.25, then it decreases with the further increase of SLES-to-OSW ratio.

The percentage of LOC increased from 38.79% to 59.87% as SLES/OSW ratio increased from 0.17 to 0.25, respectively at 20 min of operation. At SLES/OSW ratio of 0.17, less monomer present at low SLES concentration hence less amount of oil can be extracted from sludge. As SLES concentration increase, more SLES monomer present hence increases the tendency of SLES monomer to extract more oil from sludge. The similar finding was observed by Zhang, et al. [14]. However, the percentage of LOC reduced to 35.91% as SLES/OSW ratio is further increase in to 1. At SLES/OSW ratio of 1, the SLES concentration is 0.48 mM, which identical with critical micelle concentration (CMC) of SLES (4 EO) [15]. At CMC, the hydrophobic tail of SLES will bind together to produce aggregates or micelles [16]. As a result,

less amount of SLES monomer presence in the OSW hence reduce the tendency of oil to be extracted from sludge.

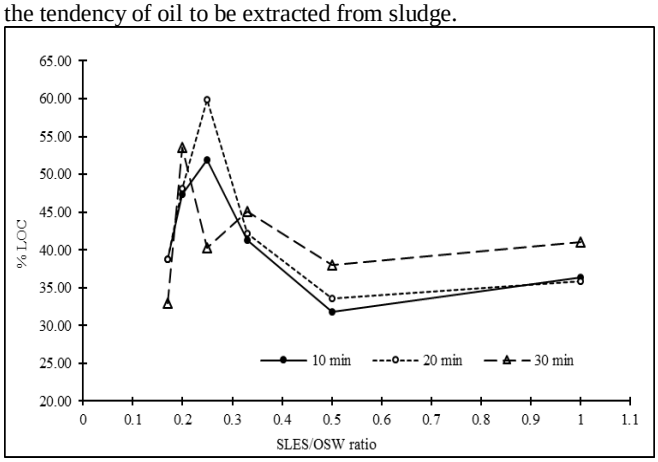


Fig. 3: Percentage of loss of oil content (LOC) for solvent extraction

The maximum percentage of LOC achieved was 59.87% at SLES/OSW ratio of 0.25 and 20 min of reaction time, respectively. The optimum reaction time of 20 min is in good agreement with Jing, et al. [17] in their study on oil recovery using AEO-9, Sodium Metasilicate and Sodium Dodecylbenzene Sulfonate.

Fig. 4 presents the FTIR spectra of treated oily sludge at 20 min of reaction time. From this figure, it is noticeable that the transmission peak reduced which indicate from the loss of oil from oily sludge. The lowest transmission peak observed is at SLES/OSW ratio of 0.25 which proved the highest percentage LOC was achieved at this condition.

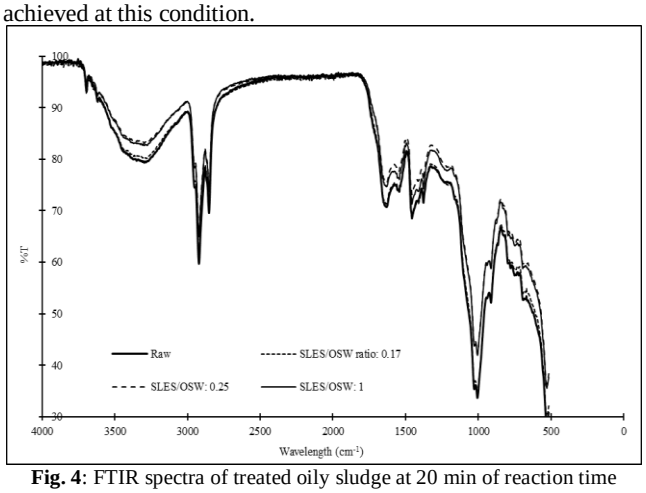
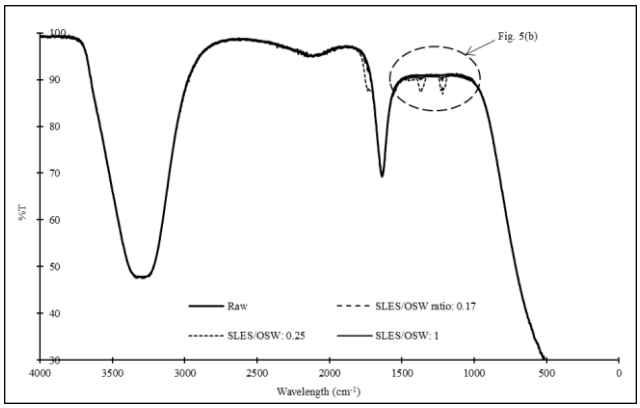
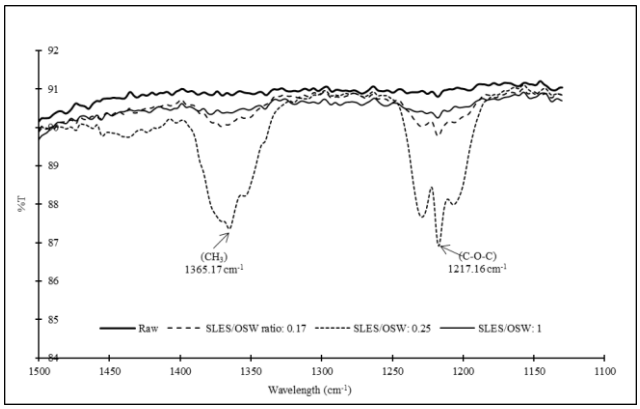


