adjusted by a three-way flexible tube in order to vary the foam height. The air bubbles ascended through the solution generated foam. The foam overflown from the column was collected. After that, the froth was collapsed to analyze diesel concentrations in the froth. In addition, effluent samples were also collected for analysis of diesel and surfactant concentrations by using the methylene chloride extraction method and titration method with methylene blue chloride, respectively. All experiments of the forth flotation were carried out at room temperature of 25-27 °C.

RESULTS AND DISCUSSION

In this study, wt% is based upon the aqueous system consisting of water, salt, and surfactant. Foamability is defined as the ratio of maximum foam height to initial solution height whereas foam stability ($t_{1/2}$) is the time required for the foam to collapse a half of the maximum height. Enrichment ratio is defined as the concentration of diesel in the collapsed froth divided by concentration of diesel in the feed.

Microemulsion Formation

The microemulsion formation of diesel with Alfoterra shows only two obvious phases, which were the excess water and excess oil phases. The layer of the middle phase (Winsor Type III microemulsion) was very thin, and it could not be clearly observed visually. Consequently, the measurement of the phase transformation became difficult to identify whether the system had a middle phase or not. Hence, the phase diagram of diesel with Alfoterra is not shown here. The IFT of the system was measured by the spinning drop tensiometer to examine the existence of Winsor Type III microemulsions. Figure 2 shows IFT as a function of Alfoterra concentration, The minimum IFT was found with 0.10 wt% Alfoterra. Figure 3 illustrates the IFT as a function of salinity scan at 0.1 wt% Alfoterra and an oil:water ratio of 1:1. The result shows that the minimum IFT occurs at 5 wt% NaCl concentration. According to the result from the effe2ct of agitation of single surfactant (Alfoterra) concentration on performance of froth flotation as will be shown later, it was found that the oil removal decreased as the solution was further agitated. Consequently, adding SDS as another frother to the solution is desirable because it provides good foamability and foam stability. The system consists of Alfoterra at 0.1 wt% and NaCl at 3 wt%, SDS concentration was varied from 0.1, 0.5, 0.7, and 1 wt%. The reason that 3 wt% of NaCl was used instead of 5 wt% NaCl is because foamability and foam stability at high NaCl concentration of the system are very poor because the repulsive force between the anionic head groups decreases when the NaCl concentration increases leading to a board foam lamella and high water content in a foam lamella. Hence, foam can break easily and froth flotation cannot be achieved. As shown in Figure 4, increasing the SDS concentration increases the IFT and the minimum IFT appears at 0.1 wt% of SDS.

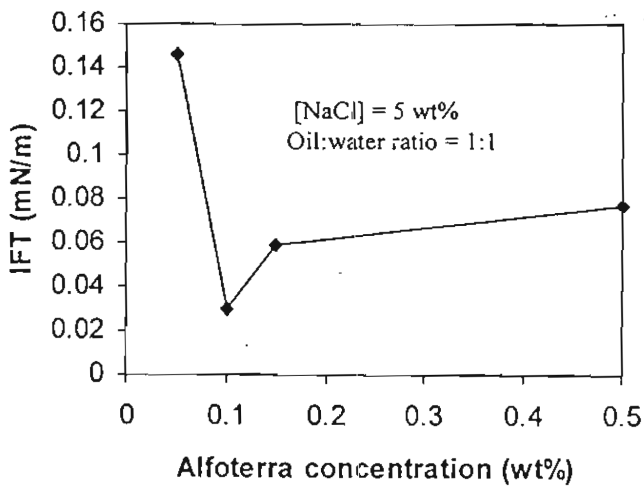

Figure 2. IFT as a function of Alfoterra concentration at 5 wt% NaCl with oil:water ratio = 1:1 (v:v)

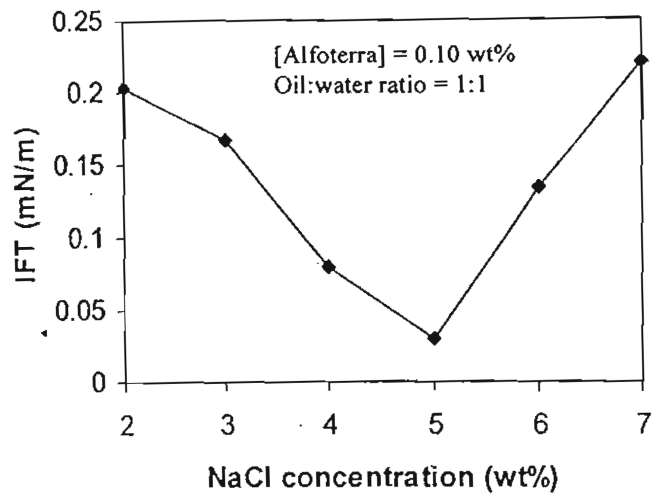

Figure 3. IFT as a function of salinity at 0.1 wt% of Alfoterra, oil:water ratio = 1:1 (v:v)

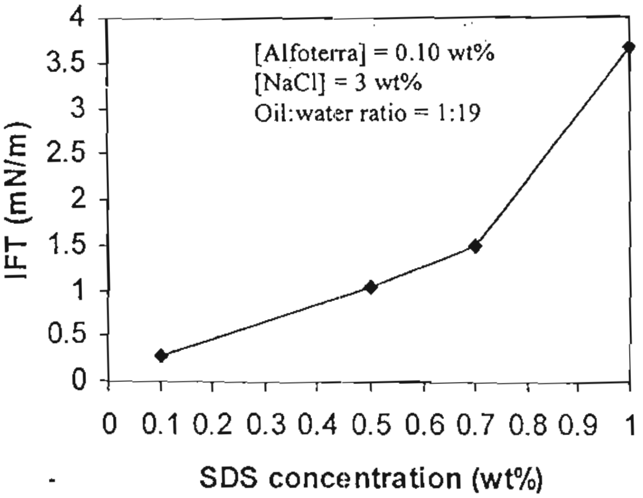

Figure 4. IFT as a function of mixed surfactant concentration at 0.1 wt% Alfoterra, 3 wt% NaCl, oil:water ratio = 1:19

Froth Flotation Results

Effect of single and mixed surfactant system

Figure 5 shows that the oil removal decreases with time of the froth flotation unit in batch mode of operation. This is because as the solution is agitated longer, foam stability decreases due to the decrease in the oil droplet size, but still higher than 2-10 μm which is the range of droplet size providing a high foam stability results in the decreasing of oil removal. Because of the speed of mixing between the surfactant solution and diesel oil used in this research is 2000 rpm, but the speed that can reduce the oil droplet size to 2-10 μm is between 5000-10000 rpm (Jarudilokkul *et al.*, 2003). The dependence of stability on the oil drop size can be explained by the oil accumulation mechanism. The small droplets tend to accumulate in the plateau borders of foam lamella at a lesser extent owing to their size and buoyancy force; therefore, they have less resistance for the movement in the plateau borders of foam lamella (Schramm, 1992). Consequently, they are less likely to be trapped within the plateau borders. As the drop size decreases, the accumulation of oil decreases. Nevertheless, the viscosity of emulsions increases rapidly with decreasing of the drop size under the range of 1-2 μm due to the interaction between the oil drops becomes significant. Hence, in the presence of very fine emulsion, the liquid drainage is much slower, and thus the foam stability is much greater. The foam stability can be increased by having small oil drop size in the range of 1-2 μm. This phenomena can be explained by the effect of size of droplets effect of size of droplets as mentioned before. However, reducing size of oil droplets into the range of 1-2 μm is very difficult and not commercially practical. Hence, an addition of a frother to the solution was selected to solve this problem. Figure 6 compares the foam stability of agitated-solution and non-agitated solution of the system with different Alfoterra concentrations. The non-agitated system was found to provide higher foam stability than that of the agitated-system. As shown in Figure 7, the maximum oil removal is at 0.5 wt% SDS. This can be explained by using the result of foamability as shown in Figure 8. Hence, this system was selected to study effects of other parameters.

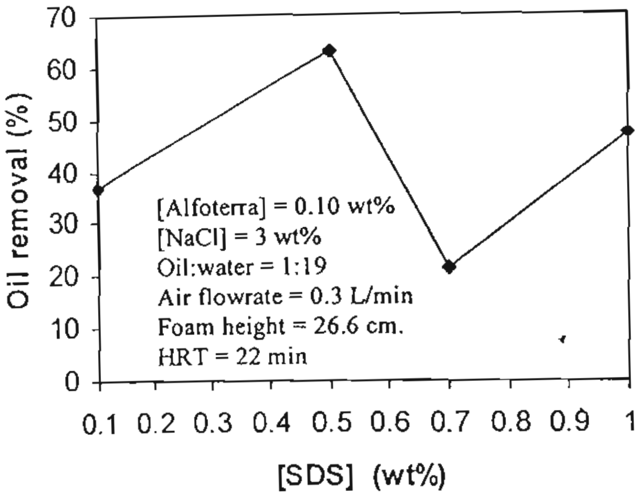

Figure 7. Oil removal efficiency of mixed surfactant system at different SDS concentrations

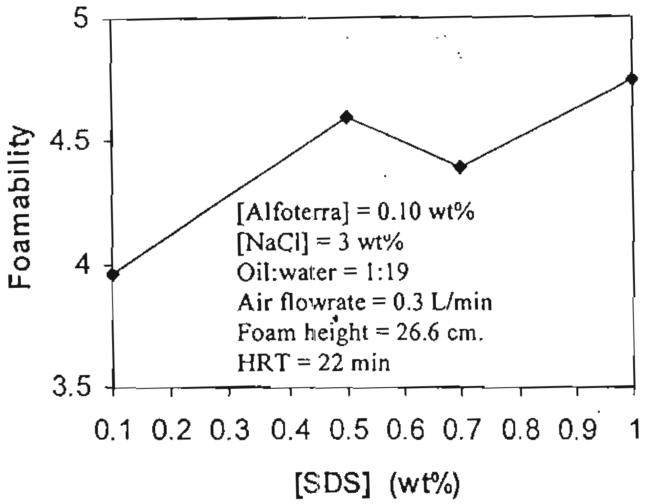

Figure 8. Foamability of mixed surfactant system at different SDS concentrations

Effect of NaCl concentration

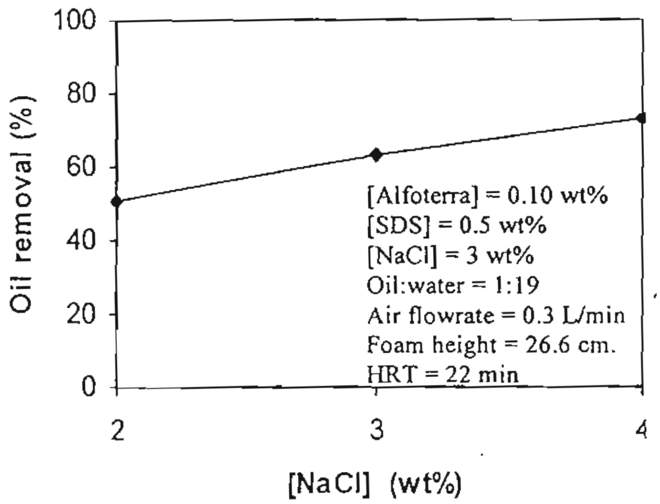

Figure 9. Removal efficiency of diesel at different NaCl concentrations

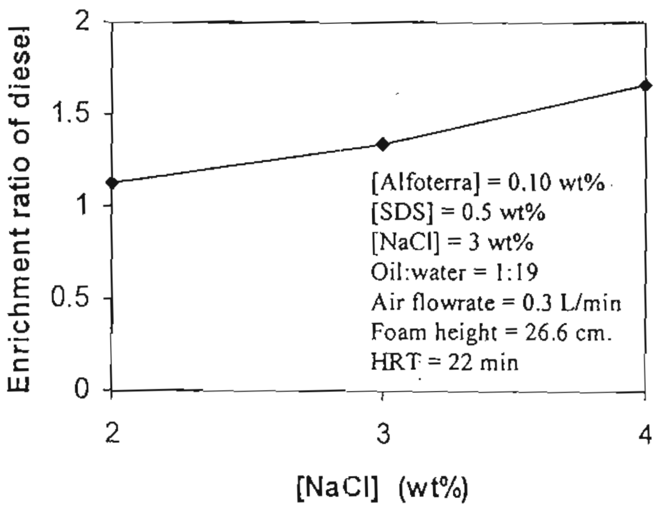

Figure 10. Enrichment ratio of diesel at different NaCl concentrations

The effect of NaCl concentration on the operation of froth flotation was carried out by varying NaCl concent

