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Optimization of Nanobubble-Assisted Bunker Oil Flotation from Oil-Wet Sand via Response Surface Methodology (RSM)

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Flotation technology is an effective method for the separation of oil from sand via gas-liquid-solid system. The mechanism of flotation lies in the generation of gas bubble that attaches itself to the hydrophobic particles. Therefore, one of the main parameters which could affect the efficiency of flotation is the bubble size distribution. This research aims to investigate the efficiency of nanobubbles (NBs) in the flotation process to remove high density bunker oil from oil/sand slurry in a laboratory-scale flotation cell. Experiments were carried out using NBs (approximate diameter of 200 nm) generated via ultrasonication for the flotation studies. In this investigation, four different variables including amplitude (sonication power), pH, duration of sonication (min) and input flowrate of NBs (ml/s) were studied. The second order response function was used for obtaining flotation efficiency, and was further optimized using response surface methodology (RSM) to maximize flotation efficiency within the experimentally studied range. The optimum parameters were found to be, 70% amplitude, pH 12, 10 min of flotation and an input flowrate of 57 ml/s to achieve the predicted maximum flotation efficiency of 19.83%. This was in agreement to the experimental results which show an optimum flotation efficiency of 19.98%. The test results indicated that the use of NBs alone provided unsatisfactory flotation. Even though NBs (larger surface area) are expected to increase the bubble-particle attachment and decrease the detachment probabilities, the low buoyancy/low rising velocity of NBs prevents efficient flotation despite the advantages they have. Future studies would include the optimization of bubble size to improve the flotation efficiency.

Keywords: Flotation, nanobubbles, bunker oil, ultrasonication, response surface methodology.

INTRODUCTION

Flotation technology is a combination of chemical, physiochemical and physical methods which uses gas bubbles to remove contaminants. The mechanism of flotation lies in the attachment of gas bubbles to the hydrophobic particles. Due to the difference in buoyancy, the contaminant rises to the surface of the system, enabling the separation of oil from soil. The flotation mechanism is dependent on: (a) collision between particles and bubbles, (b) attachment of particle and bubble to form bubble-particle, (c) flotation of bubble-particle and (d) detachment of particles from bubble-particle (Tao, 2005). Hydrodynamic parameter or more specifically bubble size plays an important role in determining the success rate of flotation efficiency. Smaller bubble size often leads to high flotation efficiency. This is because small bubble diameters enhance the bubble-particle attachment due to the high probability of collision and low probability of bubble-particle detachment.

Other than the effect of hydrodynamic parameter on flotation process, wettability also affects the separation of oil from contaminated sand. Wettability is illustrated as the type of liquid in contact with solid (Czarnecki *et al.*, 2005). For instance, "water-wet" sand type is defined as wet sand (immersed in water) before being contaminated with oil. In contrast, "oil-wet" sand is defined as dry sand contaminated with oil. "Water-wet" sand is easier to be separated in the flotation process as the oil contaminant is not in direct contact with the sand (presence of a thin film of water). Oil-wet" sand type is considered difficult to remove due to the difficulty in dislodging oil from the oil-wet sand (Painter *et al.*, 2010).

While most removal of oil from contaminated sand studies focused on water-wet sands (Long *et al.*, 2007), there are limited studies on the removal of oil from oil-wet sands (Al-Otoom *et al.*, 2009). In addition, the optimization of flotation parameters for oil-wet sands has not been significantly investigated. Therefore, this study aims to optimize the removal of high density bunker oil from oil-wet sands via flotation technology using nanobubbles (NBs) through response surface methodology (RSM), a statistical tool used for empirical model building and response optimization. The influence of sonication power, pH, sonication time and NBs input flowrate were investigated to achieve the maximum flotation efficiency.

MATERIALS AND METHODS

Materials

Bunker oil with a maximum viscosity of 380 cSt was obtained from Port Klang, Malaysia. Sand samples were obtained from a clean designated site. The slurry pH was adjusted using preparing 0.5 M of analytical grade NaOH (Sigma-Aldrich).

Preparation of Oil-Wet Sands

Sand was initially dried in the oven for two days at 60°C, followed by dry sieving using a Retsch AS 200 sieve shaker. 200 g of bunker oil was introduced to 500 g of sand sample with the particle size ratio summarized in Table 1, and allowed to mix homogeneously overnight before flotation experiments.

