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Explore the Impact of Surfactant Type on the Stability and Separation Efficiency of Oil-Water Emulsions of Real Wastewater from Al-Basrah Crude Oil Using Microbubble Air Flotation

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ABSTRACT

Among several separation processes, the air flotation distinguish as remarkably high potential separation process related to its high separation efficiency and throughput, energy-efficient, simple process, cost-effective, applicable to a wide range of oily wastewater and no by-products. The current study aimed to investigate the effect of the type and concentration of surfactant on the stability of oil-water emulsion and efficiency of the separation process. For this purpose, three types of surfactant where used (anionic SDS, mixed nonionic Span 85/Tween 80, and cationic CTAB). The results demonstrated that the Span 85/Tween 80 surfactant has the best stability, and it increases with the surfactant concentration augmentation. The removal efficiency with CTAB surfactant reached to approximately 95% at concentration of 0.3%, and decreased by increasing the surfactant concentration. The mean diameter of bubbles generated in emulsion with CTAB surfactant was 71 µm, which was lower than that obtained with the other two surfactants.

Keywords: surfactant, microbubble, oil-water, emulsion, flotation.

INTRODUCTION

The removal of oil from wastewater is widely recognized as a significant challenge in the treatment procedure. The removal of oil from wastewater is recognized to be a major challenge in the treatment process. The oil phase in the wastewater often comprises many types, such as free floating oil, Dispersed oil, emulsified oil and dissolved oil, which depends mainly on oil drop size and stability (Rocha e Silva et al., 2018). Mechanical treatment processes such as centrifuging, gravity settling, or others can rapidly separate the free oil. Also Adsorption or biological treatments have been adopted for separate the dissolved oil (Han and Kang, 2017). On the other hands, a significant portion of the oil is typically found in the emulsified phase, which is formed as a result of steric interaction or structural barriers, and electrostatic repulsion between oil droplets, and it is difficult to be separated by traditional treatments methods (Pérez-Calderón, Santos and Zaritzky, 2018; Xu et al., 2017). The substantial environmental risks and difficulties in managing emulsified oil wastewater, it's crucial to handle this type of wastewater carefully, efficiently, and economically prior to discharge into the water source. Several methods have been proposed for the remediation of the mater-oil emulsion such as microfiltration (Faiq Al-Alawy and Jabbar Madlool, 2014), member separation process (Alkarbouly and Waisi, 2022), coagulation/flocculation (Salih, Al-Alawy and Ahmed, 2021), Microwave technology (A.M. Mohammed and K. Salih, 2014), and other hybrid technology like magnetic nanoparticles (Jawad and Al-Alawy, 2020). Air flotation is a wildly employed as cost-effective separation technology for several applications such as wastewater treatment, fermentation, plastic recycling, etc. (Ogunbiyi and Liu, 2023; Rao et al., 2023; Chen et al., 2023). The flotation process is basically relied on air bubbles are employed to capture the particles that their surfaces have varying degree of hydrophobicity and hydrophilicity.

The hydrophobic molecules are pick up by the air bubbles and transport to the liquid surface, thereby a foaming layer is developed which can be removed easily, while hydrophilic particles can be discharged from the bottom as a waste. The effectiveness of the flotation technique is controlled by the likelihood of a particle-bubble collision, particle-bubble attachment, and particle-bubble detachment (Kumar and Selvam, 2018; Prakash, Majumder and Singh, 2018)

Usually, surfactants or functional molecules in a certain concentration are added in the flotation operation in order to enhance the emulsion stability and the process performance (Mohammed and Fadhil, 2015). The word "surfactant" is a contraction of the three words "surface active agents". They are amphiphilic molecules that contain both a polar (hydrophilic) (water-loving) head and a non-polar (hydrophobic) (water-hating) R-C chain. The hydrophobic tail is directed towards the organic phase and the hydrophilic head is directed towards the aqueous phase. By placing itself in this direction at the interface, the surfactant affords an expanding force against the natural tension between the continuous phase and the dispersed phase, which results in a reduction of the interfacial tension. Reducing the interface tension reduces the free energy linked with the interface and increases the chances of the continuous and dispersed phase remaining emulsified (Tadros, 2016). However, in addition to lowering interfacial tension, surfactants may also possibly increase the interfacial viscosity, resulting in a mechanical resistance to coalescence. It will also generate an electrostatic repulsive force between each molecule of the surfactant and minimize the chances of flocculation. Thus, the combination of these effects will ultimately stabilize the emulsion (Zembyla, Murray and Sarkar, 2020; Dziza et al., 2020). Surfactants are categorized into four types depending on the ionic nature of the head group (Belhaj et al., 2020; Yang and Pal, 2020; Mozaffari, 2015; Dziza et al., 2020). The anionic surfactants carry a negative charge on their hydrophilic heads, offering a peculiar capacity to adhere to positively charged particles, like dirt and oil, to raise and suspend these particles in a micelle-like structure. Contrarily, cationic surfactants have a positive charge on their hydrophilic head groups, makes them suitable for anti-static products, including hair conditioners and fabric softeners. Acidic solutions are favored for most formulations involving cationic surfactants as these retain the positive charge on the cationic structure. Nonionic surfactant is a kind of surfactant that has no charge on its hydrophilic head group and, as a result, is milder in nature. Due to the mildness of nonionic surfactants, they are widely used in the home, cosmetics, and personal care markets, and in the agrochemical industry. In addition, the absence of charge contributes to nonionic's ability to quickly emulsify oils, rendering them a major player in the elimination of grease and oil from dirty surfaces. However, for Zwitterionic (amphoteric) surfactants, the polar head-group has both a positive and a negative charge, rendering the total net charge zero. Amphoteric surfactants generally show poor toxicity, low eye and skin inflammation, tolerance to hard water, and excellent foaming and compliance with other surfactants. They act differently according to the pH of the final formulation(Anestopoulos et al., 2020; Belhaj et al., 2020). The current study dedicated to evaluate the impact of the surfactant type and concentration on the stability of Al- Basrah crude oil and the de-emulsification efficiency of oil-water (O/W) emulsion by microbubbles air flotation. For that purpose, three types of surfactants were chosen, SDS-Sodium dodecyl sulfate as an ionic surfactant, CTAB-Cetyltrimethyl ammonium bromide as a cationic surfactant, and mixed of Span 85/Tween 80 as a non-ionic surfactant.