The effect of NaCl concentration on the operation of froth flotation was carried out by varying NaCl concentration at 0.1 wt% Alfoterra and 0.5 wt% SDS. Figure 9 shows that an increase in the NaCl concentration from 2 to 4 wt% results in increasing oil removal. This is because the repulsive force between the anionic head groups decreases when the NaCl concentration increases. Consequently, the hydrophobic characteristics of the foam surface increase resulting in increasing amount of oil attached to the foam. A part from the removal efficiency the separation efficiency of the froth flotation can be indicated by the enrichment ratio. Figure 10 illustrates the effect of NaCl concentration on the enrichment ratio. It shows that an increase in the NaCl concentration from 2 to 4 wt% increases the enrichment ratio of diesel. This is because NaCl reduces the repulsive force between the anionic head groups of the surfactant so foam lamella becomes thinner leading to lower water content in the foam and higher oil content.

Effect of oil to water ratio

Most available work on froth flotation involves 1:1 oil to water ratio (Chavadej *et al.*, 2003, Feng *et al.*, 2000). Practically, a ratio of emulsified oil to wastewater is much less than 1:1. Consequently, in this work, the effect of oil loading on the performance of froth flotation was investigated by varying the oil to water ratio at 0.1 wt% Alfoterra, 0.5 wt% SDS, and 4 wt% NaCl. As illustrated in Figure 11, the effect of oil to water ratio on diesel removal corresponds to the result of foam production rate as shown in Figure 12. This is because with a high foam production rate, the drainage rate of water in the foam lamella decreases resulting in decreasing back-entrainment of oil content into the solution in the column leading to a high oil removal. It was found that the oil to water ratio does not affect significantly on the oil removal efficiency. Figure 13 shows the effect of oil to water ratio on the enrichment ratio of diesel. The enrichment ratio decreases slightly when the oil to water ratio increases from 1:199 to 1:99. This is because at an oil to water ratio of 1:99, the foam production rate is increased resulting wetter foam than a low oil to water ratio of 1:199. As a result, the collapsed foam contains a high amount of water leading to a lower enrichment ratio of

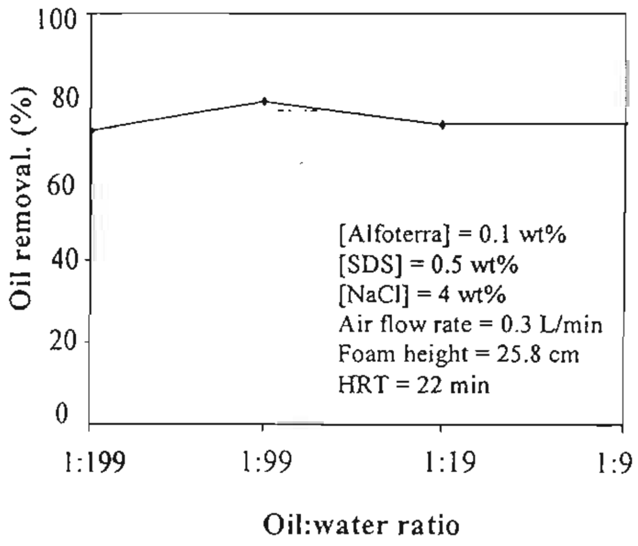

Figure 11. Removal efficiency of diesel at different feed NaCl concentrations

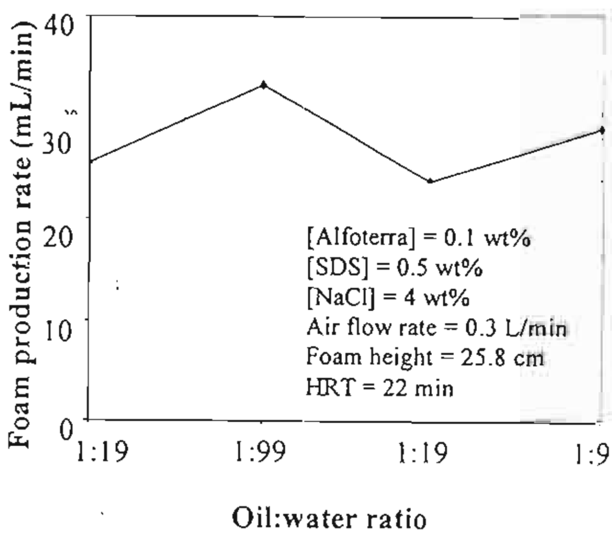

Figure 12. Foam production rate of system at different feed oil to water ratios

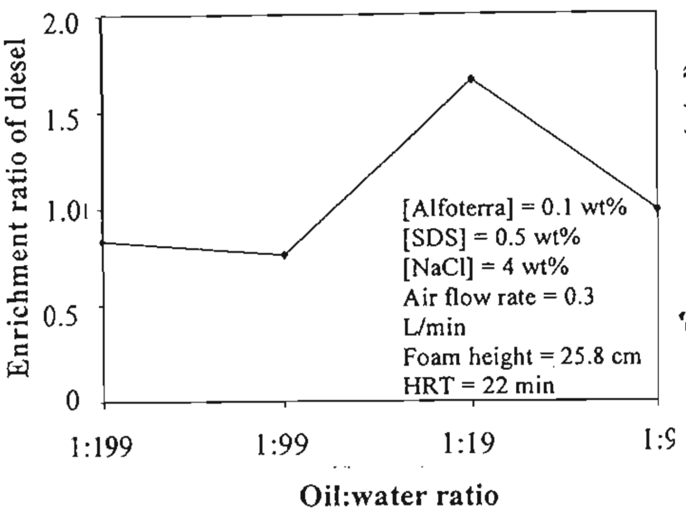

Figure 13. Enrichment ratio of diesel of system at different feed oil to water ratios

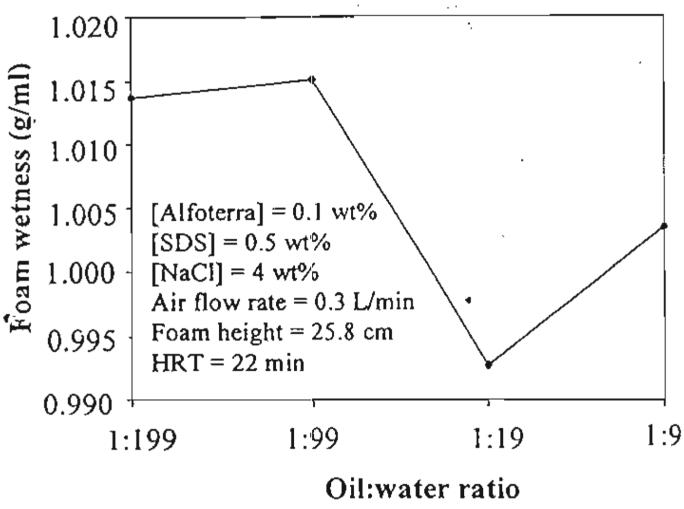

Figure 14. Foam wetness of system at different feed oil to water ratios

diesel. After that, when an oil to water ratio is further increased to 1:19, the enrichment ratio of oil increases substantially because at the system has the smaller amount of surfactant leading to the narrower foam lamella. When an oil to water ratio is further increased to 1:9, the enrichment ratio of diesel decreases again. The explanation is still the same as described before. As expected, the profile of foam wetness (see Figure 14) is the opposite trend of the enrichment ratio of diesel. The higher foam wetness, the higher water content is or the lower oil content is.

Effect of hydraulic retention time (HRT)

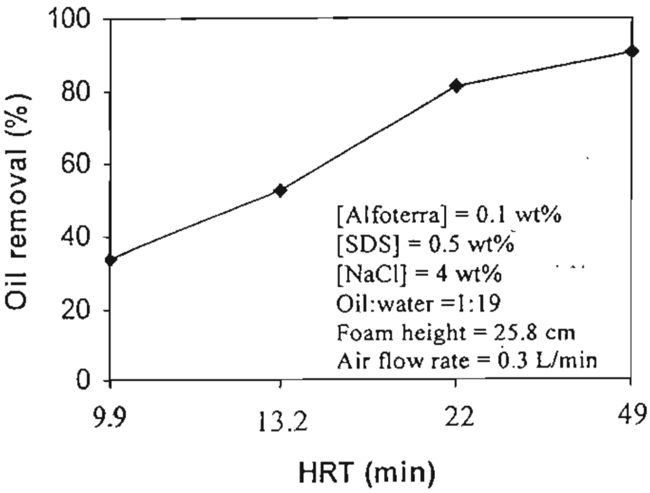

Figure 15. Removal efficiency of diesel at different HRTs

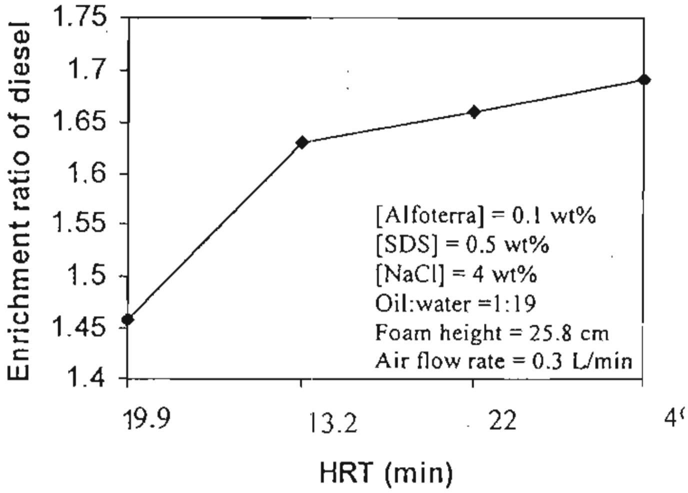

Figure 16. Enrichment ratio of diesel at different HRTs

From Figure 15, the oil removal increases when HRT increases. This is because a higher HRT gives a longer residence time for the solution to contact with air bubbles. As a result, a higher amount of oil can be carried on to the top of the column and a higher oil removal is obtained. In this work, the maximum oil removal is up to 90.37 % at a HRT of 49 min. As shown in Figure 16, the enrichment ratio of oil increases as HRT increases because a high HRT represents a lower feed flow rate resulting in longer time for oil to stay in the column as well as more time to be contacted and attached to the air bubbles and the froth at the top of the column. Therefore, the collapsed froth contains a higher amount of oil and a lower water content with increasing HRT.