Table 1. Ratio of soil content with respect to particle size

Particle Size (µm)	500-1000	250 - 500	125 - 250	<125
Percentage (%)	60	20	10	10

Experimental Procedures

Generation & Characterization of Bubbles

NBs were generated through acoustic cavitation by sonicating pure distilled water using a sonication device (Q-Sonica Q700, 20 kHz) for 3 mins. The NBs sizes were measured using Zetasizer (Malvern Instruments Ltd) using methods reported by Calgaroto *et al.*, (2014). The bubble size was found to be approximately 200 nm (average of three replicates).

Flotation Experiments

NBs generated from the ultrasonicator were introduced into the flotation cell (5L beaker filled with oil-wet sand and pH-adjusted distilled water) through a closed loop system at room temperature as shown in Figure 1. The oil was collected via freeze and thaw method, and the extracted oil was dried in the oven at 80°C to remove excess water. The efficiency of oil removal is calculated as a percentage of weight (wt%) of mass of oil recovered per mass of initial oil contaminant as shown in Eq. (1).

$$\text{Oil Removal Efficiency (\%)} = \frac{mass\ of\ recovered\ oil\ (g)}{mass\ of\ oil\ used\ (g)}\ x\ 100\% \quad (1)$$

Response Surface Methodology (RSM)

The design, mathematical modelling and optimization of the study were performed via design of experiments (DOE) using Design Expert 6.0.8 software. A central composite design (CCD) model was chosen to fit the second-order model. Eq. (2) shows the quadratic model used to estimate the optimal point :

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} {X_i}^2 + \sum_{i_{i \le j}}^{k} \sum_{j}^{k} \beta_{ij} X_i X_j + \ldots + e \quad (2)$$

where β is the coefficients of model, X_i X_j are the input variables, and Y is the output variable. The coefficients of the model were calculated using a multi-linear

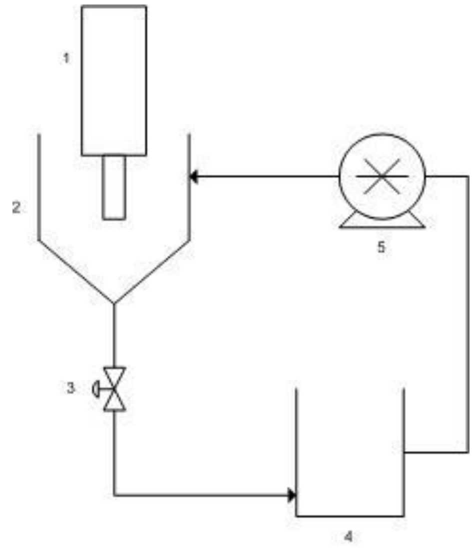

Figure 1. Schematic diagram of NBs flotation experiment setup [1-Sonicator, 2-Cup, 3-Diaphragrm valve, 4-Flotation beaker, 5-Peristaltic pump]

regression analysis and the interactive effects between the four parameters were plotted in 3D contour plots. The optimum parameters were determined based on the model obtained through RSM. A total of 30 runs were required to assess the four experimental factors, with six runs repeated at design centre to evaluate the error.

RESULT AND DISCUSSIONS

NBs Flotation Experiment

The independent variables and their coded/actual levels used in this study are shown in Table 2. The predicted response was designated as Y.

Regression model equation and analysis of variance (ANOVA)

The experimental results in Table 3 were fitted to a full quadratic second order model, selected based on the highest order polynomials, where the additional terms were significant and the models were not aliased. The model equation representing the NBs flotation efficiency (Y) was expressed as functions of amplitude (X_1), pH (X_2), sonication time (X_3), and flowrate (X_4) as shown in Eq. (3).

$$\begin{aligned} Y = {} & 83.44 + 0.33X_1 - 19.40X_2 + 0.05X_3 \\ & - 0.39X_4 + 0.0017{X_1}^2 + 0.93{X_2}^2 + 0.045{X_3}^2 \\ & + 0.0011{X_4}^2 - 0.029X_1X_2 - 0.023X_1X_3 \\ & + 0.0051X_1X_4 + 0.095X_2X_3 + 0.054X_2X_4 \\ & - 0.021X_3X_4 \end{aligned} \tag{3}$$

For the estimation of quality of the model, the coefficient of determination was evaluated together with the ANOVA statistical analysis. The ANOVA results for the quadratic model for flotation efficiency are shown in Table 4. Based on the results obtained, the model used is statistically significant where the P-value with 95% significance level was less than 0.05 for all independent variables. The high coefficient of multiple determination R^2 of 0.9584, shows that the model- values are in good agreement with the experimentally obtained values which indicates that the quadratic system could represent the system given the experimental domain.

