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Experimental Study and Analysis on Degradation of Oily Sludge from Process Equipment by Continuous Hybrid Treatment

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ABSTRACT

It is well known that petroleum refineries are considered the largest generator of oily sludge which may cause serious threats to the environment if disposed of without treatment. Throughout the present research, it can be said that a hybrid process including ultrasonic treatment coupled with froth floatation has been shown as a green efficient treatment of oily sludge waste from the bottom of crude oil tanks in Al-Daura refinery and able to get high yield of base oil recovery which is 65% at the optimum operating conditions (treatment time = 30 min, ultrasonic wave amplitude = 60 micron, and (solvent: oily sludge) ratio = 4). Experimental results showed that 83% of the solvent used was recovered meanwhile the main water which was separated from solid particles was reused. Three types of sonic probes were used to compare effects of their amplitude created. Results revealed that beyond optimum ultrasound intensity, the treating time has an adverse effect on process efficiency. Results proved that usage 0.05% NaOH during the proposed hybrid process increased the oil recovery from 50 to 65%. The proposed hybrid treatment method could represent an environmentally friendly treatment of waste sludge produced from an oil refinery.

Keywords: oily sludge, ultrasonic waves, froth flotation, oil recovery.
1. INTRODUCTION

Large quantities of sludge can be produced from different activities of the oil industry. However, a petroleum refinery is considered the largest generator of oily sludge. Abramov, et al., 2009 reported that for every 550 tons of crude oil refined one ton of oily sludge is produced. This oily sludge is characterized by a predominant content of petroleum hydrocarbons as listed in Table 1. Disposal of such oily sludge without pretreatment may cause serious threats to the environment. It is well known that many factors could affect the generation rate of oily sludge-like crude oil specification, a method of refining, petroleum store mode, and the refining production rate. Table 2 shows a range of percentage of heavy metals included in different petroleum sludge.

As a highly viscous medium, oily sludge forms a sticky blanket on the surface of the soil. Moreover, it has been adsorbed into the soil pores. Consequently, a long-term contamination of soil takes place. Hu, et al., 2013 presented different methods of oily sludge treatment as shown in Fig. 1.

Environmental engineers favor the recycling option for oily sludge due to its many advantages such as reducing the disposal of hazardous materials, increasing the recovery of petroleum hydrocarbons, and utilizing the wastes from oily sludge as a source of energy. Many techniques have been reported for remediation of hydrocarbons from oily sludge such as solvent extraction, Gazineu, et al., 2005, centrifugation treatment, Conaway, 1999, surfactant-enhanced oil recovery (EOR), Neuma, et al., 2001, ultrasonic irradiation, Li, et al., 2013 and Song, et al., 2012, and froth flotation, Scala, and Chirone, 2004. Furthermore, in remediation techniques, some methods are

American Petroleum Institute (API) reported in 1989, that enhancement of oil recovery is the main goal for environmental issues. Hahn, 1994, claimed that, in the USA, 80% of oil is recovered from oily sludge wherein the balance is further recovered by other methods of treatment. Hahn, 1994 and Ramaswamy, 2007 revealed that it is always preferable to recover oil from oily sludge if it contains concentrations of oil and solid of more than 10% and lower than 30% respectively. It is well known that the energy effects of a wave depend on the amplitude and duration (time) of the wave. Wave's energy is directly proportional to its amplitude squared. Considering these factors, the intensity is defined as power per unit area. Based on this principle, sonic wave treatment can be assumed as a green treatment technique which may treat sludge within a short time. In ultrasonic irradiation method, the ultrasonic potential supply transforms 50/60 Hz line voltage to high-frequency electrical power. This high-frequency electrical power is transported to the piezoelectric transmitter within the adapter, where it is varied to mechanical oscillations. The oscillations from the adapter are concentrated by the probe, making pressure waves in the solution. This work composes a massive number of very small bubbles which extend over the negative pressure inversion and explode strongly over the positive inversion. This phenomenon, nominated as cavitation, makes a massive number of impact waves in the solution, in addition, higher pressures and temperatures at the failure spots, the progressive influence brings about high grades of power to be liberated into the solution, Zhang, et al., 2012. Xu, et al., 2009 indicated that oil remediation could be as high as 64.1% at an ultrasonic frequency of 20 kHz and applied power of 60 W. Xu, et al., 2009 and Abramov, et al., 2009 utilized ultrasonic cavitation with a frequency of 28 kHz in an ultrasonic purifying vessel to remove oil ingredients from the surface of particles in oily sludge, and a global oil segregation rate of 55% was gained. They also reported that the optimum temperature, pressure, and frequency to obtain maximum oil recovery from sludge were 310 K, 10 bar, and 28 kHz, respectively, but both too higher or lower ultrasonic power input may retard oil removal technique because high supersonic power input may prohibit oil droplets from combining and low ultrasonic power input makes it difficult for oil to separate from particles. The main objective of the present study was to investigate solutions for enhancing the removal of oily sludge using the continuous hybrid method. Another objective was to suggest a mathematical correlation related efficiency of the removal with studied operating parameters.

