Statistical Modelling of Oil Removal from Surfactant/Polymer Flooding Produced Water by Using Flotation Column

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Abstract: The objective of this study was to investigate the effect of polymer (GLP-100) and surfactant (MFOMAX) towards the efficiency of oil removal in a flotation column by using the Response Surface Methodology (RSM). Various concentrations of surfactant (250, 372 and 500 ppm) and polymer (450, 670, and 900 ppm) produced water were prepared. Dulang crude oil was used in the experiments. Flotation operating parameters such as gas flow rate (1–3 L/min) and duration of flotation (2–10 min) were also investigated. The efficiency of oil removal was calculated based on the difference between the initial concentration of oil and the final concentration of oil after the flotation process. From the ANOVA analysis, it was found that the gas flow rate, surfactant concentration, and polymer concentration contributed significantly to the efficiency of oil removal. Extra experiments were conducted to verify the developed equation at a randomly selected point using 450 ppm of polymer concentration, 250 ppm of surfactant concentration, 3 L/min gas flow rate and duration of 10 min. From these extra experiments, a low standard deviation of 1.96 was discovered. From this value, it indicates that the equation can be used to predict the efficiency of oil removal in the presence of surfactant and polymer (SP) by using a laboratory flotation column.

Keywords: enhanced oil recovery; produced water treatment; flotation process; statistical model

INTRODUCTION

Management of produced water from Enhanced Oil Recovery (EOR) is one of the problems associated with the oil recovery since it produces large volumes of saline water, which should be managed as the by-product. The produced water contains several contaminants such as mineral ions, dispersed oil, grease, organics, heavy metals and other different contaminants [1] such as surfactant, polymer or the mixture of both surfactant and polymer (SP) resulting from the EOR injection. Good management of the produced water is important since it plays a major role in the environmental concern for reuse or discharge. Therefore, the produced water treatment is economically reasonable and technically feasible. The objectives of the produced water treatment are to remove the oil, desalination, removal of soluble organics, naturally radioactive materials, dissolve gases, suspended particles and sand, disinfection and softening [1]. These polluting components must be minimized to allow the level and threshold of oil in the produced water is limited by legislation during the discharging [2]. In Malaysia, the limit of monthly oil discharged is below 40 ppm [3].

The technologies used for the produced water treatment depends on whether the installation is based on onshore or offshore. The most commonly used techniques for separation of the oily wastewater include gravity separation [4], membrane filtration separation [5], flotation [6-8] and hydrocyclone [9-11]. For offshore installation, the footprint is generally a critical factor compared to the onshore installation because of the space limitation. Low energy, simple and high footprint technologies must be employed to remove the contaminants to maintain water quality target and for cost reduction purpose. Such a treatment process can be
improved by implementing the flotation process. A flotation process uses gas injection to create gas bubbles that help to increase the oil removal by attaching themselves to the oil droplets and bring the oil droplets to the surface for removal.

However, the efficiency of the flotation process in the produced water treatment system has degraded during the implementation of SP flooding in EOR due to the stable emulsions that are formed in the production fluids [4] caused by the SP chemicals. The function of SP in EOR is to increase oil recovery. In the past research, studies on the effect of the SP concentration to the viscosity, IFT and oil droplets size distribution that includes the coalescence and breakup of the oil droplets have been widely carried out. Some of them found that in the presence of a large amount of polymer, the viscosity of the produced water tend to increase which made the oil droplets rise very slowly to the surface. As a result, this makes the separation between the oil and water become inefficient [12]. However, several types of research found the presence of polymer in a lower concentration has triggered the separation of the oil and water by making the oil droplets bigger in size which decreases the time for oil droplets to rise to the surface [13]. Surfactant, on the other hand, has lower interfacial tension (IFT) between the oil and water which prevents the oil droplets from coalescing and decreases the separation efficiency between the oil and water.