CONCLUSIONS

From this work, foamability is another factor that affects on oil removal efficiency. Adding small amount of salt can enhance a froth flotation efficiency, but a high amount of salt deteriorate the foam stability. Oil to water ratio is not affected significantly on oil removal ěfficiency. This may be due to the same solubilization power of each sytem because it contains nearly the same Alfoterra and SDS concentration as well as NaCl concentration. Moreover, an increase in HRT increases the oil separation efficiency. The system with 0.1 wt% Alfoterra, 0.5 wt% SDS, 4 wt% NaCl, an oil:water ratio of 1:19, an air flow rate of 0.15 L/min, a foam height of 26 cm, and a HRT of 49 min gave the maximum oil removal (90.37 %).

ACKNOWLEDGMENTS

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PROGRAM & ABSTRACTS

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Surfactant Recovery from Aqueous Phase Using Multi-Stage Foam Fractionation

On-line Number 980

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ABSTRACT

Surfactants are widely found in many products such as detergent, cosmetics, shampoo and drugs. As environmental regulations tightened, there is increasing concern about reducing the surfactant concentration in effluent streams. Foam fractionation is the direct and continuous treatment which would allow for the reuse of both water and surfactant. In this study, two multi-stage foam fractionators with different tray spacing were set up to investigate the recovery of cetylpyridium chloride (CPC), a cationic surfactant, from aqueous solution. Effects of several important variables, including surfactant feed concentration and flow rate, air flow rate, foam height, number of trays and recycle position ratio, were systematically studied. It can be seen from the results that increasing air flow rate and surfactant concentration resulted in lowering enrichment ratio but increasingly % surfactant recovery. Effect of foam height on surfactant recovery was not as significant as it was on the enrichment ratio. With increasing feed flow rate, both enrichment ratio and surfactant recovery decreased. On a contrary, increasing number of trays was found to enhance both enrichment ratio and recovery. Lastly, changing recycle position was shown to have more impact on the column performance than changing the recycle ratio or tray spacing.

KEYWORD

Foam Fractionation / Surfactant recovery

INTRODUCTION

Surfactants appear in the effluent wastewater from a number of industries such as textile, pulp and paper, food processing and detergent manufacturing. As environmental regulations tightened, there has been growing concern about reducing the surfactant concentration in aqueous streams. In addition, surfactant-based separation processes have gained increasing interest in the remediation of wastewater and ground water in recent years (Scamehorn and Harwell, 1992). In these processes, surfactants are added to remove toxic pollutants from the waste streams. Consequently, the resultant effluent streams often contain

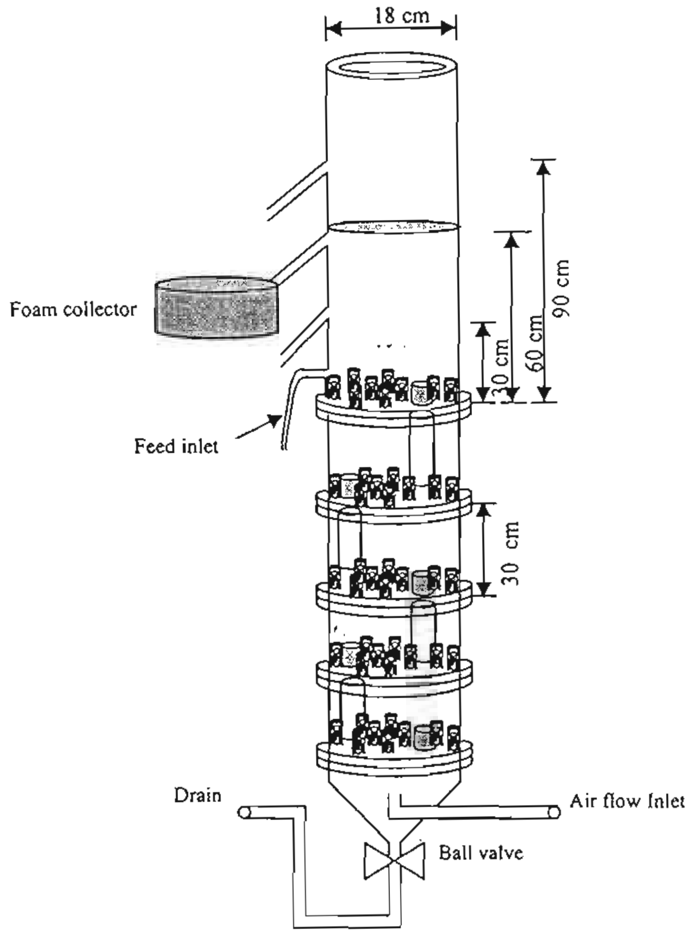


Figure 1 Schematic Diagram of a Multi-Stage Foam Fractionation Column

The compressed air was introduced at the bottom tray. Foamate at the top of the column was collected at three different foam height of 30, 60 and 90 cm from the liquid surface of the top tray.The foam was collected, frozen, thawed and then weighted to get the collapsed foamate volume.

The surfactant separation efficiency of the foam fractionation system was studied under steady state conditions. Steady state was insured when all measured parameters were invariant with time. After steady state was achieved, samples of the outlet stream and foam were taken for analysis and measurement. All experimental runs were performed at room temperature (25-27°C).

In each experiment, volumetric foam production rate (l/min.m^2), foam wetness (grams of foam solution/L of foam), and the surfactant concentration (g/l) in the collapsed foam solution were measured. The concentrations of CPC in collapsed foams, feed solutions and effluents were measured by an UV visible spectrophotometer at wavelength of 260 nm.

The critical micelle concentration (CMC) of CPC was also measured experimentally by plotting the specific surface tension versus surfactant concentration showing an abrupt change in slope.

RESULTS AND DISCUSSION

The multistage foam fractionator used in this study was first put through a series of tests in order to check when steady state could be established. Operating under the base conditions, the foam fractionation unit showed to reach steady state within approximately 6 hours. After this period of time, the surfactant concentration measured in each tray from the sampling port became constant, meaning that the steady state was established.

After the steady state was established, effects of several parameters on the separation efficiency of the multistage fractionator operated in a continuous mode were studied and evaluated in terms of surfactant recovery (%) and enrichment ratio as shown below:

$$\text{Surfactant Recovery (\%)} = \frac{(C_i - C_e) \cdot 100}{C_i}$$

$$\text{Enrichment Ratio} = C_f / C_i$$

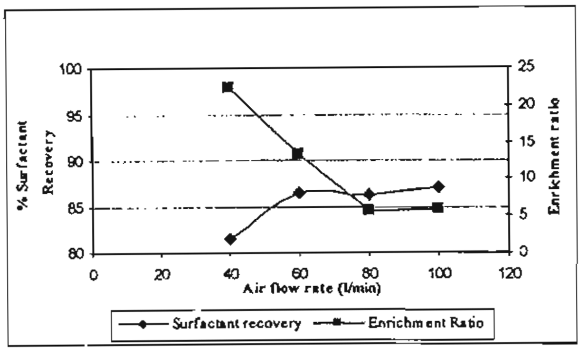
Where C_i and C_e are surfactant concentrations (mg/L) in the influent and effluent streams, respectively, and C_f is a surfactant concentration in the collapsed foam.

Effect of Air Flow Rate

From Figure 2, it can be seen that increasing air flow rate results in a reduction in the enrichment ratio but it leads to an increase in % surfactant recovery. An increase in the air flow rate increases the interfacial area between gas and liquid or the mass transfer area, thus increases the surfactant recovery. However, increasing air flow rate tends to generate wet foam which contains a lower amount of surfactant, resulting in a lower enrichment ratio.

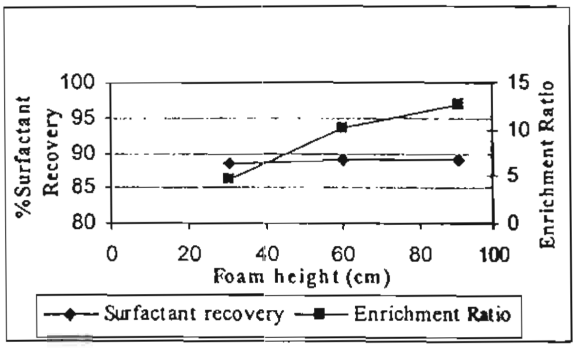
Effect of Foam Height

Effect of the foam height in the foam fractionation column was studied by varying a distance between the surface of liquid in the highest tray and the foam draw-off pipe. From Figure 3, it can be seen that increasing foam height results in an increase in the enrichment ratio but has little effect on the surfactant recovery. Increasing foam height leads to a longer foam residence time, which allows more drainage of the liquid in the films. Thus, the concentration of the adsorbed surfactant molecules increases as foam height increases, resulting in a higher enrichment ratio. On a contrary, within the range of foam heights investigated here, the effect of foam height on the surfactant recovery was not as significant as observed with the enrichment ratio.



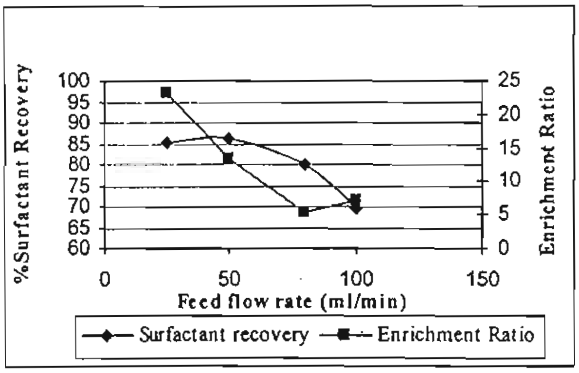
Conditions: [CPC] = 0.25 CMC; feed flow rate = 50 ml/min; foam height = 30 cm; tray spacing =15 cm and number of tray =5

Figure 2 Effects of air flow rate on surfactant recovery and enrichment ratio.



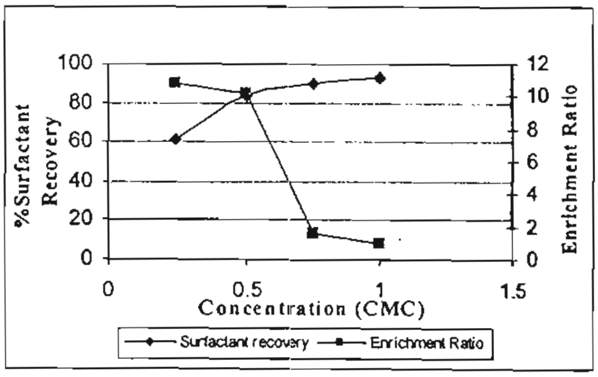
Conditions: [CPC] = 1 CMC; Air flow rate = 40 L/min; Feed flow rate = 25 ml/min; tray spacing =30 cm and No. of tray =5

Figure 3 Effects of foam height on surfactant recovery and enrichment ratio.



Conditions: [CPC] = 0.25 CMC; Air flow rate = 60 L/min; foam height = 30 cm; tray spacing = 15 cm and No. of tray = 5

Figure 4 Effects of feed flow rate on surfactant recovery and enrichment ratio.



Conditions: [CPC] = 0.5 CMC; Air flow rate =40 L/min; Feed flow rate = 50 ml/min; foam height = 30 cm; and tray spacing = 30 cm

Figure 5 Influence of CPC concentration in feed on surfactant recovery and enrichment ratio.