MATERIALS AND METHODS

Crude oil sample

To accomplish the objective of this study, a light crude oil sample was supplied by Al- Basrah refinery in Iraq. The physical properties of the crude oil sample are documented in Table 1.

Surfactants

Four types of surfactants were utilized in preparing the oil emulsions in this study, specifically, Span

Table 1. Physical properties of Al- Basrah crude oil

API	28.4
Sp. Gr	0.8849 (at 15.6 °C)
Viscosity (Cst) at 26.7 °C	19.4
Salt content (ppm)	0.0006
Water and sediment content (vol. %)	0.05
Asphaltene (wt. %)	2.22
Sulfur content (wt. %)	3.43
Nickel content (ppm)	4.04
Vanadium content (ppm)	2.76

85 (Fluka AG, USA), Tween 80 (Alpha Chemika, India), Sodium dodecyl sulfate (SDS) (Sigma Aldrich, Germany), Cetyltrimethylammonium bromide (CTAB) (Interchimiques SA, France).

Experimental setup and procedure

The experiments were accomplished with 40 L cylindrical column (100 cm in height and 20 cm in diameter) and five equally spaced holes were outfitted along the column to withdrawn the samples. The main source of air was an air compressor which supplied constant air flow rate of 0.5 L/min, and the air microbubbles were provided with microbubble diffuser (MBD) which has an average pores size less than 20 µm fitted in the bottom of the column. The crude oil concentration of the emulsions was kept constant, i.e. 200 ppm with pH of 7 and this emulsion was introduced into the flotation column from the top and the liquid height was kept at 50 cm. Figure 1 shows the setup of the Microbubble air flotation system and the other conditions namely temperature of 25±1 °C, mixing speed of 10000 rpm, air pressure at 1 bar, and duration of 10 min were maintained constant in all experiments. The time of flotation was 250 min and before each experiment, an initial sample of O/W emulsion was taken and other samples were withdrawn along the experiment and they were instantly analyzed with TD-500D UV-fluorescence analyzer to detect the oil concentration. The oil removal efficiency is calculated by Eq. (1) (Al-Dulaimi and Al-Yaqoobi, 2021).

$$Oil\ Removal\ \%\ (R_{oil}\%) = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

where: C_o and C_f are the initial and final oil concentration in ppm, respectively.

To test the emulsion stability, the emulsion sample was kept into 0.5 L glass beaker to settle under gravity at room temperature. The oil removal percentage with respect to experimental time was monitored to evaluate the stability of the emulsion.

RESULT AND DISCUSSION

Effect of surfactant type and concentration on O/W emulsion stability

The outcomes of O/W emulsion stability tests for each of the three surfactants (anionic SDS, mixed nonionic Span 85/Tween 80, and cationic CTAB) are demonstrated in Figures 2, 3, and 4 by plotting the emulsion stability against time where the concentration of all surfactants varied from 0.3 to 5 wt.%. The results demonstrated that all emulsions exhibited excellent stability for up to 24 hours. With time, stability began to

