Removal of oil from produced water by ionic flocculation using saponified babassu coconut oil

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Original Article

Oil and gas productions yield a by-product designated as produced water (PW). The high oil content of this effluent prevents its disposal or reuse. This study presents a novel alternative for the removal of oil from produced water using saponified babassu coconut oil (SBCO), as the ionic surfactant part which captures the oil by micellar solubilization, followed by ionic flocculation with Ca\(^{2+}\) ions. A factorial experimental design was applied to optimize the oil removal (RE) process. The experiments investigated the influence of SBCO + CaCl\(_2\) concentration, temperature (T), and stirring speed (ω). Extraction Percentages (RE) in the range from 64.901\% to 88.44\% were achieved. Subsequently, the influence of pH, CaCl\(_2\)/surfactant ratio and oil removal kinetics in the highest RE% system were evaluated, whereby for pH > 7, (calcium chloride/surfactant) ratio of 1:1, and 15 min of stirring, the RE obtained was 100\%. The same maximum removal result was obtained using a microemulsion containing SBCO. Thus, it can be affirmed that the application of ionic flocculation using SBCO is an efficient technique in the treatment of PW.

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1. Introduction

The activities performed by oil industries, besides being responsible for the production of hydrocarbons (oil and gas), can generate environmentally harmful effluents such as produced water (PW) [1]. Produced water is an effluent with high salinity and content of organic compounds. The composition of the produced water depends on the natural geological formation where water has accumulated (connate water) and the amount of water that is often injected into wells to increase oil recovery, becoming contaminated in the process [2,3]. Usually,
large amounts of PW are generated during oil and gas production. The volume of produced water generated is three times greater than the volume of oil and natural gas obtained [4,5]. Being an effluent that can be harmful to the environment and human health, great emphasis has been given in recent years to the treatment of produced water for proper disposal or reuse [6]. Methods such as photo catalysis, membrane technology and microbial cells [7–9] have been promising in this scenario, but the use of flotation and coagulation/floculation is still widely used due to its low operating cost and high oil removal rate [10–12]

Coagulation is a physicochemical process that decreases the repulsive potential of the electrical double layer of colloids, allowing colloidal microparticles to develop and agglomerate into larger particles [13]. Thus, these particles collide with each other forming larger structures [14]. This process usually occurs with the addition of chemicals known as coagulants and floculants, which are water soluble and classified in terms of charge as cationic, anionic or non-ionic [15,16]. These substances upon contact with bivalent or trivalent metal ions form a complex insoluble in water [17]. Cations such as Ba2+, Ca2+ and Mg2+ have a strong tendency to bond to the polar part of surfactant, while oil present in the medium is captured by the non-polar part of the surfactant, precipitated together with insoluble complex and removed out of the medium by filtration [18]. Thus, the higher the amount of oil present in the medium, the greater will be the demand of the amount of surfactants and cations present for the removal of non-polar organic substances [19]. Some studies suggest carboxylic acid salts for the removal of metals and oil [20–22], but there is no information in the literature on the use of saponified babassu coconut oil (SBCO) for this purpose.

The babassu coconut (Attalea speciosa) belongs to one of the most abundant palm trees in northern and northeastern Brazil, producing up to 15.6 tons of fruits per hectare/year [23]. The oil contains natural oxidants such as carotenoids and tocopherol, being composed in greater quantity by oleic acid (c9-18; 75.7%) [24,25]. The oil represents 7% of the fruit total weight and is currently being used for various research purposes as a source of energy production and in the food and cosmetics industry [26–28]. In addition, coconut mesocarp is a material also used in the production of ethanol [29] and bioactive film coating [30], which shows a wide variety of utility of such fruit.

Microemulsions are systems of high stability and low interfacial tension at low surfactant concentrations, and stand out for their ability to combine large amounts of two immiscible liquids into a single macroscopically homogeneous phase and exhibit a large interfacial area between the micro heterogeneous phases, being able to solubilize polar and non-polar substances. They are formed by two immiscible fluids, usually oil and water, stabilized by surfactant molecules, either pure or in combination with a co-surfactant that can be a short-chain alcohol [31,32]. Moreover, they are thermodynamically stable systems with 10–300 nm droplet diameter [33].