2. MATERIALS and METHODS

2.1 Materials

Chemicals and reagents utilized in this work were n-Hexane (95%) and sodium hydroxide (> 98 wt.% NaOH), purchased from Sigma-Aldrich. The waste oily sludge was drawn from the storage vessels of crude oil vessel in Al-Daura refinery, Baghdad, Iraq.
2.2 Methods

2.2.1 Characterization of oily sludge

Water content (CW)
Water content was estimated using the procedure indicated in the (ASTM- D95). 25 g of oily sludge was placed in a flask and 75 ml of hexane as a solvent was added in (sludge/ solvent) volumetric ratio= 1/3. The oily sludge and solvent were then fractionated and the mixture of (water and solvent) was separated and collected in a measurable container. Due to the difference in density between water and solvent, the accumulated water at the lower part of the separation funnel was measured. The water content in oily sludge was calculated according to Eq. (1), Taiwo and Otolorin, 2009.

\[
CW (wt\%) = \frac{\text{weight of water}}{\text{weight of sludge sample}} \times 100 \tag{1}
\]

Volatile hydrocarbons (VH)
Volatile hydrocarbons (VH) and moisture content were determined by weighing 8 g of the oily sludge samples in ceramic crucible and warming in an electric oven at 110 °C for 24 h. The reduction in mass was due to (VH) and (CW). (VH) was estimated by Eq. (2), Zubaidy and Abouelnasr, 2010.

\[
VH (wt\%) = \frac{\text{reduced weight (g)}}{\text{initial weight of sample (g)}} \times 100\% - \text{water content (100\%)} \tag{2}
\]

Solid content (SC)
The content of solid materials (deposits and cinder) was estimated following the procedure cited in Li, 2005. After estimating the (VH) and (CW), the dehydrated oily sludge was further calcined in an electric oven to 500 °C for 45 minutes, Zubaidy and Abouelnasr, 2010, and the residual mass was re-weighed. Eq. (3) was utilized to estimate the solid content:

\[
SC (wt\%) = \frac{\text{remaining weight (g)}}{\text{initial weight of sample (g)}} \times 100\% \tag{3}
\]

Non-volatile hydrocarbons content (NVH)
NVH was estimated following the procedure cited in Zubaidy, and Abouelnasr, 2010, and utilizing Eq. (4):

\[
NVH (wt\%) = 100\% - (VH + SC + CW) \tag{4}
\]