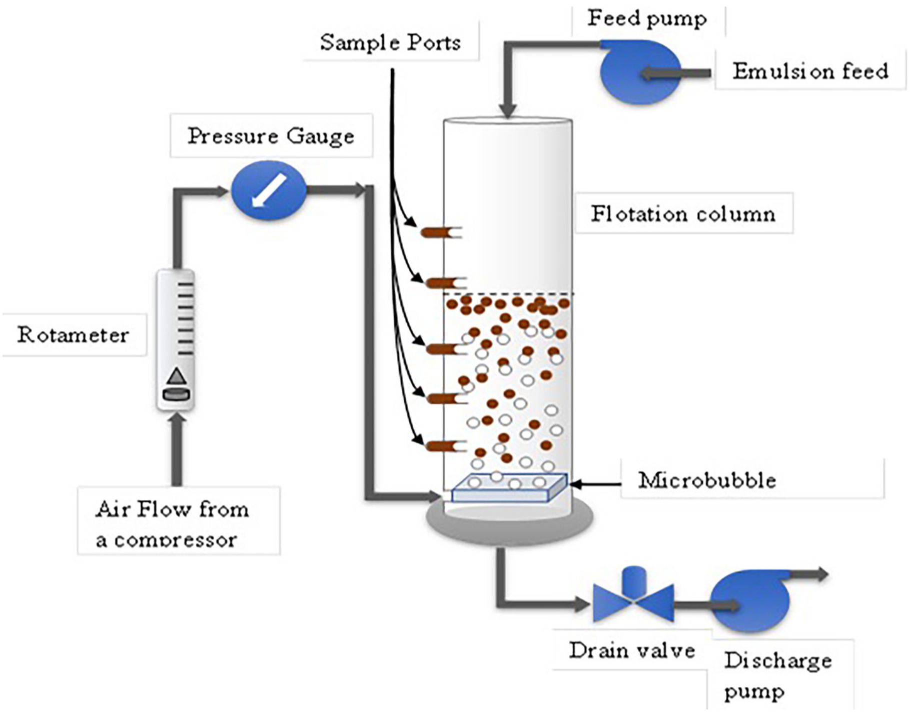

Figure 1. The microbubble air flotation scheme

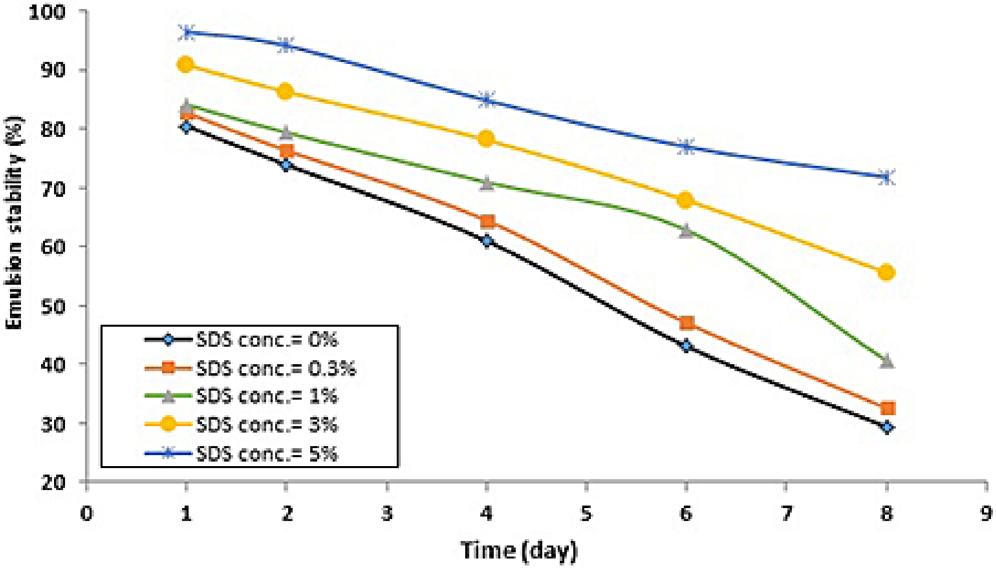

Figure 2. The effect of anionic surfactant (SDS) concentration on stability of crude O/W emulsion

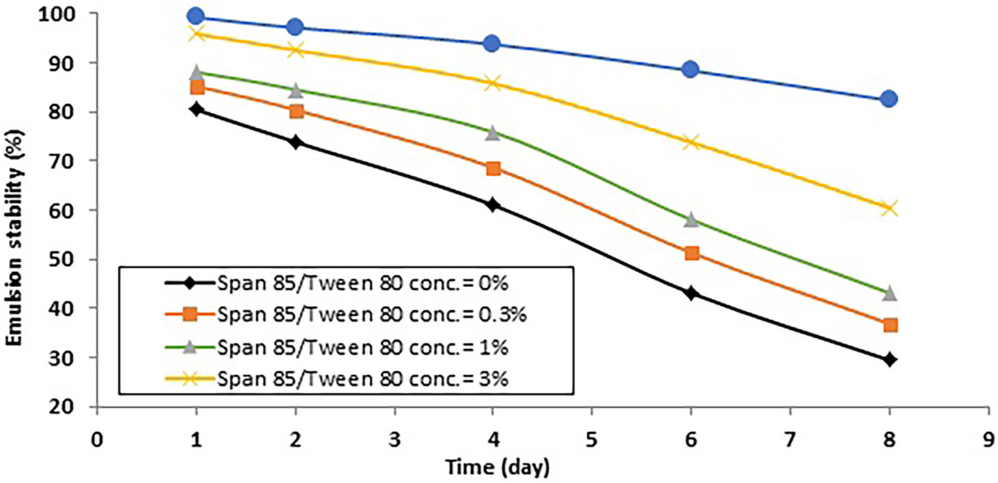

Figure 3. The effect of mixed surfactants (Span 85/Tween 80) concentration on stability of crude O/W emulsion

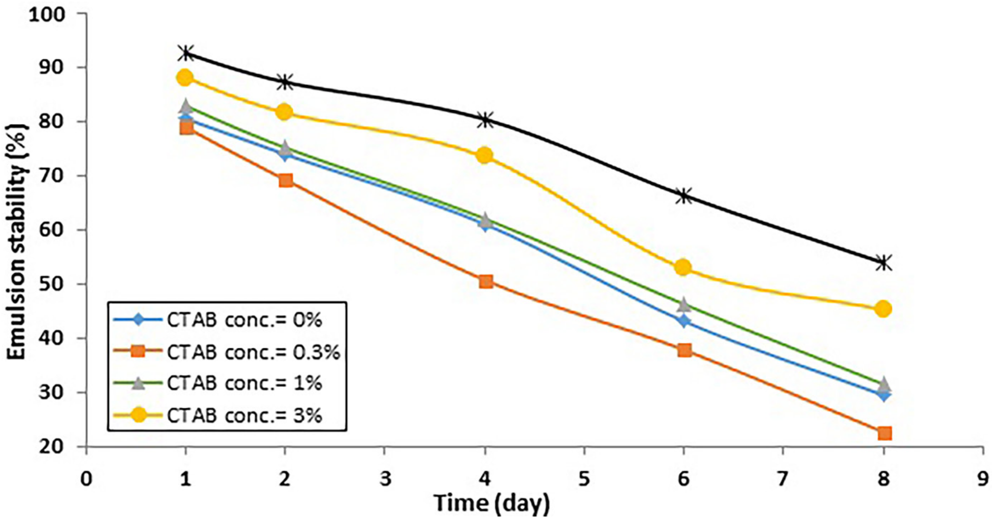

Figure 4. The effect of cationic surfactant (CTAB) concentration on stability of crude O/W emulsion