Although the effect of SP to the oil-water separation have been investigated in the water treatment industry [13-19], little attention has been given to its effect by specifically using the flotation process. The oil and water separation in the flotation unit with the presence of gas bubbles is a complex process which is not well understood. This knowledge gap further increases the difficulty to optimize the flotation system. Moreover, the currently available flotation models failed to improve the efficiency of oil removal in the presence of SP [20-22] since it was tested in the conditions without SP chemicals.

Therefore, the main objective of this study was to investigate the performance of the flotation process in the removal of oil droplets from the SP containing produced water. The effect of SP, as well as other flotation operating parameters such as the gas flow rate and the duration of the flotation to the efficiency of oil removal, have been analyzed. Based on the experimental results, a statistical model was developed to predict the efficiency of oil removal by using the flotation process in the presence of SP chemicals.

■ EXPERIMENTAL SECTION

Materials

The type of surfactant, polymer and crude oil used in the study were MFOMAX, GLP-100, and Dulang crude oil respectively. These chemicals were supplied by PETRONAS Research Sdn Bhd. Brine was prepared by adding the different type of salts at a different concentration as shown in Table (1). All of these salts were purchased from R&M Chemicals, India.

In this research, the Dulang crude oil has a low water content of 0.01%, a low waxy point of 25.9 °C with the density 0.7987 g/cm³ and viscosity of 3.1 cP at 60 °C. The viscosity was measured by using rheometer Anton Paar Model MCR302 and the oil droplets size distribution was measured by using particle size analyzer, DT-1202 from the Dispersion Technology.

Procedure

Synthetic produced water preparation

The synthetic SP produced water was prepared by mixing the brine, Dulang crude oil and various SP concentration based on the previous research. Synthetic SP produced water emulsion was prepared by mixing the MFOMAX (250–500 ppm) [4,23], GLP-100 (450–900 ppm) [23-24], Dulang crude oil with initial concentration of 1000 ppm [18,25] and brine at 14000 ppm (Table 1).

Table 1. Brine compositions

<table>
<thead>
<tr>
<th>Salts</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂·(H₂O)₂</td>
<td>0.7251</td>
</tr>
<tr>
<td>MgCl₂·(H₂O)₆</td>
<td>0.7726</td>
</tr>
<tr>
<td>NaCl</td>
<td>10.0267</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>0.0009</td>
</tr>
<tr>
<td>SrCl₂·(H₂O)₆</td>
<td>0.0295</td>
</tr>
<tr>
<td>KCl</td>
<td>0.3129</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>3.6065</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.7840</td>
</tr>
</tbody>
</table>
under the shear rate of 13000 rpm at 10 min [23,26] by using the Ultra Turrax mixer model T18. The range of the chemicals was selected based on the actual conditions used in Dulang Oilfield.

**Experimental set-up and procedure**

The as-prepared synthetic SP produced water was then fed into the flotation column. The schematic diagram of the process is shown in Fig. 1. The diameter of the flotation column is 5 cm and a length of 100 cm.

Nitrogen gas was injected through a 40–100 µm pores sparger plate at the bottom of the flotation column for the total time of 10 min. The pores size and duration of the flotation process was estimated from the work according to the work by Eftekhardadkhah et al. [2]. Samples at the water outlet were collected for every 2, 6 and 10 min and the oil concentration in the effluents was measured by a TD-500D device (UV-fluorescence technique). The efficiency of oil removal of the flotation column can be calculated by using Eq. (1).

\[
e = 1 - \frac{C_{\text{effluent}}}{C_{\text{inlet}}} \times 100\%	ag{1}
\]

where \(C_{\text{effluent}}\) is the oil concentration in the effluent and \(C_{\text{inlet}}\) is the oil concentration in the inlet.

**Statistical model**

The statistical analysis was performed by using Design Expert 9.0. A total of 45 runs were conducted based on the response surface methodology study by using randomized quadratic design to observe the experimental parameters. Based on the data obtained using this experimental design, a quartic equation was generated to establish the correlation between the independent variables and dependent variables. The independent variables in this study are the gas flow rate (L/min) \(X_1\), duration (min) \(X_2\), the concentration of MFOMAX (ppm) \(X_3\) and concentration of GLP-100 (ppm) \(X_4\). The predicted response of flotation efficiency (%) was designated as \(Y\). The actual and coded values were summarized in Table 2.