Table 2. Actual and coded values of independent variables chosen for CCD

Variable	Symbol	Code variable level		
		Low (-1)	Center (0)	High (+1)
		Actual value		
Sonication power [a]	X_1	30	50	70
pH	X_2	8	10	12
Sonication time (min)	X_3	10	15	20
Flowrate (ml/s)	X_4	27	42	57

[a] Expressed as sonication amplitude in %

Table 3. Design matrix of experimental runs with coded values and results

Standard Order	Run order	Coded level of variables				Observed results
		Amplitude	pH	Duration (min)	Flowrate (ml/s)	Flotation efficiency (%)
1	12	-1	-1	-1	-1	0.01
2	16	1	-1	-1	-1	4.96
3	11	-1	1	-1	-1	1.08
4	24	1	1	-1	-1	7.20
5	29	-1	-1	1	-1	8.81
6	26	1	-1	1	-1	5.84
7	19	-1	1	1	-1	16.51
8	7	1	1	1	-1	7.98
9	17	-1	-1	-1	1	2.63
10	8	1	-1	-1	1	15.74
11	18	-1	1	-1	1	13.98
12	23	1	1	-1	1	19.62
13	14	-1	-1	1	1	4.26
14	22	1	-1	1	1	10.05
15	6	-1	1	1	1	19.41
16	27	1	1	1	1	18.81
17	10	-2	0	0	0	0.00
18	1	2	0	0	0	10.88
19	28	0	-2	0	0	12.01
20	9	0	2	0	0	23.25
21	2	0	0	-2	0	3.44
22	20	0	0	2	0	11.01
23	25	0	0	0	-2	0.41
24	30	0	0	0	2	6.87
25	15	0	0	0	0	3.47
26	3	0	0	0	0	3.96
27	13	0	0	0	0	4.21
28	5	0	0	0	0	2.74
29	4	0	0	0	0	2.99
30	21	0	0	0	0	4.05

Table 4. Analysis of variance (ANOVA) of the response surface model to predict flotation efficiency

Source/Operating parameters	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model (Y)	1200.05	14	85.72	24.68	< 0.0001
A ($\boldsymbol{X_1}$)	85.37	1	85.37	24.58	0.0002
B ($\boldsymbol{X_2}$)	232.91	1	232.91	67.06	< 0.0001
C ($\boldsymbol{X_3}$)	72.07	1	72.07	20.75	0.0004
D ($\boldsymbol{X_4}$)	176.09	1	176.09	50.70	< 0.0001
A^2	12.97	1	12.97	3.73	0.0724
B^2	382.89	1	382.89	110.24	< 0.0001
C^2	35.31	1	35.31	10.17	0.0061
D^2	1.55	1	1.55	0.45	0.5142
AB	20.82	1	20.82	6.00	0.0271
AC	81.58	1	81.58	23.49	0.0002
AD	37.11	1	37.11	10.68	0.0052
BC	14.47	1	14.47	4.17	0.0593
BD	42.20	1	42.20	12.15	0.0033
CD	40.11	1	40.11	11.55	0.0040
Residual	52.10	15	3.47		
Lack of Fit	50.27	10	5.03	13.78	0.0049
Pure Error	1.82	5	0.36		

Interaction Effects of Parameters

Figure 2(a) – (f) shows the 3D surface response and contour plots, where two factors were varied and the other factors were held constant. Figure 2(a) shows the relationship between amplitude (X_1) and pH (X_2) on the flotation efficiency, keeping sonication time (X_3) and flowrate (X_4) constant. It is obvious that the flotation efficiency is greatly affected by the change in amplitude and pH. An increase in flotation efficiency could be significantly achieved with an increase in both the amplitude and pH. Figure 2(b) shows the relationship between amplitude (X_1) and duration of flotation experiment (X_3), keeping the other factors constant. The increase in the sonication time from 10 to 20 min at constant amplitude does not significantly affect the flotation efficiency which suggests that the duration of experiment could be kept to the minimum for minimal operational costs.