3. EXPERIMENTAL SETUP

The experimental setup of the present work is shown in Fig. 2. It consists of a 1-L glass container (no. 1) in which a mixture of oily sludge and prepared reagents (95% hexane and 0.05% NaOH) is placed with various volumetric proportions (1, 2, and 4) of prepared solvent-to- oily sludge. Three
sonic titanium solid probes of diameters (13, 19, and 25 mm) are immersed respectively into container (no. 1) and connected to an ultrasonic generator (Model VCX-750, vibra-cell, Sonics) (no.5) which is operated at different ultrasonic wave amplitude (40, 60, and 100 micron) in various operating times (10, 20, 30 and 40 min), respectively. The mixture (oily sludge, hexane, and NaOH) is homogenized by a stainless steel electric-driven mixer (no. 6), and discharged continuously to another 1-L glass container (no. 2) where a froth flotation process is carried out by inserting a low-pressure air ( at 1 L/min) via a 6 mm tube into the bottom of the second container. A layer of a mixture of oily froth with solvent is accumulated at the upper part of the container where it is removed continuously and fed to a separating funnel via container (no.3) to recover the oil and solvent. The lower layer in a container (no.2) which contains water and solid sediment was filtered to separate the suspended solids from the water. Then the separated water can be reused. To eliminate the thermal effect on sludge viscosity during ultrasonic treatment, container (no.1) was immersed in a water bath (not shown in Figure 1.). The viscosity of oily sludge in the first container is measured periodically using a Viscometer Brookfield DV-II+Pro device (no.7).

4. EXPERIMENTAL DESIGN

The factorial method was utilized for the arrangement of the experiments due to its precision in figure out the mutual influences between the process parameters of the studied system. The real values of controlled variables (F) and their corresponding levels (L) are shown in Table 3. Each experiment was repeated twice to get accurate results.

5. RESULTS and DISCUSSION

5.1 Analysis of a Sample of Oily Sludge

Table 4 lists the ingredients of oily sludge obtained from the storage vessels of heavy oil in Al-Daura refinery and analyzed according to the procedure cited in section 2.2. Results listed in Table 4 revealed that oily sludge drawn from the storage vessels of heavy oil in Al-Daura refinery contains a high percentage of hydrocarbons (870%) which need to be extracted.

5.2 Influence of Ultrasonic Treatment on Oily Sludge Viscosity

Figs. 3 and 4 illustrate the variation of sludge viscosity against ultrasonic intensity at the different operating time (10, 20, 30, and 40 min) and (solvent: oily sludge) ratio of 1:1 and 4:1, respectively. It can be seen in Fig. 3 that at the particular operating time (e.g., 30 min), as the ultrasonic wave amplitude increased from 40, 60, and 100 microns, the mixture viscosity decreases in the order of 630, 620, and 627 cp respectively. Regarding Fig. 4, at the same particular time (i.e., 30 min) as ultrasonic wave amplitude increased from 40, 60, and 100 microns the mixture viscosity decreases from 300, 250, and 270 cp respectively. Many researchers, Li, et al., 2005 and Grönroos, 2010 have reported that when ultrasonic intensity increased, the rate of disintegration of the more dense materials which have higher molecular mass, speeds up in the direction of lower density material. According to what has been observed, it is concluded that there is an optimal value for the sonic...
intensity that can be used for a system to attain the best performance. Our results agree well with the published data of Mohammed, et al., 2013, who have reported that at the higher supersonic frequency the performance of sonic proses could be reduced, due to the scattering of sonic waves because of the high concentration of cavitation bubbles which are generated at higher ultrasonic frequencies.

As can be observed from Figs. 3 and 4, at the specific operating conditions of (time = 30 minute and wave amplitude = 60 microns), when the (solvent: oil sludge) ratio increased from 1:1 to 4:1, the percentage decrease in viscosity was 59.6%. However, at the particular operating time (30 min) and (solvent: oil sludge) ratio= 4 as the ultrasonic wave amplitude increased from 40, 60 to 100 micron, the viscosity of oily mixture decreases from 300, 250 to 270 cp which is equivalent to a reduction in viscosity equal 16.6%.