This paper presents a new study for removal of oil from produced water using soap obtained from saponified babassu coconut oil (SBCO), which will be used in its pure form and in a microemulsion formulation, being aided by calcium chloride in the flocculation process.
hexane \((C_8H_{14}, 100\% – \text{Synth})\) and stirring for 2 min. The next steps were collecting 2 g of the filtrate, adding 1 g of n-hexane \((C_8H_{14}, 100\% – \text{Synth})\) to extract and quantify only the oil remaining in the produced water and stirring for 2 min. After mixing, the aqueous and organic phases were obtained, from which 2 ml were collected and a considerable amount of anhydrous sodium sulfate \((\text{Na}_2\text{SO}_4, 99–100\% – \text{Vetec})\) was added to completely remove all traces of water \([36]\).

The oil removal efficiency (RE) present in produced water (OPW) is determined from Eq. (1) \([37]\).

\[
\text{RE} (\%) = \left( 1 - \frac{[\text{OGC}]}{[\text{OGC}]_0} \right) \times 100
\]  

(1)

where \([\text{OGC}]\) is the oil and grease content of the treated produced water and \([\text{OGC}]_0\) is the oil and grease content of the initial produced water (OPW).

### 2.2.3. Experimental design

In order to study the efficiency of the flocculation phenomenon, the following variables were selected: surfactant \((\text{SBCO}) + \text{CaCl}_2\) concentration \((\text{SBCO} + \text{CaCl}_2, g)\), temperature \((T, ^\circ C)\) and stirring speed \((\omega, \text{rpm})\). To investigate the effects of these variables and optimize the process, a factorial experimental design \(^2^3\) was performed with three replications at the central point. The response variable was oil removal efficiency (RE\%) from the OPW. Table 1 shows the levels of each factor.

Aiming to maintain the stoichiometric relationship in forming the complex and its subsequent flocculation, the amounts of soap and calcium chloride in a ratio of 2 \((\text{SBCO}):1\) \((\text{CaCl}_2)\) were used. The water-insoluble complex is formed via reaction of carboxylate group from the soap ion with calcium chloride, as represented in Eq. (2) \([38,39]\).

\[
2\text{RCOONa}(aq) + \text{CaCl}_2(aq) \rightarrow (\text{RCOO})_2\text{Ca}(s) + 2\text{NaCl}(aq)
\]  

(2)

As for the statistical experimental design, surfactant concentration equal to the concentration of oil and grease \((150 \text{mg L}^{-1})\) of the produced water (OPW) was used as central point \((0)\). The minimum level \((-1)\) was 15 \text{mg L}^{-1} of surfactant, the minimum flocculant concentration used by the OPW industry \([40]\). The maximum level \((+1)\) was 435 \text{mg L}^{-1} of surfactant, which represents a symmetrical distance from the minimum level to the center point.

The chosen temperature levels were 40 °C (minimum level), as it represents the operating unit float temperature \([40]\), and 80 °C (maximum level), the highest possible working temperature without operating limitations and without mass loss by the process of evaporation. Agitation velocity levels were chosen based on previously published results \([41,42]\), with 700 rpm as the minimum level and 1500 rpm as the maximum level.

All experiments were performed in triplicate. The effect of each factor was analyzed by generating response surfaces with the STATISTICA 7.0 program.

### 2.2.4. Study of the best oil removal system

After the results found by the statistical experimental design, the best oil removal system (called optimum point) was chosen further to study other effects such as pH, \(\text{CaCl}_2/\text{surfactant ratio}\) and desorption kinetics.

In order to evaluate flocculants behavior as a function of pH, the produced water had its pH adjusted to values of 4, 5, 6, 7, 8, 9 and 10, as suggested in studies using anionic flocculants \([43,44]\). For pH control, 1M hydrochloric acid solution \((\text{HCl} – 37\%, \text{Synth})\) and 1M sodium hydroxide solution \((\text{NaOH} – 100\%, \text{Synth})\) were used.