**RESULTS AND DISCUSSION**

**ANOVA Statistical Analysis**

The quartic model equation represents the flotation efficiency (%) in the presence of SP \(Y\) which was expressed as the functions of concentration of polymer (ppm) \(X_1\), concentration of surfactant (ppm) \(X_2\), gas flow rate (L/min) \(X_3\) and duration of flotation (min) \(X_4\) for coded factors as shown in Eq. (2).

\[
Y = 26.32 + 11X_1 + 6.75X_2 - 5.99X_3 + 5.10X_4 - 0.00056X_1X_2 + 9.68X_1X_3 - 1.60X_1X_4 - 3.44X_2X_3 - 28.53X_2X_4 - 6.35X_3X_4 + 2.60X_1^2 - 36.64X_2^2 + 0.068X_1X_2X_3 - 8.33X_1X_2X_4 + 4.72X_1X_3X_4 + 2.31X_2X_3X_4 - 3.96X_1^2X_2 + 6.98X_1^2X_3 + 0.49X_1^2X_4 - 5.16X_1X_2^2 - 5.62X_2^2X_3 - 5.33X_2^2X_4 + 3.08X_2^3 + 6.11X_1^2X_2X_4 - 9.47X_1X_2^2X_3 + 17.01X_2^3X_4 + 30.30X_2^4
\]  

\[ \text{Eq. (2)} \]

![Fig 1. Schematic diagram of the flotation process](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Parameter Level</th>
<th>Actual value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flowrate (L/min)</td>
<td>(X_1)</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Duration (min)</td>
<td>(X_2)</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>MFOMAX concentration (ppm)</td>
<td>(X_3)</td>
<td>250</td>
<td>372</td>
</tr>
<tr>
<td>GLP-100 concentration (ppm)</td>
<td>(X_4)</td>
<td>450</td>
<td>670</td>
</tr>
</tbody>
</table>
Table 3 shows the significance of the parameters to the efficiency of oil removal in the flotation process. By referring to Table 3, the parameters that are significant in this model are the gas flow rate (L/min), MFOMAX concentration (ppm) and GLP-100 concentration (ppm) with the P-values of 0.0003, 0.0054 and 0.0148 respectively. Then, the actual and predicted values were plotted in a graph as shown in Fig. 2. The coefficient of $R^2$ was found to be 0.9435. The high value of $R^2$ is closer to 1 which indicates that the predicted model values were correlated well with the experimental values. This good correlation strongly illustrated that the quartic equation is a good representation of the experimental system. Extra experiments were conducted to validate the equation.

Validation of the Equation

Three experiments were performed to validate Eq. (2). A random condition with the gas flow rate of 3 L/min, polymer concentration of 450 ppm, the surfactant concentration of 250 ppm and duration of 10 min with the efficiency of 52.78% was selected for the validation. The results are shown in Table 4.

From the table, the mean value for the actual efficiency was 51.13% while the predicted efficiency value for the condition was 52.78%. The STD was as low as 1.96 indicating that this model can be used to predict the efficiency of the oil removal in the presence of SP at a lab condition.

Contour Plots

Contour plots for the effect of increasing surfactant concentration and gas flow rate at low polymer concentration (450 ppm) for 10 min as shown in Fig. 3.