These results revealed that effect of solvent addition on the viscosity of the mixture is predominant even when wave amplitude increased to 100 microns. Experimental results indicated that 83% of the solvent used is recovered by the separating funnel at the operating conditions (i.e., ultrasonic wave amplitude = 60 microns, operating time = 30 min, and [solvent: oily sludge] ratio = 4 which give the maximum reduction in oily sludge viscosity. Rafie, et al. 2013, and Mohammed, et al., 2013 revealed that n-Hexane was found to be a good extractive solvent which can be used effectively in flocculation process of oily sludge treatment because of its good solubility for many materials such as metals and carbon-based solid particles, and partially polar polymeric additives. The findings of Mohammed, et al., 2013, supported the selection of n-hexane for use in present work.

5.3 Influence of Ultrasonic Amplitude on Oil Extraction

As can be seen in Fig. 5, the oil recovery was increased to 43% as operating time increased from 10 to 20 minutes and undergo to its peak to 64% within 30 minutes of ultrasonic treatment (i.e., 60-micron amplitude). No further significant increase in oil recovery was observed when ultrasonic treatment was increased above 30 minutes. It seems that fewer bubbles of large size and greater energy were generated, while at a higher frequency much denser bubbles with moderate or lower energy were formed which indicates that the lower bubble threshold and higher bubble intensity at low frequency might be favorable for ultrasonic washing of oily sludge. Previous studies by Czechowski, et al., 2005, Grönoos, 2010, Mohammed, et al., 2013, and Mansur, et al., 2014, stated that beyond an optimum ultrasonic intensity, the sonication time was inversely proportional to the ultrasonic power, so that a constant amount of ultrasonic energy was always absorbed. Jin et al., 2012, claimed that a high oil recovery rate above 90% was achieved when the ultrasonic treatment parameters were 60 °C, 28 kHz, 15 min and 400 W and no further enhancement of oil recovery was observed when the ultrasonic power and treatment duration increased beyond 400W and 15 min.

5.4 Influence of NaOH Addition

Fig. 6 represents a bar chart for the influence of addition 0.05% NaOH to a mixture of (4 parts hexane: 1 part oily sludge). As can be seen, oil recovery increases from 50 to 65% as the addition of NaOH increased from 0 to 0.05%. This may be attributed to that NaOH enhances a quick
flocculation of the solid particles and assist to separate them from the mixture of oily sludge and solvent. Thus, the destabilization of the emulsion was enhanced by the addition of \( \text{Na}^+ \) ions. Consequently, separation of sludge from oil was increased. Furthermore, existence of \( \text{OH}^- \) group reduces the electrostatic estrangement and increase the rate of flocculation. The reason for this electrostatic estrangement was attributed to the linkage of additive ions with one or more groups of alcohol. Results of present wok agree well with published data of Lager, et al., 2006, investigated the influence of addition low concentration of \( \text{NaCl} \) for oil removal from sludge. They indicated that the existence of \( \text{Na}^+ \) ions can influence the adsorption of oil over the surface of mud or mineral stratums. Consequently, it is suggested that the added \( \text{Na}^+ \) assisted to cleavage the connection band between oil and aggregation of particles by growing the negative charges over the solid particles. Suri et al., 2010, suggested that the addition of sodium hydroxide may improve breakdown of bubbles and thus promote the effect of ultrasound waves.

5. MATHEMATICAL CORRELATION

According to the experimental outcomes, a polynomial was suggested to predict the oil recovery from oily sludge for the studied ranges of operating parameters of ultrasonic wave amplitude (amp), operating time (t), and using (solvent: oil sludge) ratio = 4.

\[
\%R = a_0 + a_1t + a_2t^2 + a_3t^3
\]  
(5)

Where \( a_0, a_1, a_2, \) and \( a_3 \) represent the coefficients of the polynomial. Regression analysis technique was utilized to estimate the coefficients of Eq. 5 at any amplitude of the ultrasonic wave. The empirical correlations are presented by Eqns. 6 to 8. Values of the correlation coefficients \( (R^2) \) indicate an excellent representation of the formulated equations to the operating system.