decline because of the coalescence of dispersed droplets.The stability of emulsion varies with different surfactants, formulations and emulsification methods. With SDS surfactant, the stability achieved 96.5% at concentration of 5% and 84.15% at concentration of 1% after one day, and the stability decline dramatically to 71.8% for concentration of 5% and 40.7% for concentration of 1% after eight days as in Figure 2. Similar results was obtained for the mixed surfactants of Span 85/Tween 80 as shown in Figure 3, where the stability at concentration of 5% was 99.3% and 88.15% for concentration of 1% after one day, and its reduced to 82.3% at concentration of 5% and 43.15% for concentration of 1% after eight days. Using CTAB as surfactant showed an analogous response to that observed with both of other used surfactant as shown in Figure 4. The trend obtained in the current research comes similar with that obtained by other researchers (Saad et al., 2019; Lv et al., 2014; M.S et al., 2014).

Increasing the quantity of surfactant leads to a lower ripening rate and enhanced emulsion stability. Also it induces the number of surfactant molecules to adsorb at the O/W interface and preventing the droplets from coalescing (Kumar and Mahto, 2017). Increasing emulsion levels increases the amount of the barrier between the two phases and encourages a good distribution of oil droplets (the dispersed phase) in the water (the continuous phase). Ultimately, decision about the surfactant concentration should be taken based on the cost of the surfactant and the process's economy. On the other hand, it is noted that the emulsion with the mixed non-ionic Span 85/Tween 80 surfactant had the best stability, followed by the emulsion containing anionic SDS surfactant, whereas the emulsion with CTAB from the cationic group had the least stability when compared to the other groups as illustrated in Figure 5. Non-ionic emulsifiers can transmit the interactive particles using the steric stabilization mechanism, while anionic emulsifiers can provide a repulsive force between equally charged electric double layers to the particles (Dobrowolska and Koper, 2014). The thin film droplet was well covered with non-ionic surfactant to give the emulsion less time to coalesce. A non-ionic surfactant agent like Span 85 and Tween 80 is therefore appropriate for use as an O/W stabilizer, and it is generally implying a good selection as emulsifiers, where the salinity of water does not affect them. In addition, they are inexpensive, commercially available and do not alter the oil properties.

Effect of surfactant type and concentration on oil removal efficiency

A range of anionic, nonionic, and cationic surfactants were used, including sodium dodecyl sulfate (SDS), mixed Span 85/Tween 80, and cetyltrimethyl ammonium bromide (CTAB), respectively, to investigate the effect of surfactants on oil removal efficiency by microbubble flotation, and the consequent air bubble size generated, and the doses of the surfactants were 0, 0.3, 1, 3, 5 wt.%.

Firstly, laboratory flotation trials were conducted to investigate the influence of surfactant concentration on oil removal efficiency. The experimental results of the study are seen in Figures 6, 7, and 8 by plotting (R_{oil}%) versus flotation period at various surfactant doses. It is obvious

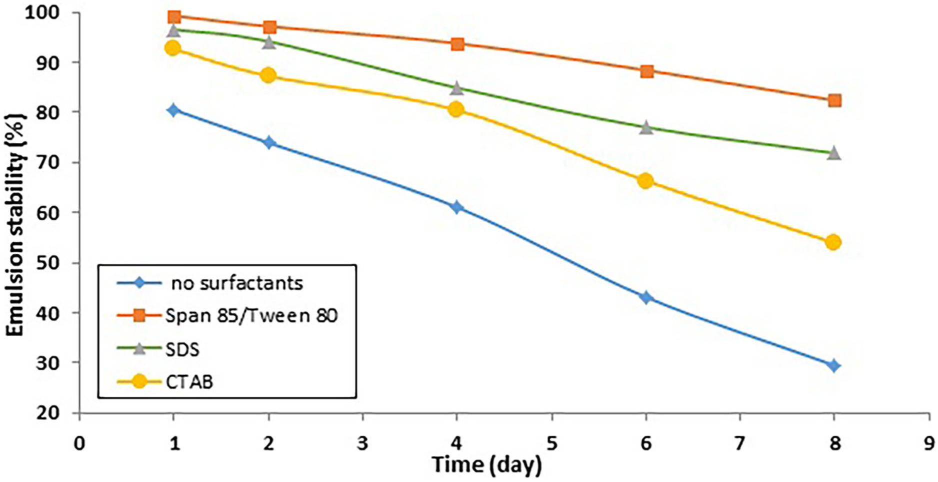

Figure 5. The effect of surfactant type on stability of crude O/W emulsion, as a function of time