Aiming to evaluate \(\text{CaCl}_2/\text{surfactant ratio}\), the mass ratios were varied as follows: 1 g/2 g (0.5), 1.2 g/2 g (0.6), 1.4 g/2 g (0.7), 1.6 g/2 g (0.8), 1.8 g/2 g (0.9) and 2 g/2 g (1).

Oil removal tests were performed as a function of the stirring time in order to evaluate the desorption kinetics. Five samples of produced water were prepared, from which aliquots were collected every five minutes until completing 25 min.

The results obtained were adjusted in zero-order, Lagergren’s pseudo-first-order, and pseudo-second-order models \([45,46]\), shown in Eqs. (3)–(5), respectively.

\[
\text{OGC}_0 - \text{OGC} = k_0 t
\]  

(3)

\[
\ln \frac{\text{OGC}_0}{\text{OGC}} = k_1 t
\]  

(4)

\[
\frac{1}{\text{OGC}_0} - \frac{1}{\text{OGC}} = -k_2 t
\]  

(5)

where \(k_0\) is the desorption rate constant for the model \((\text{gg}^{-1} \text{min}^{-1})\); \(k_1\) is the desorption rate for the pseudo first order model \((\text{min}^{-1})\); \(k_2\) is the velocity constant of the pseudo-second order of desorption \((\text{gg}^{-1} \text{min}^{-1})\) and \(t\) is the time \((\text{min})\).

### 2.2.5. Use of microemulsions

After establishing the optimum point for the removal of oil present in the produced water, a microemulsion formulation was evaluated in order to compare the efficiency of soap and calcium chloride in the two different systems. The amount of soap and experimental conditions were the same in both studies.

The microemulsion formulation was chosen after determining the Winsor regions in the pseudoternary diagram, which was obtained from the mass titration methodology of the constituents. Combinations of active matter \((\text{C/S})\) and oil phase were weighed and the aqueous phase was titrated, observing the change in appearance between clear and cloudy. In a cloudy situation the mixture is taken to a centrifuge, where the phases are separated and the system is characterized according to Winsor classification \([47]\).
Fig. 1 – Surface tension graphs (σ) versus negative logarithm of concentration (−log_{10}[SBCO]). (●) SBCO; (○) SBCO + 1510 mg L\(^{-1}\) [NaCl]; (×) OCBS + OPW.

3. Results and discussions

3.1. Critical micellar concentration of SBCO in different aqueous phases

Fig. 1 presents the critical micellar concentration (CMC) of SBCO in distilled water, saline ([NaCl] = 1510 mg L\(^{-1}\)) and produced water ([NaCl] = 1510 mg L\(^{-1}\) + 150 mg L\(^{-1}\) crude oil). The CMC for SBCO in distilled water presented a higher value (11.01 mg L\(^{-1}\), σ = 37,966 N m\(^{-1}\)) when compared to SBCO in saline solution 6423 mg L\(^{-1}\), σ = 38,454 N m\(^{-1}\) and OPW 6732 ppm; σ = 38,040 N m\(^{-1}\)). The higher CMC value for the soap in distilled water is due to the repulsion phenomenon between the anionic surfactant heads when adsorbing at the liquid-gas interface. This repulsion promotes the migration of the molecule into the solution. Thus, for interface saturation and subsequent micelle formation [32], it is necessary to add larger amounts of surfactant, which indicates a higher concentration of surfactant.

The presence of inorganic salts in the medium decreases the repulsion between the polar heads of the surfactant when they are at the liquid–gas interface. Thus, interface saturation is achieved at the lowest surfactant concentration resulting in lower surfactant concentration values to form micelles (CMC) [48,49].

The oily produced water (OPW) contains dissolved salts and suspended oil droplets, ensuring the existence of two interfaces: liquid-gas and liquid-liquid. At first, saturation will occur at the liquid-liquid interface, then at the liquid-gas interface. Thus, a slight increase in surfactant concentration in the medium is necessary to saturate both interfaces, resulting in higher CMC.