\[
\%R = 80 - 7.4167t + 0.4t^2 - 0.0058t^3
\]  
at amp= 60 microns, \( R^2=1 \)  
(6)

\[
\%R = 54 - 3.2833t + 0.2t^2 - 0.0032t^3
\]  
at amp= 100 microns, \( R^2=1 \)  
(7)

\[
\%R = 15 + 0.8333t + 0.025t^2 - 0.0008t^3
\]  
at amp= 40 microns  \( R^2=1 \)  
(8)

As can be observed, in Eqns. 6 to 8 that the amplitude of ultrasonic wave has a noticeable effect on the significance of the polynomial terms. \( a_0 \) represents the intercept with the axis of the objective function. It has the highest value at 60 microns. The coefficients of the second, third, and fourth terms represent the significance of the linear, quadratic, and cubic trends of the polynomial which have the highest values at the 60 microns.

6. CONCLUSIONS

Throughout the present research, it can be said that a hybrid process including ultrasonic treatment coupled with froth floatation has been proved as a green effective treatment of waste oily sludge collected from the bottom of crude oil tanks in Al-Daura refinery and able to get high yield of base
oil recovery which is 65% at the optimum operating conditions (treatment time = 30 min, ultrasonic amplitude wave 60 microns, and (solvent: oily sludge) ratio = 4). Experimental results showed that 83% of the solvent used was recovered meanwhile the main water which was separated from solid particles was reused. Three types of sonic probes were used to compare the effects of their created amplitude. Results revealed that beyond an optimum ultrasonic intensity, the treating time has an adverse effect on process efficiency. Results proved that usage of 0.05%NaOH during the proposed hybrid process increased the oil recovery from 50 to 65%. The proposed hybrid treatment method could represent an environmentally friendly treating of waste sludge produced from oil refinery during relatively short time compared with other treatment processes.

REFERENCES


NOMENCLATURE

a= ultrasonic wave amplitude, μm.
API = American Petroleum Institute.
CW = Water content, g.
H = Volatile hydrocarbons, g.
NVH = Non-volatile hydrocarbons content, g.
R= correlation coefficients
SC = Solid content, g.
t = operating time, min.

**Table 1.** Characteristics of oily sludge. Ramaswamy et al., 2007.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon content</td>
<td>5 - 86.2</td>
</tr>
<tr>
<td>Water content</td>
<td>30 – 85</td>
</tr>
<tr>
<td>Solid content</td>
<td>5 – 46</td>
</tr>
</tbody>
</table>

**Table 2.** Typical metal concentrations in oily sludge, API, 1989.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc (Zn)</td>
<td>7–80</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.001–.12</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>32–120</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>17–25</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>27–80</td>
</tr>
</tbody>
</table>
Table 3. Design of experiments.

<table>
<thead>
<tr>
<th>Level no.</th>
<th>Ultrasonic wave amplitude (micron)</th>
<th>solvent:sludge (volume ratio)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>2</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>40</td>
</tr>
</tbody>
</table>

Table 4. Classification of oily sludge from the storage vessels of heavy oil in Al-Daura refinery.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content</td>
<td>23 %</td>
</tr>
<tr>
<td>Volatile hydrocarbons</td>
<td>10 %</td>
</tr>
<tr>
<td>Solid content</td>
<td>7.6 %</td>
</tr>
<tr>
<td>Non-volatile hydrocarbons content</td>
<td>59.4%</td>
</tr>
<tr>
<td>Viscosity</td>
<td>750cp</td>
</tr>
</tbody>
</table>
Figure 1. Oily sludge treatment methods. Hu et al., 2013.

Figure 2. Snapshot for main parts of the experimental setup.
Figure 3. Variation of dynamic viscosity against operating time and different ultrasonic wave amplitude and [Solvent: Oily Sludge] ratio = 1:1.

Figure 4. Variation of dynamic viscosity against operating time at different ultrasonic wave amplitude and [Solvent: Oily Sludge] ratio= 4:1.
Figure 5. Variation of Oil recovery against operating time at different ultrasonic wave amplitude and (solvent ratio: oily sludge) ratio = 4:1.

Figure 6. Effect of NaOH on oil recovery at optimum operating conditions (ultrasonic wave).