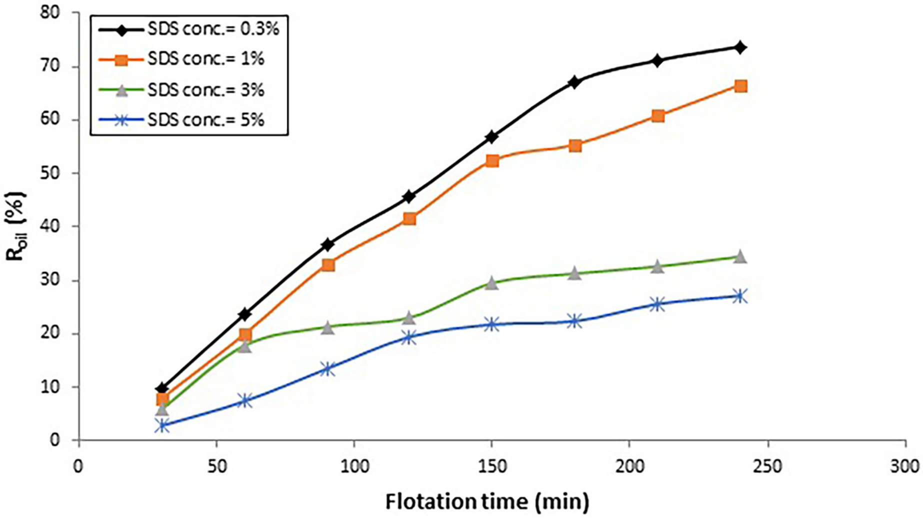

Figure 6. The effect of adding anionic surfactant (SDS) on the oil removal efficiency

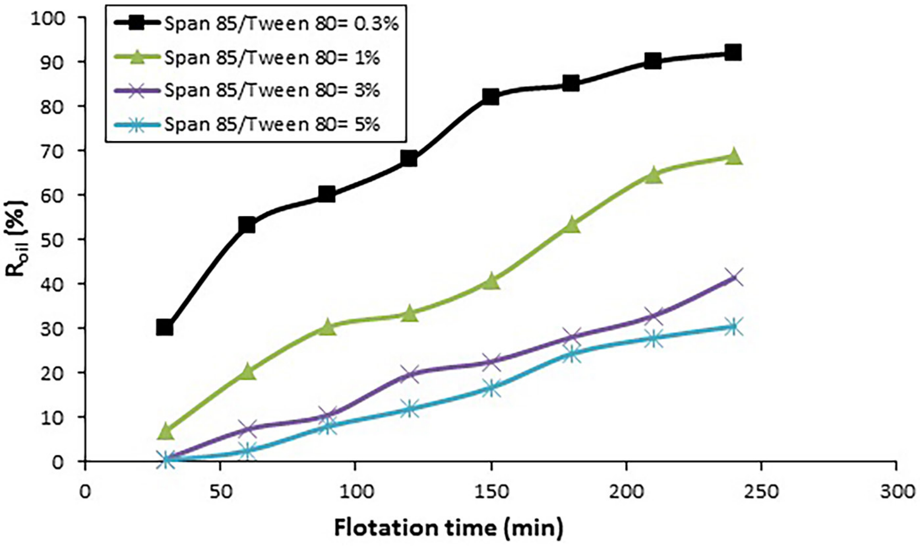

Figure 7. The effect of adding mixed non-ionic surfactant (Span 85/Tween 80) on the oil removal efficiency

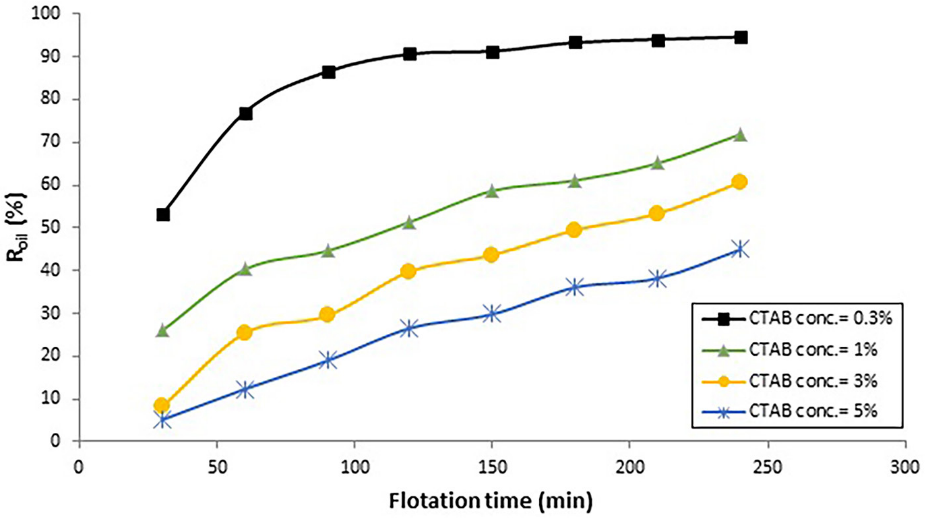

Figure 8. The effect of adding cationic surfactant (CTAB) on the oil removal efficiency