Fig. 4: FTIR spectra of treated oily sludge at 20 min of reaction time

Fig. 5 presents the FTIR spectra of treated wastewater at 20 min of reaction time. There are additional peaks were observed for SLES/OSW ratio of 0.25 (Fig. 5(a)). Fig. 5(b) focused on the FTIR spectra of selected wavelength. From Fig. 5(b), it is noticeable that there is an increase in transmission peak with the increase of SLES/OSW ratio until it reaches SLES/OSW ratio of 0.25, then it decreases with the further increase of SLES/OSW ratio. This observation supports the finding obtained in Fig. 3. The strongest peak was observed at SLES/OSW ratio of 0.25 which also evidence the highest percentage LOC was achieved at this condition. The bending CH_3 alkanes (1365.17 cm^{-1}) and C-O-C stretch (1217.16 cm^{-1}) observed in Fig. 3 proved the presence of oil extracted from oily sludge in treated wastewater.



(a)



(b)

Fig. 5: FTIR spectra of treated wastewater at 20 min of reaction time

3.2.2. Loss of moisture content from oily sludge

Fig. 6 shows the percentage of LMC from oily sludge at SLES-to-OSW volume ratio range from 0.17 to 1. The removal of water from oily sludge for blank study is 24.06%. Similar to LOC, it is clearly shown in Fig. 6 that the percentage of LMC increases with the increase of SLES/OSW ratio until it reaches SLES/OSW ratio of 0.25, then it decreases with the further increase of SLES/OSW ratio.

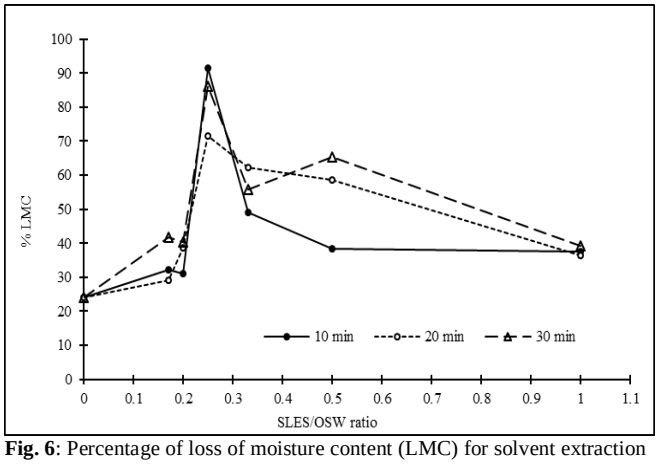


Fig. 6: Percentage of loss of moisture content (LMC) for solvent extraction

The percentage of LMC increased from 29.02% to 71.39% as SLES/OSW ratio increased from 0.17 to 0.25, respectively at 20 min of operation. Long, et al. [18] also reported that the percentage of dewatering increases with the increase in rhamnolipid surfactant concentration. However, the decrease in percentage of LMC observed as SLES/OSW ratio increase to 1 show that the SLES aggregates influence the dewatering process. The maximum percentage of LMC achieved was 91.54% at SLES/OSW ratio of 0.25 and 10 min of reaction time, respectively.

3.3. Regression Analysis

A multilinear regression model via Excel Software was used to analyze and verify the relationship between percentage of LMC (y_1) and LOC (y_2) response with parameters studied in this research. The parameters selected were SLES/OSW ratio (x_1) vary from 0.17 to 1 and reaction time (x_2) in range of 10 min to 30 min. The mathematical expression obtained for prediction of percentage LMC can be expressed as:

$$\%LMC = 24.682 - 129.507x_1^2 + 141.351x_1 \quad (3)$$

The regression statistics and ANOVA for the expression above is presented in Table 1. From equation (3), it is observed that the reaction time (x_2) is insignificant with the percentage of LMC.