3.2. Experimental design

Table 2 presents conditions and experimental results of oil removal from produced water (OPW) expressed as oil and grease content (OGC) of treated water and oil removal efficiency (RE%). The results of the tests presented removal percentages (RE%) between 64.901 ± 0.226% and 88.444 ± 0.235%, proving that the removal of the oil present in the produced water is directly related to selected variables ([SBCO + CaCl\(_2\)], T and ω). The increase in the concentration (SBCO + CaCl\(_2\)) was the most influential, explained by the greater formation of Ca\(^{2+}\)(R−COO\(^-\)) complex, responsible for the oil droplet flocculation phenomenon.

By adding surfactants to the produced water, lipophilic tails capture the oil droplets dispersed in the medium, forming micellar agglomerates. By adding CaCl\(_2\), the Ca\(^{2+}\) ion is released and ionically interacts with the carboxylate group present in the surfactant, forming Ca\(^{2+}\)(R−COO\(^-\)) complex and consequently causing micelle rupture. Once free, the complexes migrate out of the aqueous solution, taking with them the adsorbed oil droplets on their tails.

These experimental results were modeled by linear regression, obtaining a first order polynomial model (95% confidence interval). The estimated main effects and interactions (up to 3-way) are shown in Table 3.

It can be observed that only the interactions [(SBCO + CaCl\(_2\))(ω)] and [(T)(ω)] were not significant. Moreover, (SBCO + CaCl\(_2\)) and (ω) influence positively the system, but start to have a negative effect when interacting with other variables in binary form, which shows how sensitive these two variables may be to the action of other factors. The temperature (T) shows a constant pattern of negative influence and in binary interactions, which demonstrates strong negative influence of this variable in the system. However, it is noted that interaction between the three variables acquires a positive value, which allows to evaluate that the studied variables complement each other in order to achieve better removal efficiencies (RE%).

Variance analysis (ANOVA) and F test were performed in order to validate the proposed model as significant and/or predictive. The results are presented in Table 4, where the calculated value of F\(_1\) (30.813) is greater than F\(_{0.05}\) (3.466) and the calculated value of F\(_2\) (3.449) is less than F\(_{0.05}\) (0.186). Thus, the proposed model is considered predictive and significant, and it is possible to predict results within the domain of the factors without performing new experiments.

Fig. 2 illustrates the response surfaces for oil removal efficiency (RE%) relative to: SCBO + CaCl\(_2\) vs. T, SCBO + CaCl\(_2\) vs. ω and T vs. ω. By analyzing the response surface given by Fig. 2(a), it is confirmed that the relationship between SCBO + CaCl\(_2\) and temperature are inversely related, since better RE% are achieved at higher values SCBO + CaCl\(_2\) (1.0 encoding) and low T values (−1.0 encoding). In Fig. 2(b), it is possible to observe that if SCBO + CaCl\(_2\) concentration remains at high values (close to 1.0 coding), the stirring speed (ω) will not be a risk factor in decreasing the efficiency of the process. The rate of destabilization of chemical structures will be lower when compared to the formation rate of structures at low speeds. In Fig. 2(c), it is observed that a high stirring speed (ω) (coding greater than 0) will not negatively affect the system as long as the temperature (T) remains low (coding below 0).

The removal efficiency of oil present in the produced water was increased by increasing the stirring speed. Such behavior can be explained by the decrease of droplet volume and
### Table 2 – Test conditions and results of experimental design for OGC (mg. L⁻¹) and RE (%).