Effect of Liquid Feed Flow Rate

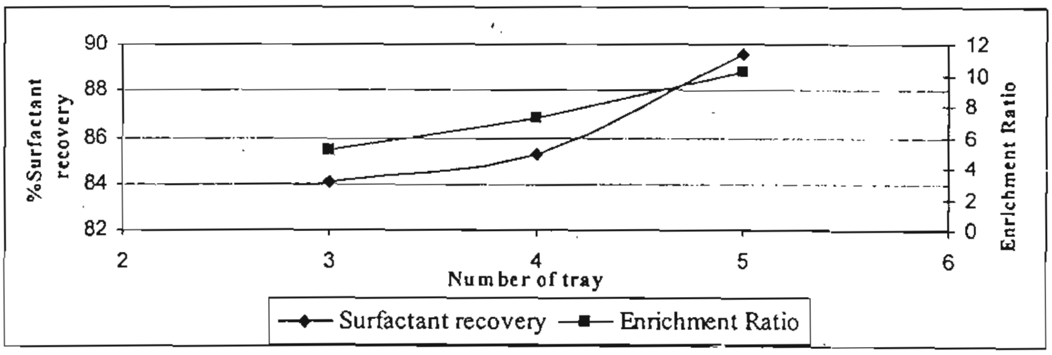
From Figure 4, it shows that increasing feed flow rate results in a decrease in both enrichment ratio and surfactant recovery. The decrease in the enrichment ratio and surfactant recovery upon increasing feed flow rate may attribute to a shorter residence time at a higher liquid flow rate. As a result, considerable amount of surfactant still remains in the liquid which drains out of the column and the surfactant becomes more concentrated at the higher trays.

Effect of Feed Concentration

. The surfactant concentration in the feed solution was varied in the range of 25-100% of the CMC of CPC. From Figure 5, increasing surfactant concentration from 0.25 CMC to 1 CMC results in a drastical decrease in the enrichment ratio. In contrast, within the same range of the surfactant feed concentration, the surfactant recovery increases slightly. A higher surfactant concentration in the thin liquid film in the foam lamellae may make this liquid more stable as well as causes an increase in surface viscosity and surface concentration, leading to a decrease in the rate of film drainage, thus causing the surfactant to quickly go out off the column. On the other hand, foam that formed over a fluid with a low surfactant concentration is less stable and results in a much higher enrichment ratio than that formed over high-surfactant fluid. The foam formed over a fluid with a higher concentration is characterized by smaller, more stable bubbles.

Effect of Number of Trays

From Figure 6, it can be seen that increasing number of trays from 3 to 5 results in an increase in both enrichment ratio and surfactant recovery. Under the conditions studied, the highest % surfactant recovery of 90 % and enrichment ratio of 10 were achieved when 5 trays were used. This is due to the fact that increasing number of trays provides a longer residence time and, consequently, allowing the surfactant to become more concentrated in foam as well as a higher surfactant recovery. The present study is in good agreement with the previous result (Boonyasuwat et.al, 2003)



Conditions: Air flow rate =50 L/min; feed flow rate = 50 ml/min; foam height = 60 cm; tray spacing = 30 cm and number of trays =3

Figure 6 Influence of Number of tray on surfactant recovery and enrichment ratio

Effect of Recycle Position and Recycle Ratio

From Table 2 it can be seen that the change in recycle position and recycle ratio of the effluent had only little effect on both surfactant recovery. However, slight increase in the enrichment ratio was observed when the recycle feed was fed into the trays at higher position (trays 4 and 5). Therefore the effect of recycle ratio was further studied by using 3 different ratios (3/1, 1/1, and 1/3). It can still be seen that no significant change was observed upon varying the recycle ratio. The results suggested that the recycle feed position and recycle ratio may not have much effect on this small column.

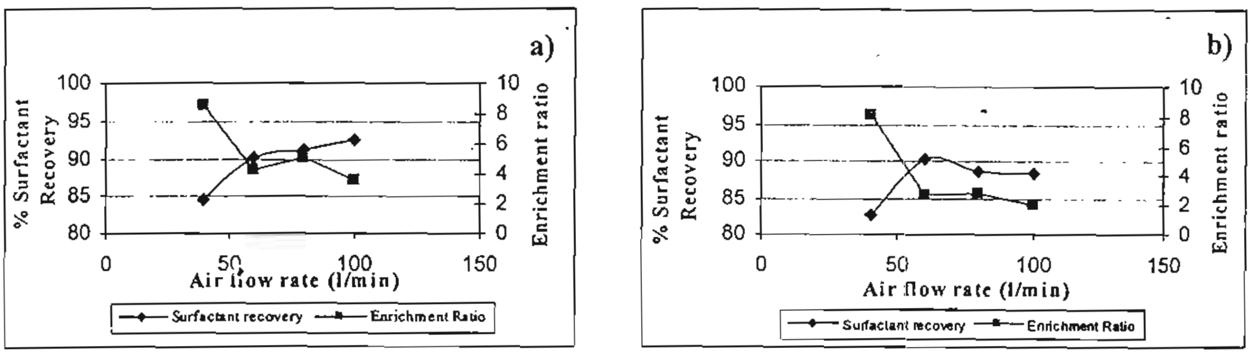
Table 2 Effect of recycle ratio and recycle position on surfactant recovery and enrichment ratio.

Condition: [CPC] = 0.50 CMC air flow rate =40 L/min; feed flow rate = 50 ml/min; foam height = 30 cm; tray spacing = 15 cm; and number. of tray =5

Recycle Position	No recycle		Recycle					
	% Surfactant Recovery	Enrichment Ratio	Recycle/Feed = 1:1		Recycle/Feed = 1:2		Recycle/Feed = 3:1	
			% Surfactant Recovery	Enrichment Ratio	% Surfactant Recovery	Enrichment Ratio	% Surfactant Recovery	Enrichment Ratio
tray5	88.99	7.66	84.33	12.16	85.31	9.62	88.62	9.53
tray4	89.12	10.44	83.76	14.18	88.69	13.24	86.54	11.24
tray3	88.47	9.99	81.78	12.15	87.56	10.29	87.65	9.11
tray2	88.62	11.11	84.53	9.32	87.23	9.85	82.62	12.54
tray1	87.75	9.54	84.46	11.53	84.29	10.35	86.81	10.89

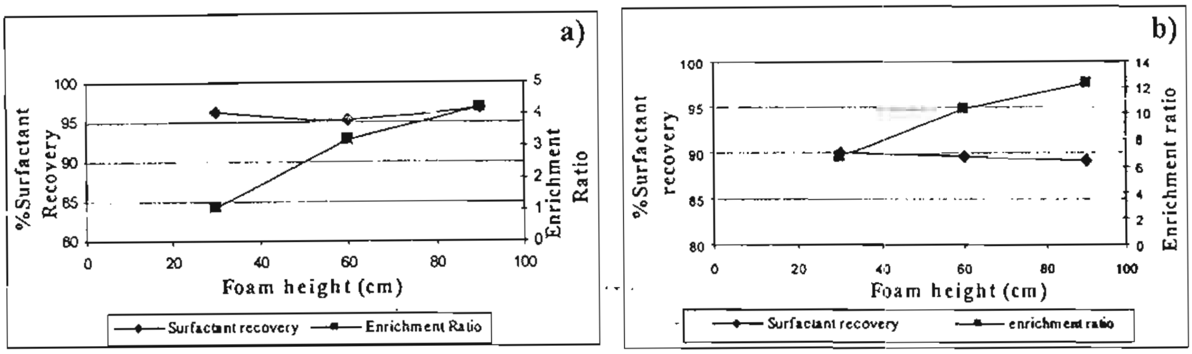
Effect of Tray Spacing

The results observed from Figure 7-11 indicated that under the conditions studied increasing tray spacing from 15 cm to 30 cm did not show any significant effect on the performance of the multistage foam fractionation in terms of both surfactant recovery and enrichment ratio. Very similar results and comparable values of surfactant recovery (%) and enrichment ration were obtained from the two columns using different tray spacing. This may be due to the limited size and dimension of the column which might not large enough to see the effect. In addition, the number of bubble caps on each tray may be too few which limited the extent of the mass transfer occurred in the column.



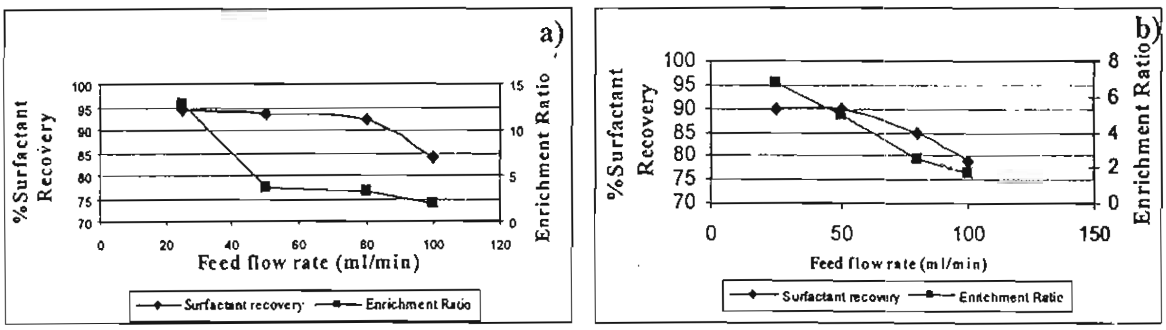
Conditions: [CPC] = 0.5 CMC; Feed flow rate = 50 ml/min; Foam height= 30 cm, and No. of tray = 5

Figure 7 Effects of superficial air velocity on surfactant recovery and enrichment ratio. a) 15 cm tray spacing b) 30 cm tray spacing



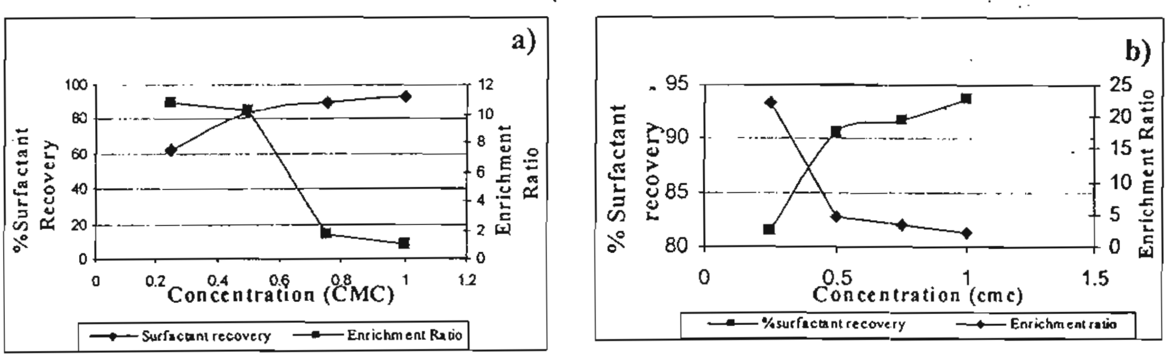
Conditions: [CPC] = 0.75 CMC; Air flow rate = 60 L/min; Feed flow rate = 50 ml/min and No. of tray =5

Figure 8 Effects of foam height on surfactant recovery and enrichment ratio a) 15 cm tray spacing b) 30 cm tray spacing