Table 1: Regression statistics and ANOVA for percentage of LMC (y_1)

Regression statistics and ANOVA	
Multiple R	0.54
R Square	0.29
Adjusted R Square	0.20
Standard Error	17.11
Observations	19
Significance F	0.06
P-value for intercept	0.05
P-value for x_1^2	0.02
P-value for x_1	0.03

It is depicted from Table 1 that the significance F and the P-value reported for intercept, x_1^2 and x_1 are nearly or less than 0.05 evidently shows that the results are quite reliable, and variable has statistically significant [13, 19]. However, the value of R^2 and adjusted R^2 obtained were 0.29 and 0.20, respectively which indicate the data are not well fitted. The best mathematical expression obtained for prediction of per-centage LOC can be expressed as:

$$\%LOC = -0.137x_2^2 + 0.228x_1x_2^2 - 8.885x_1x_2 + 62.262x_1 + 5.479x_2 \quad (4)$$

The regression statistics and ANOVA for the expression above is presented in Table 2.

Table 2: Regression statistics and ANOVA for percentage of LOC (y_2)

Regression statistics and ANOVA	
Multiple R	0.99
R Square	0.97
Adjusted R Square	0.89
Standard Error	8.00
Observations	19
Significance F	6.70×10^{-10}
P-value for intercept	Not available
P-value for x_2^2	6.43×10^{-5}
P-value for $x_1x_2^2$	0.02
P-value for x_1x_2	0.02
P-value for x_1	0.05
P-value for x_2	6.95×10^{-7}

From Table 2, it is clearly seen that the significance F and the P-value reported for x_2^2, $x_1x_2^2$, x_1x_2, x_1 and x_2 are less than 0.05 evidently shows that the results are quite reliable, and variable has statistically significant. Unlike LMC, the R^2 and adjusted R^2 observed were 0.973 and 0.893, respectively which indicate the data are well fitted. Both SLES/OSW ratio (x_1) and reaction time (x_2) are significant with the percentage of LOC. It is also noticeable from variables $x_1x_2^2$ and x_1x_2 that SLES/OSW ratio (x_1) and reaction time (x_2) are dependent on each other.

Fig. 7 shows the comparison between experimental and predicted value of percentage LMC and LOC. It is clearly shown that the scatter plots of LOC are denser at around 45 degree line which indicates that the experimental data were close to predicted value calculated from mathematical expression. Meanwhile, some of LMC's scatter plot are distant from 45 degree lain which in agreement with results of R^2 obtained in Table 1.

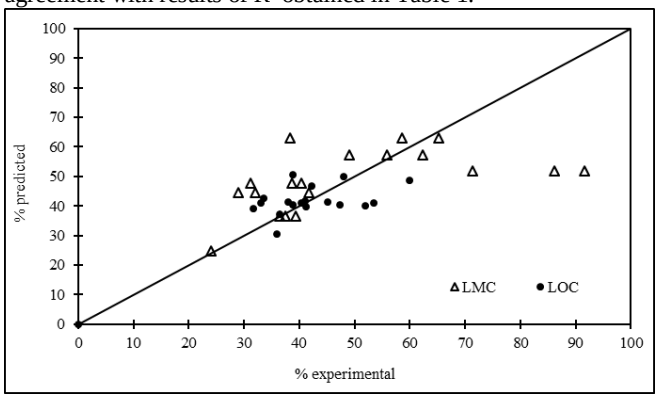


Fig. 7: Comparison between experimental and predicted value of percentage LMC and LOC.

4. Conclusion

Oil removal from refinery oily sludge was investigated in this study by solvent extraction method using anionic surfactant. The treatment of oily sludge using SLES surfactant is found to be capable of significantly reduces the waste sludge mass as well as increase the rate of oil removal from oily sludge. SLES surfactant could effectively remove oil content from the oily sludge ranging from 30% to 60%. Under the experimental condition, the maximum percentage loss of oil content (LOC) and loss of moisture content (LMC) achieved were 60% and 90%, respectively.

The best operating condition obtained were at reaction time of 20 minutes with SLES/OSW ratio of 0.25. This achieved about 59.87% of LOC from the oily sludge and 71.39% of LMC. This shows the effectiveness of using SLES surfactant as the solvent for the treatment process.

The efficiency of oil removal by using SLES surfactant was verified in this study by using multilinear regression via Excel software. It is proved from ANOVA analysis that the reaction time was insignificant for LMC and the scattered data plot are not well fitted. Meanwhile, ANOVA analysis of the mathematical expression obtained for LOC proved that the developed expression can be used to predict the percentage of LOC at SLES/OSW ratio varies from 0.17 to 1 and reaction time in range of 10 to 30 minutes, respectively.

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