from these graphs that regardless of the type of surfactant used, raising the surfactant concentration from 0.3 wt.% to 5 wt.% reduces oil removal efficiency. It can be observed from Figure 6 that, when SDS surfactant is used, the removal efficiency decreased from 73.3% at surfactant concentration of 0.3% to 27.3% at concentration of 5% during 240 min of treatments. Comparable trends were obtained when Span 85/Tween 80 and CTAB surfactants were used as can be noticed from Figures 7 and 8. This outcome corroborated the findings of other previous studies (Majumder and Kumar, 2016). The results may be contributed to fact that the presence of surfactant affects the emulsion's stability. Increasing surfactant concentrations result in emulsions that are very stable, due to tightly binding of surfactant particles with the oil-liquid interfaces, which causes a reduced coalescence of oil droplets, and hence poor removal efficiency. In contrast, emulsion is less dense and stable at a reduced surfactant concentration, which enables for greater separation efficiency. A further justification of the high oil drop removal efficiency observed at low surfactant concentration is the generation of big flocs (oil droplets and surfactants) (Al-Dulaimi and Al-Yaqoobi, 2021). Besides the increased collision possibility they provide, big flocs are an excellent means of transportation and can act as a collision and trap carrier for nearby flocs in the liquid. Furthermore, the negative correlation of the size of the oil droplet to surfactant quantity could be the most effective parameter behind this response. Since oil droplets are comparatively small at high surfactant concentrations, the possibility of collision between oil drops and air bubbles is minimized (Arafat, 2014). In addition to their low buoyancy, which maintains them deflected when approaching an ascending bubble, finer oil droplets have a lower rise velocity and longer retention durations, all of which are significant factors in their removal from a liquid medium. A further potential reason for this result is the possibility of bubbles being attached to the oil droplets, either by point contact or by spreading all over the surface of the bubble. The point contact attachment mechanism is ineffective and mostly results in oil-bubble separation throughout aggregate ascension. In return, the spreading attachment mechanism is much more effective. However, its effectiveness depends upon the size of oil droplets. Bigger oil droplets in relation to air bubbles spread in a more uniformly way over a broader area on the bubble surfaces during collisions with bubbles, which create a fairly strong attachment to the bubbles. On the other hand, tiny oil droplets spread less over the surface of the bubble according to their small size, smoothness and low spreading rate (Yan et al., 2020; Wang et al., 2023).

The results illustrated in Figure 9 demonstrated the impact of surfactant type on oil removal efficiency by comparing the three surfactants. The R_{oil}% where plotted versus surfactant concentration at different types of surfactant. It can be concluded from this graph, that the oil could be separated efficiently with the cationic surfactant, but less with the anionic and non-ionic surfactants.

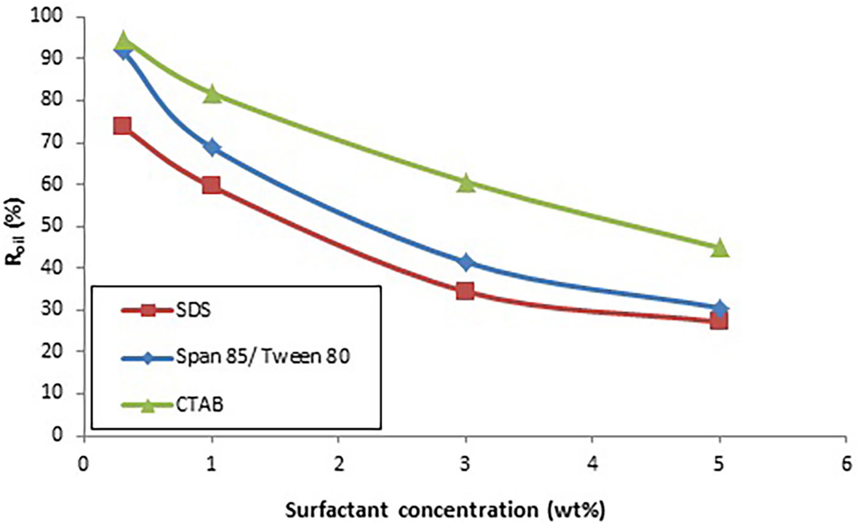

Figure 9. The effect of surfactant type on the oil removal efficiency, as a function of surfactant concentration

The removal efficiency with CTAB surfactant reached to approximately 95% for concentration of 0.3%, and it is decreased by increasing the surfactant concentration until it hit value of 44.9% at concentration of 5%. With nonionic Span 85/Tween 80 surfactants, the removal efficiency was about 90% at concentration of 3%, and it receded to about 30% at concentration of 5%. Finally, the efficiency was dramatically tumbled to 73.3% at concentration of 0.3% when anionic SDS surfactant was utilized, and the efficiency recorded its lowest value of 27% at concentration of 5%. This results may be attributed to the fact that the form and dosage of surfactant has a major influence on interactions between oil drops and gas bubbles, most likely by altering surface charge (Zeta potential) and interacting surfaces' hydrophobicity (Basařová and Zedníková, 2019).

The impact of anionic SDS, nonionic Span 85/Tween 80, and cationic CTAB surfactants on the oil droplet's surface charge at various concentrations was thereby investigated, and the results are presented in Figure 10. When an oil droplet is put into contact with aqueous solutions, it gains an electrical surface charge. In the absence of any surface active chemicals, the surfaces of the majority of petroleum oil droplets have been stated to be highly negatively charged (Poh et al., 2014) and, as a consequence, the negatively charged oil drops were unable to adhere to the anionic (SDS) surfactant molecules which also carry a negative charge. Alternatively, the oil drops could be solubilized in the SDS micelles, as other researchers have found (Lee et al., 2014). The surface of emulsion drops stabilized by SDS may be more negatively charged compared to nonionic Span 85/Tween 80. The zeta potential was about -33 mV at concentration of 1% for Span 85/Tween 80, and it reduced to about -59.5 mV at concentration of 5%, while it recorded a value of -67.9 mV at concentration of 1% with SDS surfactant and it reduced slightly to -70.2 mV at concentration of 5%. Consequently, limiting the number of effective collisions with the bubbles due to electrostatic repulsive forces.

However, it has been well recognized that in the absence of surfactants the air microbubbles in distilled-deionized water have a very strong negative surface charge at neutral pH values (Satpute and Earthman, 2021). During the industrial floatation process, if the particles required to attach a floating gas bubble are also negatively charged, the usage of anionic emulsifiers would be unfavorable to the floatation method due to the electrostatic repulsive force among the particles and gas bubbles.