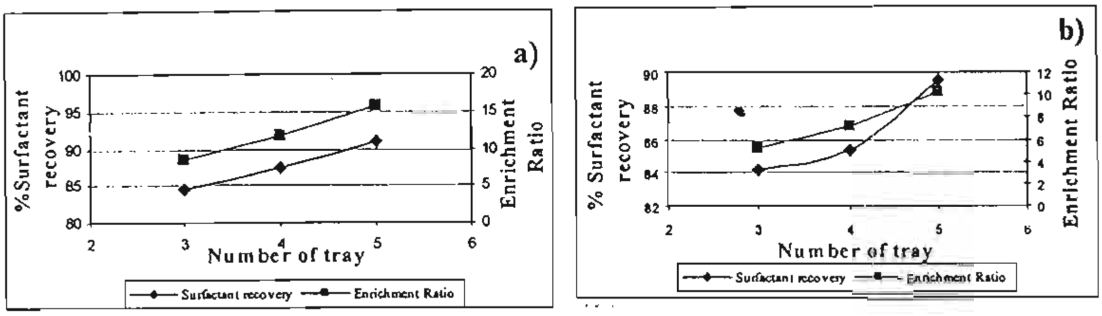
Conditions: [CPC] = 0.75 CMC; Air flow rate = 40 L/min; foam height = 30 cm and No. of tray = 5

Figure 9 Effects of feed flow rate on surfactant recovery and enrichment ratio a) 15 cm tray spacing b) 30 cm tray spacing



Conditions: Air flow rate =40 L/min; Feed flow rate = 50 ml/min; foam height = 30 cm and No. of tray =5

Figure 10 Effects of CPC concentration on surfactant recovery and enrichment ratio a) 15 cm tray spacing b) 30 cm tray spacing



Conditions: [CPC] = 0.5 CMC; Air flow rate =40 L/min; Feed flow rate = 50 ml/min and foam height = 60 cm

Figure 11 Effects of Number of tray on surfactant recovery and enrichment ratio
a) 15 cm tray spacing b) 30 cm tray spacing

CONCLUSIONS

The influence of the system parameters can be concluded as follows:

1. Increasing liquid feed flow rate results in both decreases in the enrichment ratio and % surfactant recovery.
2. An increase in air flow rate results in a reduction in the enrichment ratio but the surfactant recovery increases.
3. The efficiency of surfactant recovery does not change with increasing foam height but has more positive impact on the enrichment ratio.
4. The efficiency of surfactant recovery increases with surfactant feed liquid concentration but enrichment ratio decreases as feed liquid surfactant concentration increases.
5. With increasing number of trays both surfactant recovery and enrichment ratio are increased.

ACKNOWLEDGEMENTS

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PROGRAM & ABSTRACTS

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Separation of Carbon Black from Silica by Froth Flotation Technique as an Approach for Single-Walled Carbon Nanotubes Purification

On-line Number 884

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ABSTRACT

To produce single-walled carbon nanotubes (SWNT) by catalytic decomposition of carbon-containing molecules on silica support, as-prepared SWNT are grown on the surface of catalyst support. A very high purity of SWNT is required in various specific applications. Therefore, a purification step is considerably important in commercial production of SWNT. The conventional method for purifying SWNT is chemical treatment with acid or base. However, drawbacks of chemical treatment are toxicity, high cost, and the structural change of purified SWNT. To purify SWNT, froth flotation was focused as a better technique to separate SWNT from the spent catalysts. In this research, carbon black was used as model for investigation of effect of various parameters in froth flotation operation on purity and recovery of carbon. Nonionic surfactant was founded to be superior to ionic surfactants in the separation process between carbon and silica because both of silica and carbon are negatively charged. Effects of surfactant concentration, carbon loading, air flow rate, and foam height were investigated in this work.

KEYWORDS

froth flotation, purification, carbon nanotubes, surfactant

INTRODUCTION

Since single-walled carbon nanotubes were first discovered in 1993 (Ijima, et al., 1993, and Bethune, et al., 1993), they have captured attention from researchers worldwide because they exhibit many unique and exceptional physical and chemical properties that can be extended to several potential applications (Yakobson, et al., 1997).

In the present, SWNT are produced by 3 main methods: arc discharge (Bethune, et al., 1993), pulsed laser vaporization (Guo, et al., 1995), and catalytic decomposition of carbon-containing molecules (Kitiyanan, et al., 2000). Among these techniques, the catalytic method has been considered as a promising approach for large-scale production at a relatively low cost. However, in some processes that use silica as a catalytic support, it is difficult to separate as-prepared SWNT from the spent catalyst. Therefore, purification might be one of the important concerns that limit the scaling up to commercial scale. Currently, the conventional method to separate SWNT from silica support is chemical treatment by using concentrated HF or concentrated NaOH (Matarredona, et al., 2003). After that, membrane extraction is utilized to recover purified SWNT. However, both chemical treatment and membrane extraction display some negative impacts such as toxicity, high operating cost, and structural change of purified SWNT. Therefore, this work focused on applying froth flotation as an alternative separation process for SWNT purification.

Froth flotation is one of the surfactant based separation processes (Fuerstenau, et al., 1989) which is widely used in several applications. The schematic of froth flotation process is shown in Figure 1. In froth flotation operation, surfactant is added to the solution to promote the separation while air is sparged into the solution through sintered glass disk because air bubbles are used as a mean of separation in this technique (Zouboulis, et al., 1994). Hydrophobic particles such as SWNT could be carried by generated air bubbles to the top of the column. There are several advantages of flotation operation such as rapid operation, low space requirement, high removal efficiency, and low cost of operation (Choi, et al., 1996). Therefore, in this work, froth flotation was focused to separate SWNT from catalytic support because its advantage is superior to the conventional purification methods.

In fact, the as-prepared SWNT are grown on the surface of catalytic support, it needs some additional steps to break the interaction between SWNT and catalytic support before operated in froth flotation. In this study, the step of breaking the SWNT-support interaction has been neglected. To investigate the appropriate conditions in froth flotation operation for SWNT purification, physical blending between carbon black and silica was used as a model at the starting point of novel algorithm for SWNT purification.

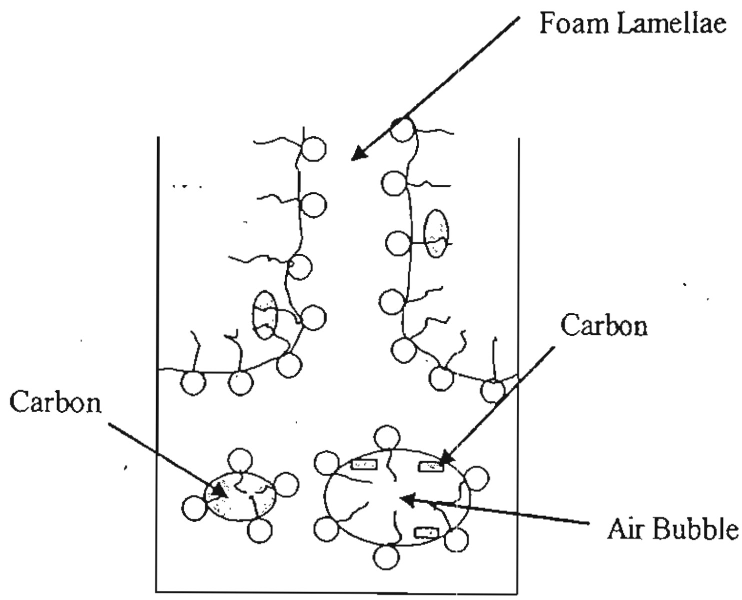

Figure 1. Schematic of the froth flotation process

MATERIALS AND METHODS

Carbon black type 400R having average particle size of 0.24 μm was supplied from Cabot Company. The as-received carbon black was rinsed with deionized water, centrifuged and dried to remove impurities before use. Surfonic L24-7, containing linear alcohol ethoxylate with seven-mole ethoxylate of linear, primary 12 – 14 carbon number alcohol, nonionic surfactant was obtained from Huntsman Company, USA. The surfactant was used as received. Deionized water was used in all experiments.

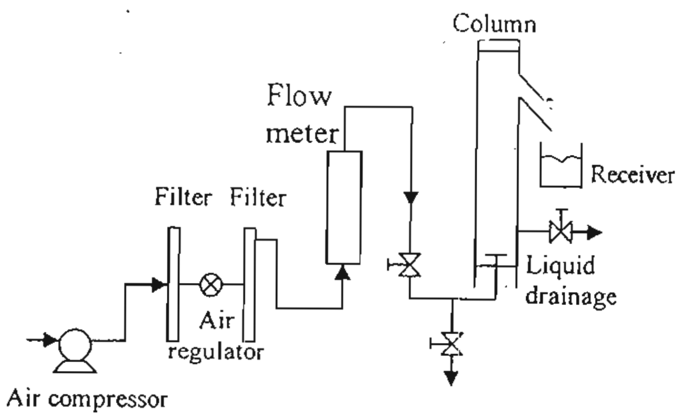

Figure 2. Schematic diagram of the froth flotation apparatus

The schematic diagram of flotation apparatus used in this work is shown in Figure 2. Flotation column is a glass column with 3.8 cm of inside diameter and 120 cm in length. Filtered air was introduced at the bottom of the column at constant flow rate of 200 mL/min through a sintered glass disk having pore size diameters about 16 – 40 μm. However, the air flow rate can be varied from 150 to 300 mL/min for investigation of the effect of air flow rate. The effects of surfactant concentrations ranging from 0.25 - 1 CMC (82.1 μM) were also observed. Foam was collected at the top of the column and then broken for analysis. All of flotation experiments were performed at room temperature (25-27° C). Deionized water was used to wash surfactant out of carbon-containing solid in the overhead froth. After that, the weight of the solid after dried in the oven at 110° C and after heated in the presence of air at 700° C was recorded and used to evaluate the purity and recovery of carbon black.

RESULTS AND DISCUSSION

To purify SWNT by using froth flotation technique, many parameters such as concentration of surfactant, and air flow rate should be first investigated. Since there are other additional parameters affecting the purification of the as-produced SWNT such as the interaction between SWNT and catalyst support, carbon black was utilized to represent SWNT after the interaction with the support is broken and to investigate the appropriate operating conditions in flotation column. In this research, purity of carbon is defined as a weight percentage of carbon on total solid (carbon and silica) in the overhead froth, while recovery is a weight percentage of carbon in the overhead froth on carbon in the initial feed.