The relationship between amplitude (X_1) and input flowrate (X_4) is shown in Figure 2(c), keeping pH (X_2) and duration (X_3) constant. The increase in input flowrate together with the increase in amplitude showed an increasing trend in flotation efficiency. The increase in flowrate was expected to increase the flotation efficiency, as it increases the rate of bubble flow into the flotation cell. With the increase in bubble flow, this subsequently leads to increased bubble

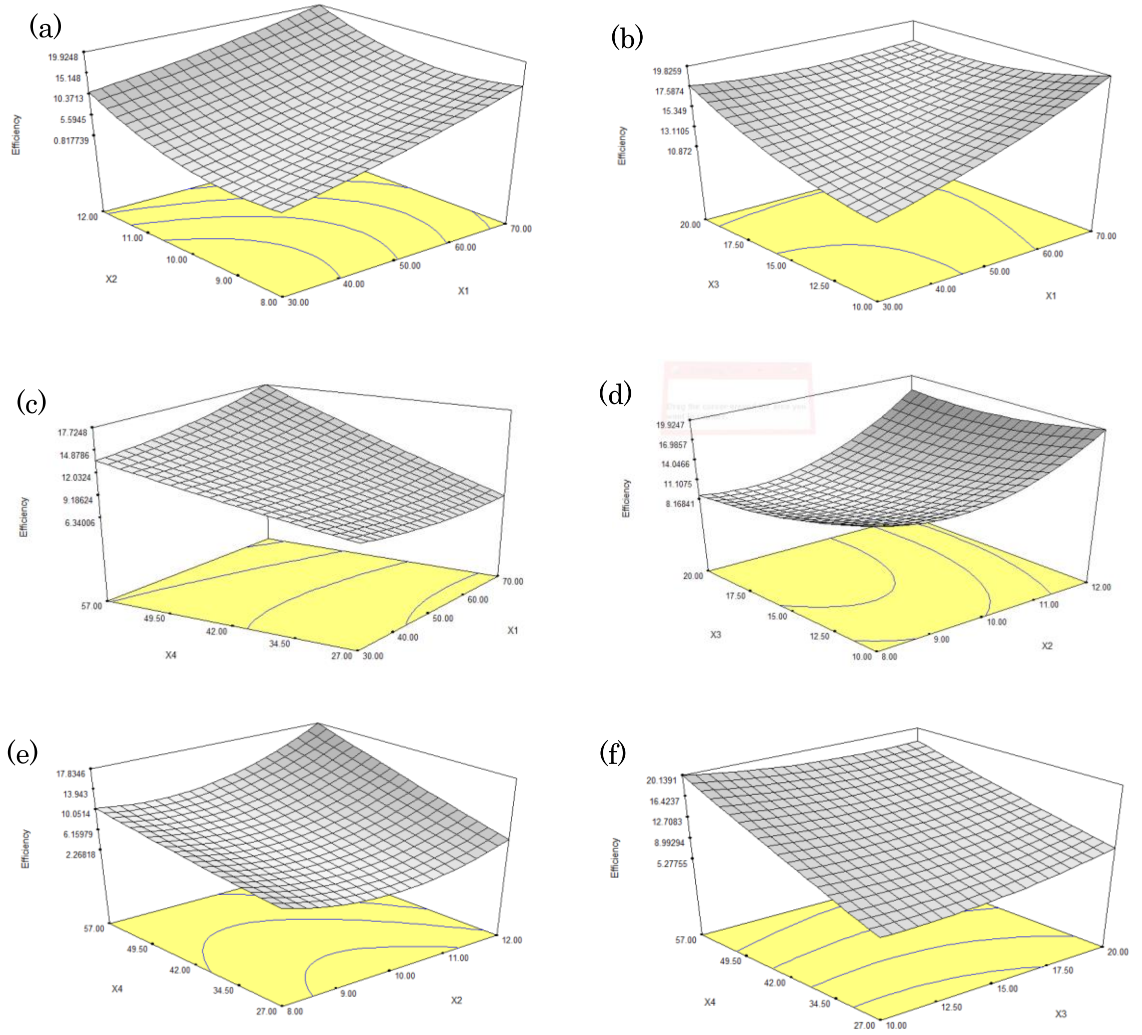

Figure 2. Response surface plots of flotation efficiencies (%) due to: (a) effect of amplitude (X_1) and pH (X_2); (b) effect of amplitude (X_1) and duration (X_3); (c) effect of amplitude (X_1) and input flowrates (X_4); (d) effect of pH (X_2) and duration (X_3); (e) effect of pH (X_2) and input flowrates (X_4); (f) effect of duration (X_3) and input flowrates (X_4)

concentration within a constant time frame, which attributed to the higher efficiency as observed. Figure 2(d) instead shows the relationship between pH (X_2) and duration (X_3) on flotation efficiencies (%). As observed, pH showed an increasing trend over duration of experiment on the flotation efficiency output. This suggests that pH has a more significant effect towards flotation efficiency compared to duration of flotation, as aforementioned.

In Figure 2(e), the response surface plots shows the effect of pH (X_2) and input flowrates (X_4) on flotation efficiencies (%). Both parameters were observed to play significant roles in the flotation efficiency, with the increase in both pH and input flowrate to maximum showed highest flotation efficiency recorded. Lastly, Figure

2 (f), shows the relationship between duration (X_3) and input flowrates (X_4), keeping the other values constant. The maximum flotation efficiency could be observed at the maximum input flowrate (57 mL/s), and minimum duration of flotation (10 min). At this condition, the oil removal efficiency is predicted to 19.83%.

Optimization Studies for Flotation Efficiency

Based on the model, the optimum flotation variables were found to be at an amplitude of 70%, pH of 12, duration of 10 min, and input flowrates of 57 mL/s with a prediction of 19.83% in flotation efficiency. These values were experimentally validated with flotation efficiencies up to 19.98 % (±1.61) at the optimum conditions. This confirms that RSM could be effectively used to optimize the process parameters using the statistical design of experiments.