Oil drops were highly attracted to the cationic surfactant (CTAB). It bears a positive residual burden. Thus, CTAB is capable of reducing the negative charge density on the oil droplet surface and as well as changing the charge polarity from negative to positive. The surface charge of the oil droplet rose (tended to be positive) as a result of the CTAB inclusion, achieving a positive value of 22.24 mV at a CTAB concentration of 1 wt.% and 55.32 mV at a CTAB concentration of 5 wt%.

In addition, CTAB can also be adsorbed on the oil droplets to form macro-flocs. After the CTAB was blended with the emulsions, many

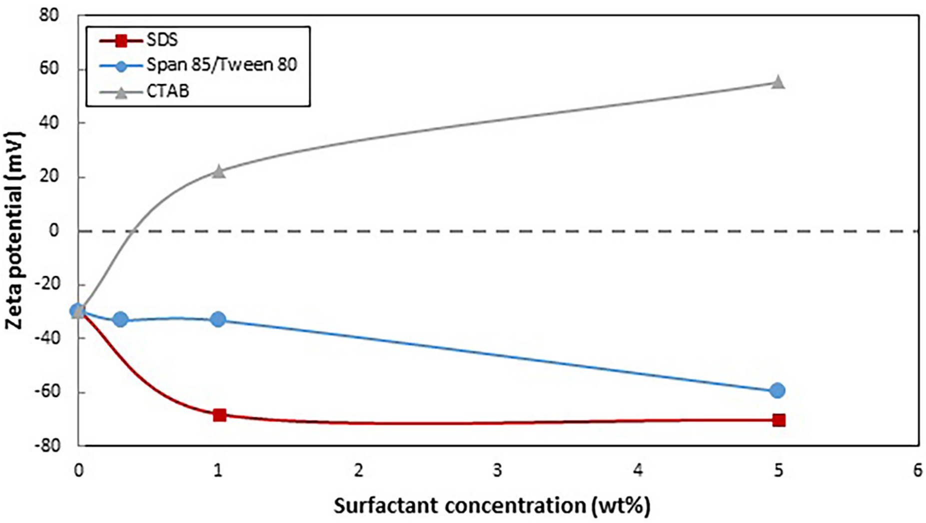

Figure 10. Surface charge (Zeta Potential) values of emulsion oil droplets as a function of surfactant concentration in the presence of SDS, mixed Span 85/Tween 80, and CTAB surfactants

flocs were noticed. The flocs, which were made up of the CTAB and oil, adhered to and floated with the air microbubbles, even at very low levels of the surfactant. CTAB, may also adsorbed at the microbubble-liquid interface and might render the microbubbles less negatively charged, consequently weakening the electrostatic repulsive force between the gas bubbles and oil droplets as negative charges on the bubble surface becomes weaker, thereby enhancing the likelihood of microbubbles attaching to oil droplets and/or flocs, thus raising the oil-gas-floc sizes.

Effect of surfactant type on air bubble size

Laboratory flotation investigations were performed to explore the effect of surfactant type bubble size and size distribution. In flotation methods, bubble size is an essential factor. According to previous studies, surfactant or foaming agents may render air bubbles finer and even more stable by reducing the solution's surface tension, thereby facilitating flotation reaction and improving collective efficiency (Xu et al., 2016; Kyzas and Matis, 2018; Al-Yaqoobi and Zimmerman, 2022). Also its may reducing the coalescence resulting from bubble collisions by the repulsive force between the air bubbles (Parhizkar et al., 2015; Watcharasing et al., 2009). Figures 11, 12, and 13 show the size distributions of bubbles generated from the MB diffuser in the systems containing anionic (SDS), mixed nonionic (Span 85/Tween 80), and cationic (CTAB) surfactants, respectively. The experiments were conducted with surfactant constant ratio of 3 wt.%. The bubbles size measurement analysis for the bubble generated in emulsion contained SDS surfactant showed that 0.58% of the bubbles were in range of 35–70 µm; only 6% of the bubble population was in range of 110–170 µm as shown in Figure 11. The Sauter mean diameter D [3, 2] for the bubbles generated was 93.7µm. for the emulsion used mixed nonionic (Span 85/Tween 80) as surfactant has mean diameter D [3, 2] of 107.6 µm. The bubble with size ranged from 30–70 µm were only 27% of the total bubble generated, while 32% of the bubble was 110–140 µm as can be noticed in Figure 12. The mean diameter D [3, 2] of bubbles generated in emulsion with CTAB surfactant was 71 µm, which was significantly lower than that obtained with the other two surfactants. Moreover, 82% of the bubbles were in range of 25–70 µm as in Figure 13. The flotation process performance is controlled by efficiencies of collision, attachment, and stability; consequently, a greater potential of collision and attachment can be provided by a higher specific bubble interfacial area, which increase of separation efficiency. The collision efficiency between bubbles and particles/drops in flotation process is a function of particle and bubble diameters. Surfactants act in a variety of ways to decrease the bubble size and increase the air holdup in a bubble column (Reis et al., 2017), but no specific mechanism has been identified. It is not only relevant to the reduction of surface tension (Zhang et al., 2020; Al-Yaqoobi and Zimmerman, 2022).