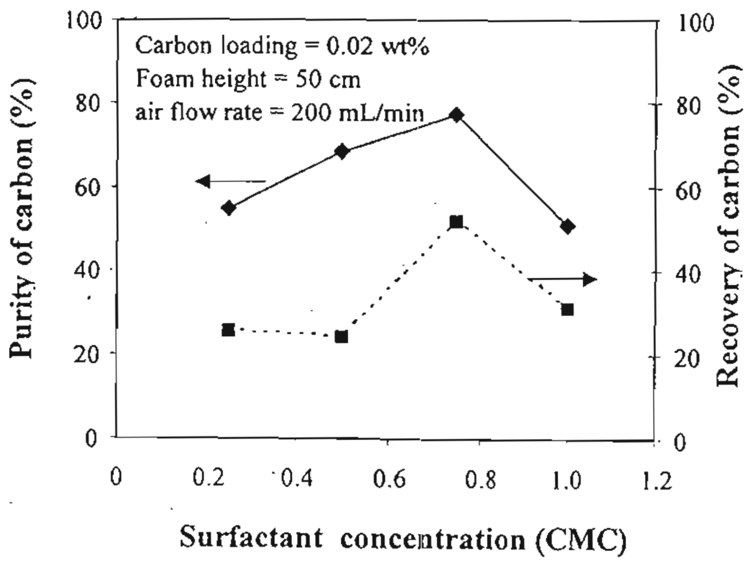

Figure 3. Effect of surfactant concentration on separation efficiency (1 CMC=82.1 μM)

Effect of surfactant concentration

Figure 3 depicts the purity and recovery of carbon as a function of surfactant concentration. At below CMC, as surfactant concentration increases, the separation efficiency increases due to more surfactant monomers adsorbed on the bubble surface as demonstrated in Figure 4. At a lower surfactant concentration, a small number of surfactant monomers adsorbed on bubble surface leads to lower solubilization power for co-adsorption of carbon on the air bubbles than that of a higher surfactant concentration. Therefore, the recovery of carbon is significantly dropped when

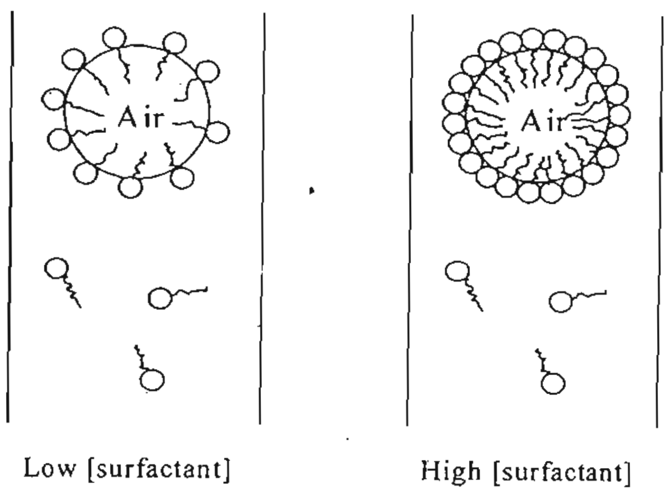

Figure 4. Schematic of froth flotation process at surfactant concentration below CMC

surfactant concentration is decreased. For the purity of carbon, at a low surfactant concentration, the steric effect from surfactant is also low. Hence, silica has higher possibility to be co-adsorbed on the bubble surface resulting in depressing the purity of carbon. However, increasing surfactant concentration beyond CMC descends both purity and recovery of carbon. This may be because micelles are formed in the solution leading to decreasing in a number of surfactant monomers on the air bubbles as demonstrated in Figure 5.

Effect of carbon loading

Figure 6 shows the effect of carbon loading on purity and recovery of carbon. From the result, the recovery of carbon decreases while the purity of carbon is almost constant, when carbon loading increases. In this investigation, surfactant concentration was kept constant to yield a constant surface concentration of surfactant on the bubbles. As a result, recovery of carbon decreases when more carbon is added into the solution.

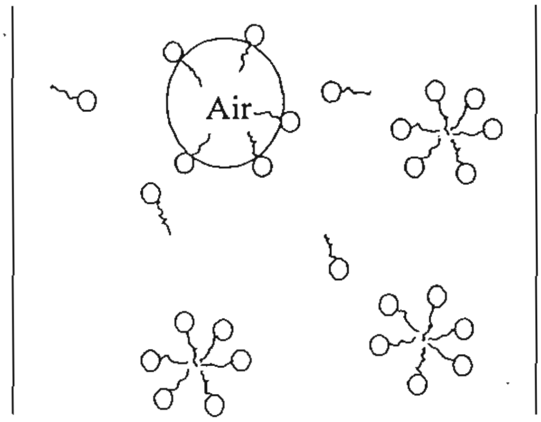

Figure 5. Schametic of froth flotation of CMC

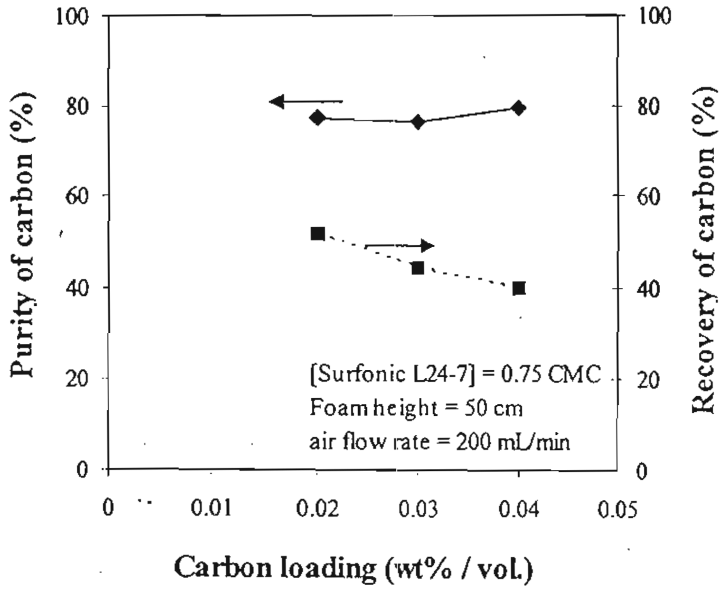

Figure 6. Effect of carbon loading on separation efficiency

Effect of air flow rate

The effects of air flow rate on purity and recovery of carbon are shown in Figure 7. Both purity and recovery decrease when air flow rate increases. Typically, the efficiency of the separation is expected to be improved when air flow rate increases due to more bubbles in the solution. However, as air flow rate increases, not only a number of bubbles passing through the solution, but also flow pattern in the column is altered. A very high air flow rate leads to severe circulation velocity in the solution; so some portion of carbon adsorbing on the bubble surface is dissolved back into the solution. Therefore, the lower the air flow rate, the better the separation efficiency is. However,

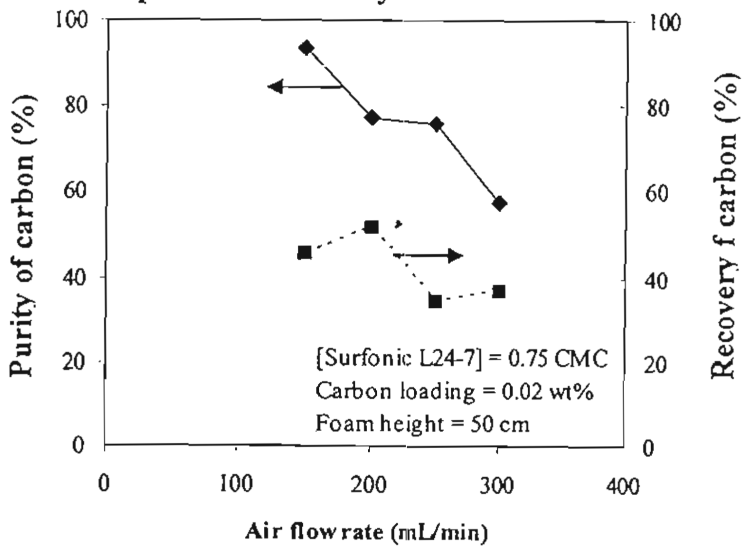

Figure 7. Effect of air flow rate on separation efficiency

in this study, air flow rate cannot be reduced to lower than 150 mL/min because no foam overflows from the column.

Effect of foam height

The separation efficiency as a function of foam height is shown in Figure 8. The purity of carbon increases from around 80 to 90% when foam height increases within the range of studied. As the foam height increases, foam has a longer retention time to stay in the froth zone before it overflows from the column. Hence, silica that has been carried to the foam lamellae is possible to be drained out of foam lamellae due to the gravitational force resulting in the improvement of purity. For the recovery of carbon, the maximum recovery was observed at a foam height of 50 cm. At a lower foam height, carbon has longer residence time to move from the bottom of the column to the froth zone because of the higher solution level. Therefore, some portion of carbon could be entrained back to the solution as a result of fluid circulation in the column. However, the recovery is decreased with further increasing foam height or decreasing solution height, because the residence time of carbon in the froth zone increases. Consequently, to achieve the maximum separation efficiency, foam height should be optimized.

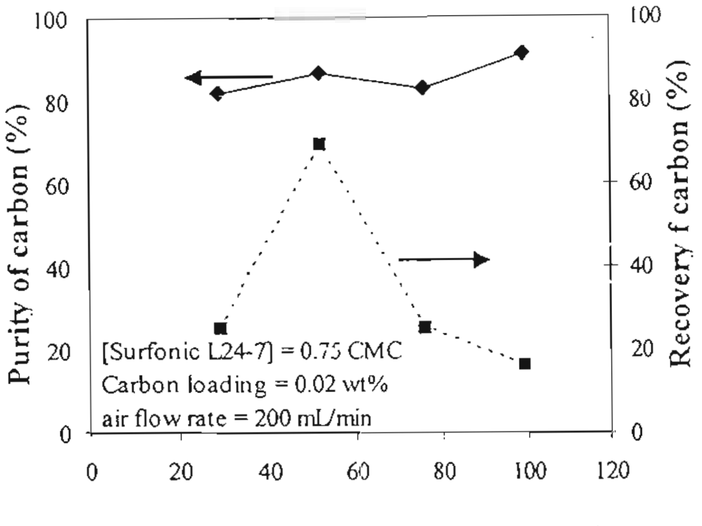

Figure 8. Effect of foam height on separation efficiency

CONCLUSIONS

In this study, the novel technique which is froth flotation operation for purification of single-walled carbon nanotubes was introduced. However, to focus only on the important parameters in froth flotation technique without effect of interaction between SWNT and catalytic support, carbon black which is physically blended with silica was used in this work as a model for purification. To achieve high separation efficiency, surfactant concentration should be lower than 1 CMC whereas a lower air flow rate yields a higher separation efficiency. Moreover, foam height should be optimized while carbon loading does not significantly affect the separation efficiency.

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Effect of Interfacial Tension and Foam Characteristics on Diesel Removal in Froth Flotation Operation

On-line Number 256

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ABSTRACT

Froth flotation is one of surfactant based separation processes which is suitable for dilute wastewater treatment. There are several advantages such as low space requirement, high removal efficiency, flexibility for various pollutants at different scales, and low cost. To achieve high performance for froth flotation, the combination of ultra-low interfacial tensions between oil and water and stable foam production must be achieved. To get the ultra-low interfacial tensions, Winsor type's III microemulsion or middle phase has to be formed. In this study, branched alcohol propoxylate sulfate sodium salt with 14 – 15 carbon and 4 PO groups (Alfoterra 145 – 4PO) was used to form microemulsion formation with diesel. The effects of surfactant concentration and NaCl concentration on phase study, foam characteristics, and performance of froth flotation operation were investigated in this work. An increase in surfactant concentration decreases interfacial tension (IFT), but increases foam stability. For the effect of NaCl concentration, the minimum IFT was achieved at 5 wt% NaCl. However, this optimum salinity cannot be operated in froth flotation experiment due to poor foam characteristics. Therefore, both IFT and foam characteristics should be optimized to achieve high efficiency of froth flotation.

KEYWORDS

Froth Flotation, ultra-low interfacial tension, Foam characteristics, Microemulsion with diesel

INTRODUCTION

In the presence, a number of vehicles have been increasing rapidly affecting the amount of fuel usage. Diesel comsumption seems is much higher than gasoline consumption. This may be because diesel provides more energy per unit volume than gasoline does (State Home Page, April 2004). In United State and Latin America, diesel is used primarily for the transportation of goods. However, In Europe, Japan, and elsewhere, diesel is a significant source of energy for personal transportation (UPO Home Page, April 2004). The demand for diesel is forecasted to grow faster than the demand for energy in general. Therefore, diesel has high possibility to contaminate in water by leakage from gas station or underground storage tank.