Table 4. Actual and prediction efficiency for the validation experiments

<table>
<thead>
<tr>
<th>Actual Efficiency (%)</th>
<th>Prediction Efficiency (%)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>49.3</td>
<td>52.78</td>
</tr>
<tr>
<td>Point 2</td>
<td>53.2</td>
<td>52.78</td>
</tr>
<tr>
<td>Point 3</td>
<td>50.9</td>
<td>52.78</td>
</tr>
<tr>
<td>Mean Efficiency</td>
<td>51.133</td>
<td>STD</td>
</tr>
</tbody>
</table>
The results for 2 and 6 min of flotation duration were not shown since the factor was not significant to the oil and water separation as indicated in Table 3. In Fig. 3, the increase of surfactant concentration at 1 L/min had an insignificant effect on the efficiency of oil removal. However, when the gas flow rate increased to 3 and 5 L/min at 250 ppm surfactant concentration, the efficiency of the oil removal increased to 52.82% for 3 L/min and 59.4% for 5 L/min. This is because the increment of gas flow rate tends to increase the potential for attachment of the gas bubbles to the oil droplets. However, at 3 L/min and 5 L/min, increasing the surfactant concentration decreased the efficiency of the oil removal from 52.82 to 34.94% (at 3 L/min) and 59.4 to 39.67% (5 L/min) respectively. In the previous research, an increment in surfactant concentration alone (with the absence of polymer) tend to decrease the efficiency of the oil removal because of the decreasing in the IFT [12]. This result was contradicting at 1 L/min of gas flow rate as the presence of the polymer has balanced out the effect of the efficiency of oil removal by making the oil droplets flocculate [13,27]. This flocculation maintained the rate of oil removal in the presence of the surfactant. The same findings [12] were observed at 3 L/min and 5 L/min whereby increment of surfactant concentration tend to decrease the efficiency of the oil removal.

Further investigation was done to study the effect of polymer concentration on the flocculation of the oil droplets. Fig. 4 shows the effect of GLP-100 concentration on the oil droplets size. From the figure, the size range of the oil droplets gradually increased as the polymer concentration increased from 200 to 900 ppm. The size of oil droplets in the absence of polymer shown the smallest compared to the size in the presence of the polymer. Polymer promotes the coalescence of the oil droplets. This trend was inlined with other researchers [12,27].

Contour plots for the effect of surfactant and gas flowrate at high polymer concentration (900 ppm) at 10 min flotation duration were shown in Fig. 5. At a higher concentration of polymer (900 ppm), the increase in surfactant concentration at 1 L/min decreased the efficiency of the oil removal from 49.51% at 250 ppm of surfactant to 6.89% at 500 ppm of surfactant concentration. At 3 L/min, the efficiency dropped from 34.36% at 250 ppm surfactant concentration to 3% at 500 ppm surfactant concentration. Similar findings were observed at 5 L/min. The efficiency of oil removal decreased from 25.21 to 9.96% at 250 to 500 ppm. Comparing Fig. 3 and 5, the decreased in the efficiency was more significant in higher polymer concentration (900 ppm) (Fig. 3).
increased the viscosity of the emulsion and restricted the movement of the oil droplets to the surface. The effect of viscosity at 900 ppm overcome the flocculation effect at 450 ppm [13].

**CONCLUSION**

A statistical model was developed to describe the efficiency of oil removal in the presence of SP (MFOMAX and GLP-100). It was found that the gas flow rate, surfactant concentration, and polymer concentration affect the efficiency of the oil removal significantly while the duration of the flotation was not significant in the flotation process. Experiments were carried out to access the developed quartic equation and the comparison of the predicted value matched the experimental value with STD 1.96. Low STD indicated that this equation can be used to predict the efficiency of oil removal at a lab scale condition. This study can provide a guideline for the flotation process optimization in SP containing produced water.

**ACKNOWLEDGMENTS**

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**REFERENCES**


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**Fig 5.** Contour plots for the effect of surfactant and gas flow rate at a high polymer concentration (900 ppm) at 10 min flotation duration

**Fig 6.** The effect of polymer concentration on the viscosity of the emulsion compared to 450 ppm polymer concentration (Fig. 5). This is due to the increase in the emulsion viscosity caused by the increase in polymer concentration [13]. To validate this statement, the viscosity of the emulsion was tested with the increasing of polymer concentration as shown in Fig. 6. By referring to the figure, the increase of the polymer concentration tends to increase the viscosity of the emulsion. Therefore, instead of making the oil droplets flocculate, the high polymer concentration


EOR on topside produced water management, SPE Improved Oil Recovery Symposium, Society of Petroleum Engineers, 12-16 April 2014, Tulsa, Oklahoma, USA.