However, some of research outcomes indicated that, as the surfactant concentration increases, the bubbles get tinier. As the size of air bubbles becomes smaller, one might predict an improvement in oil recovery. The data reveals, however, a drop in oil recovery. This behavior can be explained by the fact that mixing in the recovery zone increases with the decreased bubble size. An increased mixing can result in a reduction in the attachment efficiency, despite an increase in

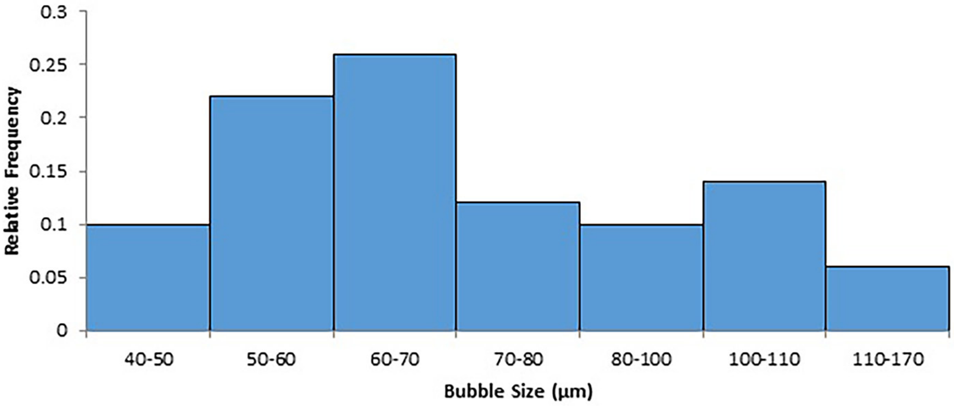

Figure 11. The plot shows distribution of microbubbles in O/W emulsion prepared with SDS surfactants

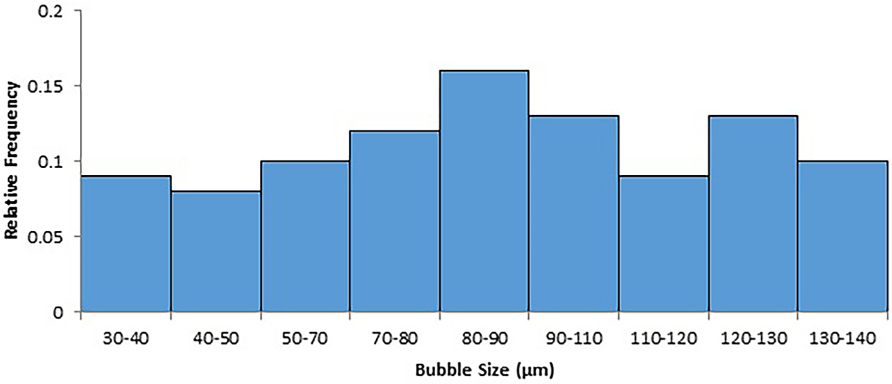

Figure 12. The plot shows the distribution of microbubbles in O/W emulsion prepared with (Span 85/Tween 80) surfactants

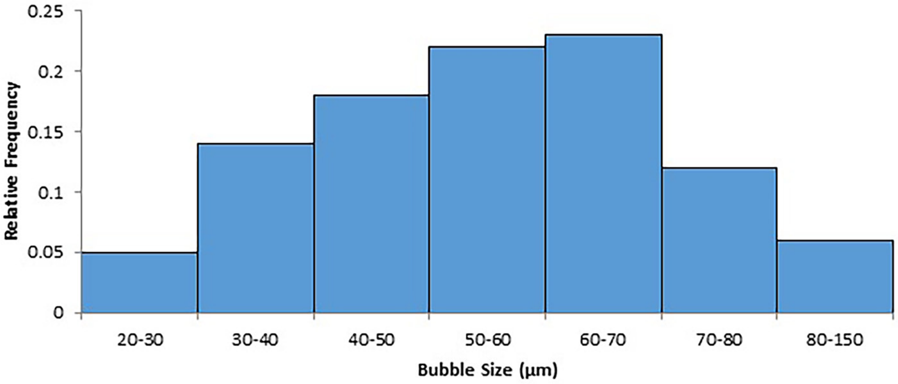

Figure 13. The plot shows the distribution of microbubbles in O/W emulsion prepared with CTAB surfactants

collision frequency (Jávor et al., 2016; Brun et al., 2015). If the time needed for film thinning was longer than the contact time, attachment would not exist. With increased mixing, the contact duration is expected to shorten. This is because surfactant addition prevents bubbles from coalescing by concentrating at the air–water interface and directing their hydrophilic groups onto the liquid film around the air bubble. This produces a repulsive electric force when two bubbles get next to each other (Brun et al., 2015; Chakibi et al., 2018).

CONCLUSIONS

The current research investigated the effect of different types of surfactant on the satiability of oil-water emulsion driven from Al-Basrah crude oil, and the ultimate effect on the separation efficiency using microbubble air flotation technology. The anionic, nonionic, and cationic surfactants represented by SDS, Span 85/Tween 80, and CTAB in rage of concentrations were used in this study. The results revealed that the stability of the emulsion was highly affected by the concentration of the surfactant and the best stability was achieved with nonionic Span 85/Tween 80 surfactant. Also the removal efficiency was remarkably relied on the type of the surfactant and its concentration in the emulsion. The highest removal efficiency were obtained with CTAB reached to around 95% at concentration of 3%, followed by 92% for Span 85/Tween 80 surfactant and 73.7% for SDS. The mean bubble size generated in the emulsion with using surfactants was in rang of 93.7µm, 107.6 µm, and 71 µm for SDS, Span 85/Tween 80, and CTAB respectively. The microbubble air flotation is efficient technology for the remediation of oily wastewater, and the choosing of the surfactant is an essential parameter in emulsion preparation.

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