To remove diesel from water, froth flotation is focused in this work. Firstly, froth flotation was utilized to separate the desired ore from unwanted substrates in the mineral processing process (Yarar, 1997). However, nowadays, froth flotation technique is widely employed in wastewater treatment application (Nabih, et al., 2003 and Walcarius, et al., 2001), and also in paper deinking processes (Zhu, et al., 1998 and Moon, et al., 1998). There are 2 main types of froth flotation which are dissolved air flotation and induced air flotation. In this work, induced air flotation was focused. Filtered air is introduced into the solution through sintered glass disk. Air bubbles generated in the solution are keys for successful separation. Droplets of emulsified oil which have hydrophobic surfaces can co-adsorb at the bubble surfaces which are also hydrophobic and can rise to the froth zone (air/bubble interface) with air bubbles. However, the stability of these bubble-droplet aggregations is low since pure liquid cannot form foam (Rosen, 1989) leading to lower separation efficiency. To achieve higher separation efficiency, surfactant is added into the solution because surfactant can stabilize foam. Chang et al. (Chang, et al., 2000) reported that the surfactant concentration should be adjusted to maintain the foam stability.

To achieve high separation efficiency, a proper amount of surfactant added into the solution is needed. In previous work (Pondstabodee, et al., 1998), it was found that the maximum oil removal corresponds to the formation of Winsor Type III microemulsion. This seems to be starting point of our group to further investigate the relationship between froth flotation and Winsor Type III microemulsion. Therefore later, Chavadej *et al.* (2004) investigated the main source of oil removed from flotation column. They found that most oils removed from the column came from excess oil phase rather than middle phase in Winsor Type III microemulsion. After that, Yanatatsaneejit *et al.* (2004) hypothesized that the maximum oil removal was achieved because of the ultra-low interfacial tension characteristic in Winsor Type III microemulsion. However, they found that interfacial tension is not the sole factor affecting the performance of froth flotation, foam characteristics are also important on flotation efficiency. In this work, the performance of froth flotation to remove diesel from wastewater as function of interfacial tension and foam characteristics was investigated systematically.

MATERIALS AND METHODS

The model oil in this study was commercial grade of diesel obtained from The Petroleum Authority of Thailand (PTT). The studied surfactant was branched alcohol propoxylate sulfate sodium salt (Alfoterra 145-4PO) which is not yet commercially available. It is specially synthesized by Sasol Company (formerly Condea Vista Company), Rosebank, South Africa. Analytical purity grade sodium chloride (NaCl) from Aldrich Chemical Company Inc. was used as electrolyte in this work. All chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

To investigate the phase behavior of microemulsions, 5 mL of homogeneous aqueous solution, prepared at various surfactant concentrations and NaCl concentrations, was mixed with 5 mL of diesel in a vial sealed with a screw cap. The vials were shaken every day for 3 days, and then allowed to equilibrate at a constant temperature of 30°C in a water bath for 1 month to reach equilibrium, which was verified by the invariant height of each phase. The interfacial tensions between equilibrated excess oil and excess water phases were measured by a spinning drop tensiometer (SITE 04, Krüss GmbH, Hamburg).

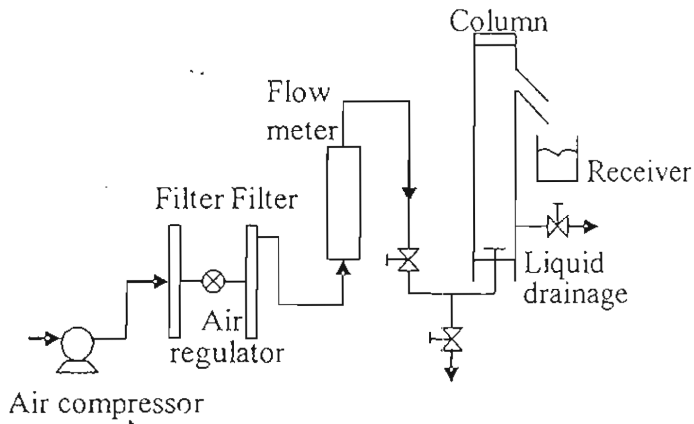

Figure 1. Schematic diagram of the froth flotation apparatus

A schematic diagram of the froth flotation unit used in this work is shown in Figure 1. A glass cylindrical column with 5 cm internal diameter and 120 cm height was used as the froth flotation column. A 750 mL sample with an initial oil:water ratio of 1:1 and various surfactant and NaCl concentrations which had been equilibrated at 30°C for 1 month in the incubator, was transferred to the froth flotation column. Filtered air at a flow rate of 300 mL/min was introduced at the bottom of the column through a sintered glass disk having pore size diameters about 16 – 40 μm. The generated air bubbles rose through the solution to the top of the column. The foam collected in the receiver over a period of time was broken by freezing for diesel concentration analysis. Moreover, the solution in the column was sampled at the same time interval as the foam collected for analysis of diesel and surfactant concentrations. All experiments were stopped when solution surfactant concentrations became too low that no more foam came overhead from the column.

In order to obtain a better understanding about the phenomena in the froth flotation process, foamability and foam stability experiments were conducted in the same flotation column. A 250 mL sample containing a given surfactant concentration and an oil to water ratio of 1:1 was transferred to the column. Filtered air was introduced at the bottom of the column through the solution at a constant flowrate of 100 mL/min until the maximum foam height in the column was achieved. The maximum foam height was then measured. Then the filtered air was stopped introducing to the column, and the time required for the foam volume to collapse to half of the maximum height was recorded to quantify foam stability. All experiments of froth flotation operation, foamability, and foam stability were conducted at a room temperature of about 25 – 27° C.

RESULTS AND DISCUSSION

In this study, wt% is based upon the aqueous system consisting of water, salt, and surfactant. The ratio of maximum foam height to initial solution height is considered as foamability while foam stability ($t_{1/2}$) is defined as the time required for the foam to collapse to half of the maximum height.

Phase behavior study

Interfacial tensions (IFT) is one of the major factors affecting the performance of froth flotation operation. To achieve high separation efficiency, a reduction of the system IFT is required. Figure 2 shows the effect of initial surfactant concentration on IFT value. At 3 wt% NaCl concentration, increasing Alfoterra 145 – 4PO concentration decreases IFT between oil and water because a number of micelles increases whereas IFT is vise versa (Huh, 1983). However, Alfoterra 145 – 4PO concentration cannot be increased to more than 0.15 wt% because macroemulsion is formed rather than microemulsion. As a result, the optimum surfactant concentration in a range of ultralow IFT (less than 10^{-2} mN/m) was not achieved.

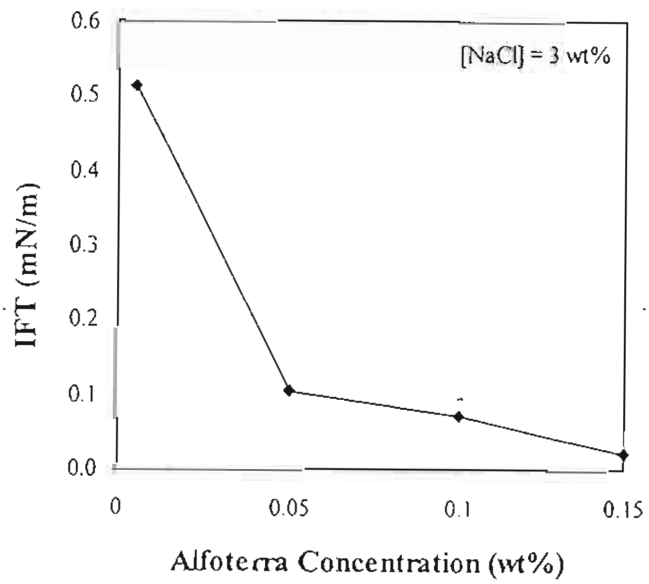

Figure 2. Effect of surfactant concentration on IFT

The Alfoterra 145 – 4PO concentration of 0.1 wt% was selected to elucidate the effect of NaCl concentration on IFT. As shown in Figure 3, the minimum IFT was achieved at 5 wt% NaCl. The explanation of the effect of NaCl concentration on IFT was already discussed in our previous work of ethylbenzene (Yanatatsaneejit, et al. 2004a).

Foam characteristics

As described in previous work (Yanatatsaneejit, et al. 2004a and Yanatatsaneejit, et al. 2004b), removal efficiency of oil in froth flotation operation is also influenced by foam characteristic (foam formation and foam stability). Therefore, the higher the foamability and the foam stability, the higher the oil removal should be obtained. Figure 4 shows the effects of Alfoterra 145 – 4PO concentration on foam stability and foamability. Foam stability tends to increase with increasing Alfoterra 145 – 4PO concentration because more surfactants adsorb at the surface of air bubbles. Therefore, the repulsive force between surfactants increases, and foam stability also increases. In addition, when Alfoterra 145 – 4PO concentration increases from 0.005 to 0.10 wt%, foamability increases. However, foamability decreases when the surfactant concentration further increases to 0.15 wt%. At low Alfoterra 145 – 4PO concentrations, formability increases with Alfoterra 145 – 4PO concentration because foam stability increases. However, when Alfoterra 145 – 4PO concentration further increases greater than 0.1%, a thicker foam lamellae is formed causing a higher water content in the foam. As a result, foamability decreases.

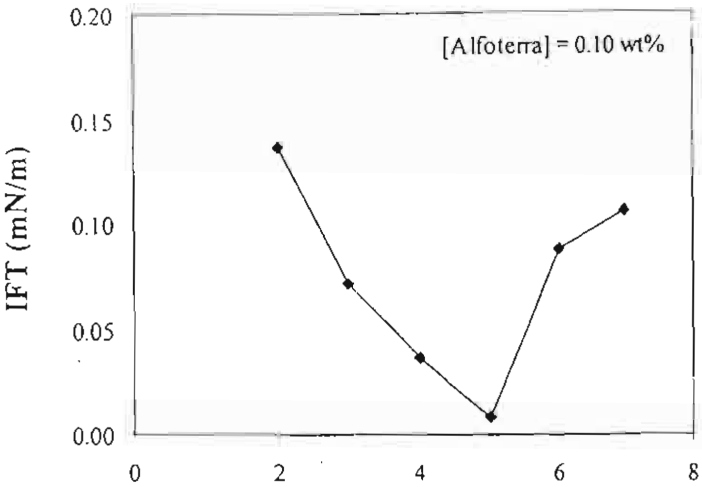

Figure 3. Effect of NaCl concentration on IFT

For the effect of NaCl concentration on foam characteristics, the descent of foam stability was observed when NaCl concentration increases as shown in Figure 5. This is because the negative charge of surfactant is neutralized by the positive charge of NaCl, causing decreasing repulsive force between head groups of surfactant. The distance between two bubbles becomes closer until the critical distance is reached resulting in coalescence of these bubbles. In case of foamability, it increases rapidly when NaCl concentration increases from 2 to 3 wt%. However, farther increasing NaCl concentration to 4 wt% substantially decreases foamability. Increasing NaCl concentration from 2 to 4 wt% causes lower interfacial tensions as in Figure 3. Therefore, at 3 wt% NaCl, the system needs less energy to form air bubbles within the liquid solution than 2 wt% NaCl does and so foams are easily formed in 3 wt% NaCl system as compared to those in 2 wt% NaCl system. However, even though the interfacial tensions of 4 wt% NaCl is much lower than that of 2 and 3 wt% NaCl, but foamability of 4

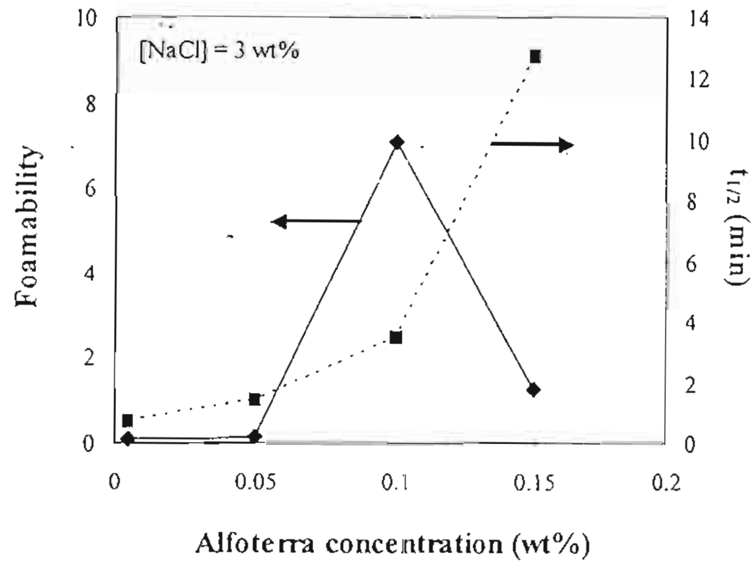

Figure 4. Effect of surfactant concentration on foamability and foam stability ($t_{1/2}$)

wt% NaCl is the lowest because foam stability of 4 wt% NaCl is the lowest. Consequently, to achieve high foamability, both of the interfacial tensions and foam stability have to be optimized.