A control experiment was also conducted using similar setup as shown in Fig. 1, without the generation of NBs (in the absence of sonication) using the optimized parameters. The purpose of this control experiment is to investigate the effect of oil buoyancy alone on the oil separation efficiency. It was observed that at the optimized conditions; the separation efficiency was found to be 6.1%.

Based on the results obtained, it could be clearly seen that the presence of NBs (≈200 nm) provided a significant enhancement of separation of oil from oil-wet sand of approximately 14%. However, a low overall flotation efficiency of 19.98% was recorded, which could be attributed to the properties of NBs and the oil-wet sand characteristics. While NBs typically have a large surface area due to the small diameter size, they have negligible buoyancy (low bubble rise velocity), low diffusivity and would remain suspended in water for a long period of time, and exist in a metastable state (Liu *et al.*, 2013) (Uddin *et al.*, 2012). In addition, it was also reported that oil-wet sands are considered difficult to remove using water-based recovery processes, due to the high attachment forces between oil and sand (Czarnecki *et al.*, 2005). Therefore due to these properties, the use of NBs alone for flotation purpose will not yield satisfactory results, because NBs lack the buoyancy and sufficient force to aid the flotation of oil contaminant.

CONCLUSION

The use of NBs for the removal of oil from oil-wet sand via the flotation method was investigated. The influence of four parameters (amplitude, pH, duration, and input flowrate) were modeled and optimized to increase the oil flotation efficiency. The optimum conditions suggested from the RSM model for amplitude (%), pH, duration (min) and input flowrate (mL/s) were 70%, 12, 10 min and 57 mL/s respectively. Under these conditions, the experimental result showed improved oil removal efficiency from 6.1% (in the absence of NBs) to 19.98% (in the presence of NBs). This finding shows that the presence of NBs is capable of enhancing the separation of oil from oil-wet sand. However, the low buoyancy and high stability of NBs in water hinder the efficient flotation of oil to the surface of water. Therefore, future experiments would include improving the buoyancy of NBs to enhance the oil removal percentage, while providing a large surface area for the enhancement of bubble-particle attachment.

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