<table>
<thead>
<tr>
<th>Assay</th>
<th>SBCO + CaCl₂ (g)</th>
<th>T (°C)</th>
<th>ω (rpm)</th>
<th>OGC (mg. L⁻¹)</th>
<th>RE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>40</td>
<td>700</td>
<td>52.647 ± 0.226</td>
<td>64.901 ± 0.226</td>
</tr>
<tr>
<td>2</td>
<td>435</td>
<td>40</td>
<td>700</td>
<td>23.265 ± 0.452</td>
<td>84.490 ± 0.452</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>80</td>
<td>700</td>
<td>44.961 ± 0.407</td>
<td>70.025 ± 0.407</td>
</tr>
<tr>
<td>4</td>
<td>435</td>
<td>80</td>
<td>700</td>
<td>43.299 ± 1.774</td>
<td>71.133 ± 1.774</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>40</td>
<td>1500</td>
<td>23.565 ± 0.195</td>
<td>84.289 ± 0.195</td>
</tr>
<tr>
<td>6</td>
<td>435</td>
<td>40</td>
<td>1500</td>
<td>17.333 ± 0.235</td>
<td>88.444 ± 0.235</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>80</td>
<td>1500</td>
<td>41.845 ± 0.345</td>
<td>72.102 ± 0.345</td>
</tr>
<tr>
<td>8</td>
<td>435</td>
<td>80</td>
<td>1500</td>
<td>22.111 ± 0.534</td>
<td>85.259 ± 0.534</td>
</tr>
<tr>
<td>9</td>
<td>225</td>
<td>60</td>
<td>1100</td>
<td>32.082 ± 0.172</td>
<td>78.611 ± 0.172</td>
</tr>
<tr>
<td>10</td>
<td>225</td>
<td>60</td>
<td>1100</td>
<td>28.966 ± 0.518</td>
<td>80.689 ± 0.518</td>
</tr>
<tr>
<td>11</td>
<td>225</td>
<td>60</td>
<td>1100</td>
<td>28.343 ± 0.113</td>
<td>81.104 ± 0.113</td>
</tr>
</tbody>
</table>

Mean of triplicates ± standard deviation. SBCO (surfactant concentration) + CaCl₂ (CaCl₂ concentration); T: temperature; ω: Stirring speed; OGC: oil and greases content; RE: oil removal efficiency.

### Table 3 – Estimated effects of key factors and their interactions on OPW oil removal efficiency. The variables in bold are statistically significant results.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effect</th>
<th>Coefficient</th>
<th>Std. error coefficient</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>78.277</td>
<td>78.277</td>
<td>0.402</td>
<td>0.000026</td>
</tr>
<tr>
<td>[SBCO + CaCl₂]</td>
<td>9.501</td>
<td>4.750</td>
<td>0.472</td>
<td>0.009734</td>
</tr>
<tr>
<td>[T]</td>
<td>−5.901</td>
<td>−2.950</td>
<td>0.472</td>
<td>0.024666</td>
</tr>
<tr>
<td>[ω]</td>
<td>9.886</td>
<td>4.943</td>
<td>0.472</td>
<td>0.009001</td>
</tr>
<tr>
<td>[SBCO + CaCl₂][T]</td>
<td>−2.369</td>
<td>−1.184</td>
<td>0.472</td>
<td>0.128824</td>
</tr>
<tr>
<td>[SBCO + CaCl₂][ω]</td>
<td>−0.846</td>
<td>−0.423</td>
<td>0.472</td>
<td>0.464700</td>
</tr>
<tr>
<td>[T][ω]</td>
<td>−1.784</td>
<td>−0.892</td>
<td>0.472</td>
<td>0.199325</td>
</tr>
<tr>
<td>[SBCO + CaCl₂][T][ω]</td>
<td>6.870</td>
<td>3.435</td>
<td>0.472</td>
<td>0.018373</td>
</tr>
</tbody>
</table>

### Table 4 – ANOVA for oil removal efficiency (% RE).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares (SS)</th>
<th>Degree of freedom (df)</th>
<th>Mean square (MS)</th>
<th>F-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>559.138</td>
<td>7</td>
<td>79.876</td>
<td>F₁</td>
</tr>
<tr>
<td>Residual</td>
<td>17.802</td>
<td>3</td>
<td>5.934</td>
<td>13.460</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>14.234</td>
<td>1</td>
<td>14.234</td>
<td>F₂</td>
</tr>
<tr>
<td>Pure error</td>
<td>3.567</td>
<td>2</td>
<td>1.783</td>
<td>7.980</td>
</tr>
<tr>
<td>Total SS</td>
<td>576.940</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

F table (95% confidence interval)

<table>
<thead>
<tr>
<th>F₁ vs.</th>
<th>F cal/F table</th>
<th>Model</th>
<th>Significant</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₁,2</td>
<td>8.89</td>
<td>1.514</td>
<td>Predictive</td>
</tr>
<tr>
<td>F₁,2</td>
<td>18.51</td>
<td>0.431</td>
<td></td>
</tr>
</tbody>
</table>

### Fig. 2 – Response surfaces for oil removal efficiency (% RE). (a) SBCO + CaCl₂ vs. T, (b) SBCO + CaCl₂ vs. ω and (c) T vs. ω.