Froth flotation

As shown in the previous work (Yanatatsaneejit, et al. 2004a), three parameters which are oil removal, surfactant removal, and enrichment ratio of oil are defined as the performance of froth flotation. Figure 6 shows the effect of Alfoterra concentration on IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability and foam stability. Similar to ethylbenzene system (Yanatatsaneejit, et al. 2004a), the total cumulative diesel removal is the highest at the Alfoterra concentration corresponding to the maximum foamability and foam stability but not the minimum IFT. The similar result of the Alfoterra removal was also found. This result implies that IFT is not the sole factor affecting performance of froth flotation. Actually, IFT should be reduced to the critical value to enhance the amount of oil attached with foam. However, for system having IFT lower than the critical value, the effect of foam characteristic on the performance of flotation is dominant.

IFT, total cumulative diesel removal, total cumulative Alfoterra removal, foamability, and foam stability as function of NaCl concentration are depicted in Figure 7. The maximum diesel and Alfoterra removals correspond to the highest foam stability. From Figure 7, the removal efficiencies of diesel and Alfoterra are not significantly affected by NaCl concentration in the range of 2 to 3 wt%. This is because the trade-off between foamability and foam stability. However, at NaCl concentration above 3 wt%, NaCl concentration substantially affects the removal efficiency since both foamability and foam stability are extremely low. From the effect of both Alfoterra concentration and NaCl concentration, foam characteristics and IFT seem to be principal parameters affecting the performance of froth flotation

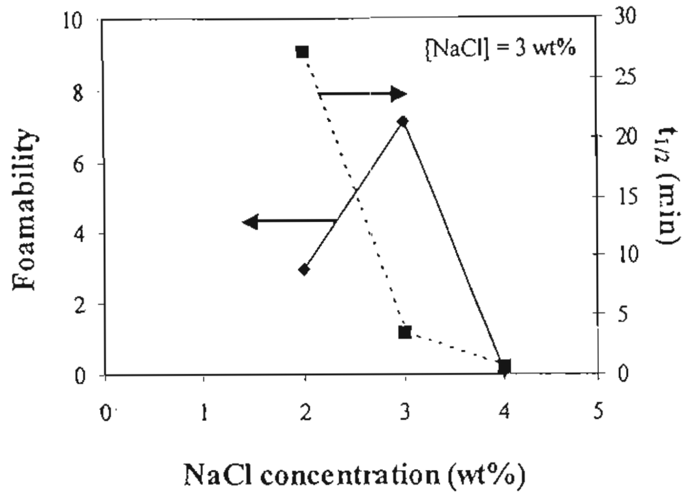

Figure 5. Effect of NaCl concentration on foamability and foam stability ($t_{1/2}$)

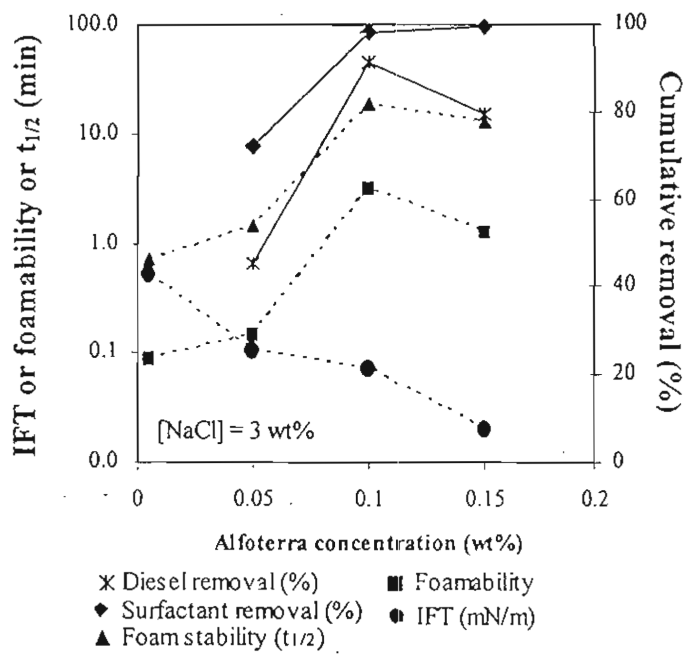

Figure 6. Effect of surfactant concentration on process parameters

CONCLUSIONS

In this study, the induced air flotation was investigated to remove diesel from wastewater. There are 3 parts of experiment in this work which are phase behavior, foam characteristics, and froth flotation operation. The effects of surfactant and NaCl concentrations on all 3 parts were studied. The optimum surfactant concentration was not achieved in this work because macroemulsion was formed at high surfactant concentrations. The highest diesel removal corresponds to the maximum foamability and foam stability but not the minimum IFT. Therefore, it can be concluded that in froth flotation operation, IFT is not the sole factor to obtain good separation efficiency but foam characteristic have to be taken into consideration in froth flotation operation.

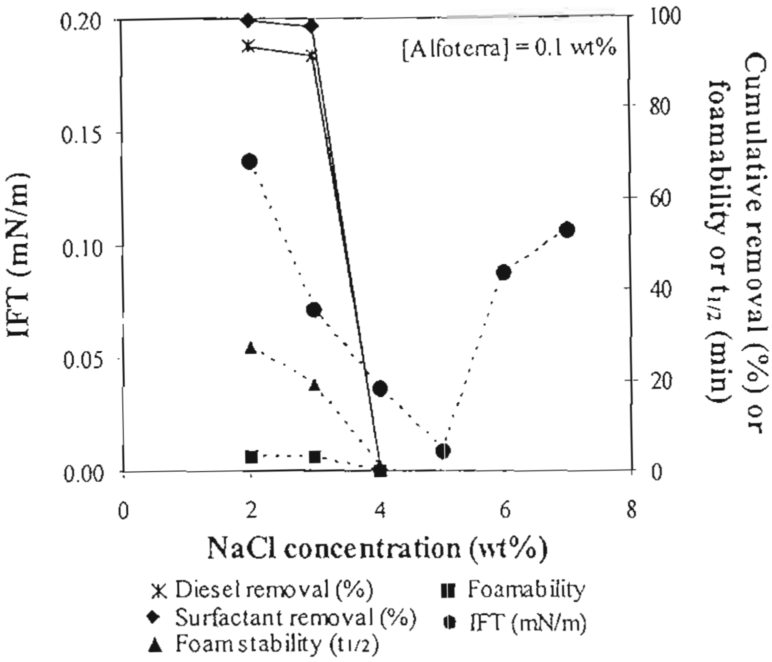

Figure 7. Effect of NaCl concentration on process parameters

ACKNOWLEDGEMENTS

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PIM-1

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BIOMASS ENERGY

TECHNICAL PROGRAM IN BRIEF

	Monday August 18, 2003	Tuesday August 19, 2003	Wednesday August 20, 2003	Thursday August 21, 2003
REGISTRATION	Foyer A 8:30-9:30			
(OWR)	Room A 9:30-10:00			
Plenary	Room A 10:00-10:40			
Workshop-I	Room A 11:00-17:40			
BioTech-I	Room B 11:00-12:40			
Separation-I	Room B 14:00-15:40			
BioTis	Room B 16:00-17:40			
BioTech-II		Room A 9:00-10:10		
Keynote		Room A 10:10-10:40		
Separation-II		Room B 9:00-10:40		
Microreactors-I		Room A 11:00-12:40		
Env. Tech.-I		Room B 11:00-12:40		
Energy-I		Room A 14:00-15:40		
Workshop-II		Room B 14:00-17:30		
Energy-II		Room A 16:00-17:40		
Microreactors-II			Room A 9:00-10:40	
Particle Tech.			Room B 9:00-10:40	
Chemical Reactor-I			Room A 11:00-12:40	
Env. Tech.-II			Room B 11:00-12:40	
Chemical Reactor-II			Room A 14:00-15:40	
Env. Tech.-III			Room B 14:00-15:40	
Catalysis			Room A 16:00-17:40	
Env. Tech.-IV			Room B 16:00-17:40	
Open Forum- Discussion			Room A 17:40-18:30	
Chemical Reactor-III				Room B 9:00-10:40
Uni. Lab Visit - Closing				University 11:00-12:40
Ref. Break (Morning)	10:40 – 11:00	10:40 – 11:00	10:40 – 11:00	10:40 – 11:00
Ref. Break (Afternoon)	15:40 – 16:00	15:40 – 16:00	15:40 – 16:00	
Lunches	12:40 - 14:00	12:40 - 14:00	12:40 - 14:00	
Welcoming Reception	19:30 - 22.30			
Symposium Banquet		19:30 – 22.30		

PROCESS INTENSIFICATION OF WASTEWATER TREATMENT THROUGH SECONDARY BIOMASS FILTRATION, Trond E. Bustnes, C. F. Kaminski and M. R. Mackley, University of Cambridge, UK (on page 68)

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p-AZO-SUBSTITUTED CALIX[4]ARENES AS "PROTON-SWITCHABLE" EXTRACTANTS FOR DICHROMATE ANIONS, Hasalettin Deligöz, Mine Sulak Ak, Mustafa Tabakci and Mustafa Yılmaz, Pamukkale University, Turkey, Selçuk University, Turkey (on page 70)

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Chair:

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BIOSURFACTANT ENHANCED TREATMENT OF SOILS CONTAMINATED BY PETROLEUM OILS USING STIRRED TANK REACTORS, Kingsley Urum, and Turgay Pekdemir, Heriot-Watt University, UK (on page 76)

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LIGHT OIL REMOVAL FROM WASTEWATER BY MIDDLE PHASE MICROEMULSION AND FROTH FLOTATION, A. Witthayapanyanon, U. Yanatatsaneejit, J. F. Scamehorn, and S. Chavadej, Chulalongkorn University, Thailand, University of Oklahoma, USA (on page 78)