The increase of its quantity in the medium, which results in a larger surface area of the droplet and, consequently, facilitating the formation of the oil in water micelles. The effect of stirring velocity is more significant than the temperature, showing that ionic attraction between the Ca²⁺ ions and the surfactant make the system resistant to the turbulence.

Thus, the highest percentage of oil removal occurred in test 6, reaching 88.444 ± 0.235 for the conditions: [SBCO + CaCl₂] = 435 g mL⁻¹, T = 40 °C and ω = 1500 rpm.
3.3. Study of the best oil removal system

Fig. 3 shows results of oil removal as a function of the pH of the produced water. For pH values below 7 (pH < 7), removal efficiency is low. In this pH range the soap regenerates to its fatty acid due to H⁺ attack on the carboxylate group. Thus, the amount of surfactant in the medium will be reduced, and there will be a reduction in the amount of complex formed by adding calcium chloride [17]. On the other hand, from pH 10, there is a reaction between sodium hydroxide and fatty acids present in in the oil producing in-situ soap, which forms oil/water micelles (emulsion) and helps the removal of larger amounts of oil by the process of flocculation or by breaking the emulsion itself. Despite these results, the authors do not recommend an excess of basicity in the medium since at pH = 7 a significant oil removal result is already achieved (RE = 88.444 ± 0.235).

Fig. 4 shows oil removal results as a function of CaCl₂/SBCO ratio. The efficiency of oil removal from the produced water is lower when CaCl₂/surfactant ratio is lower. Even though the lowest ratio (CaCl₂/SBCO = 0.5) guarantees the minimum stoichiometry required to convert all surfactant to complex, it was not possible to kinetically arrange all reagents in the structure of the product, and it was necessary an excess of calcium ions to ensure complete conversion of surfactants into complexes. Thus, as the amount of calcium chloride (ratio increase) relative to the surfactant increases, larger amounts of molecules are converted to complexes, resulting in higher percentages of oil removal, reaching maximum peak when at a ratio of 1:1 (calcium chloride/surfactant), as observed elsewhere [22,50].

Fig. 5 shows results of oil removal as a function of time. It is observed that the OGC value of produced water (OPW) reaches values close to zero after 15 min. Table 5 shows the values of the constants and the correlation coefficients of the kinetic models studied. The best model fit for the experimental data is that of pseudo-first-order. Thus, the desorption rate is proportional to the amount of oil removed by the flocculation process, a result consistent with other studies [22].

3.4. Use of microemulsions

Fig. 6 presents two pseudoternary diagrams. They differ only in the aqueous phase (AP), in which distilled water and produced water were used, with aviation kerosene as oil phase (OP), SBCO as surfactant (S), iso-amyl alcohol as co-surfactant (C) and ratio C/S = 1. In the pseudo-ternary diagrams, the region

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Table 5 – Constants and correlation coefficients (R²) obtained for the desorption models of Zero Order (zero), pseudo order (1') and pseudo order (2') modified.

<table>
<thead>
<tr>
<th>Model</th>
<th>Constant</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order zero (zero)</td>
<td>k₀ = 8.617</td>
<td>0.853</td>
</tr>
<tr>
<td>Pseudo-first order (1')</td>
<td>k₁ = 0.436</td>
<td>0.925</td>
</tr>
<tr>
<td>Pseudo-second order (2')</td>
<td>k₂ = 0.033</td>
<td>0.804</td>
</tr>
</tbody>
</table>
of Winsor WIV + unsolubilized surfactant (WIV + US) corresponds to the formation of a microemulsion phase with the precipitated surfactant. This is because the amount of oil or water present in this region is not sufficient for the complete solubilization of the surfactant. The Winsor I (W) region corresponds to the formation of two phases: a microemulsion phase and a second phase with excess oil. In this work, we chose to use the Winsor WIV (WIV) region, which corresponds to the formation of only one microemulsion phase, as it has a greater quantity of direct micelles compared to the other regions formed. The compositions for the flocculation study were chosen at a point that contains a large amount of aqueous phase and small amounts of oil phase and active matter (C/S). The two compositions used were: 75% AP, 5% OP and 20% C/S (C + S = 10% SBCO and 10% iso-amyl alcohol).

For comparative effect on the oil removal efficiency of the produced water, the microemulsion formulation was studied under the same conditions as the pure soap. Thus, the microemulsions were added in a concentration of 290 mg/L of OPW, followed by the addition of 145 mg of CaCl₂ (CaCl₂/microemulsion = 0.5 and [microemulsion + CaCl₂] = 435 mg L⁻¹). Other conditions were: 40 °C, 1500 rpm, pH = 7 and 5 min stirring.

Oil removal efficiency results from the water produced by the addition of pure soap and the two microemulsion systems are shown in Table 6. OGC was used to quantify the oil content before and after treatment. It is clear that microemulsion formulations have greater efficiency in removing oil from the water produced (100%) than pure soap does (88.444 ± 0.235%). This is because, by adding microemulsion formulations, the direct micelle oil nuclei captures the oil droplets dispersed in the aqueous medium, while on soap addition their molecules capture the oil and form the micelles. Thus, micelles present faster diffusion than pure soap in the aqueous medium, which ensures enhanced capture of oil droplets when using microemulsions. Then, with the addition of calcium chloride and subsequent formation of the complex, larger amounts of oil are removed from the produced water by soap in microemulsion form.

Another advantage of using microemulsion is its ability to treat larger amounts of produced water when compared to pure soap. The microemulsion formulation has the same amount of soap used in the process that uses pure soap, but the direct micelles also present in their composition butanol and kerosene, substances that easily solubilize the oil present in the produced water [40]. Thus, by breaking the micelle due to the formation of the complex (flocculant) after the addition of calcium chloride, iso-amyl alcohol and kerosene help to remove larger amounts of oil.

### Table 6 - Oil removal efficiency of water produced through pure soap and soap in microemulsified form.

<table>
<thead>
<tr>
<th>System</th>
<th>SBCO</th>
<th>Microemulsions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquose phase</td>
<td>–</td>
<td>Distilled water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OPW</td>
</tr>
<tr>
<td>OGC (mg L⁻¹)</td>
<td>17.33 ± 0.235</td>
<td>0.000 ± 0.367</td>
</tr>
<tr>
<td>RE (%)</td>
<td>88.444 ± 0.235</td>
<td>100 ± 0.367</td>
</tr>
</tbody>
</table>

OGC: oil and greases content of the treated sample; RE: oil removal efficiency.

4. Conclusions

The experiments using saponified babassu coconut oil for the treatment of produced water allowed the following results:

- The low CMC value for SBCO in produced water (6.732 mg L⁻¹) represents an advantage as micelles are formed with small amounts of soap.
- The highest percentage of oil removal from produced water occurred at 435 mg L⁻¹ (SBCO + CaCl₂), 40 °C and 1500 rpm; 1:1 ratio (calcium chloride/surfactant); 15 min of stirring, with 100% removal from a pH 10.
- Microemulsions showed higher efficiency in removing oil from the produced water (100%) than pure soap (88.44%).
- The application of soap to remove oil from the produced water stands out for not generating residues in the flocculation process.

Conflicts of interest

The authors declare no conflicts of interest.
Acknowledgements

The authors would like to thank the Federal University of Rio Grande do Norte (UFRN), in particular the Graduate Program in Chemical Engineering, the Laboratory of Surfactant Technology (LTI/Chemistry Institute/UFRN) and CAPES and CNPq for the financial assistance received for the realization of research.

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