



Research Article

Efficiency of the Green Surfactant Derived from *Avena sativa* Plant in the Presence of Different Salts for EOR Purposes

Amin Azdarpour ¹, Milad Norouzpour ¹, Moein Nabipour ¹, Rafael M. Santos ² and Erfan Mohammadian ³

¹Department of Petroleum Engineering, Islamic Azad University, Marvdasht Branch, Marvdasht, Iran

²School of Engineering, University of Guelph, Guelph, ON, Canada N1G 2W1

³Key Laboratory of Continental Shale Hydrocarbon Accumulation and Efficient Development, Ministry of Education, Northeast Petroleum University, Daqing 163318, China

Correspondence should be addressed to Amin Azdarpour; aminazh22@gmail.com

Received 1 March 2023; Revised 26 April 2023; Accepted 4 May 2023; Published 18 May 2023

Academic Editor: Mehdi Ostadhassan

Copyright © 2023 Amin Azdarpour et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this investigation, a unique approach using a green surfactant extracted from the *Avena sativa* (AS) plant in conjunction with three different salts, including Na_2CO_3 , NaCl, and Na_2SO_4 , was examined for enhanced oil recovery. In addition, the efficiency of NaOH as a supplementary chemical in the process was investigated. Based on the results of the interfacial tension (IFT), the optimum value of NaOH was found to be 2,000 ppm, while the green surfactant had a CMC value of 4,000 ppm. The IFT value at the CMC point of NaOH was 2.34 mN/m, when the FB was used, and the IFT value was 2.78 mN/m, when deionized water was used. In addition, in terms of IFT reduction, wettability modification, and oil recovery factor enhancement, Na_2CO_3 was the most suitable salt with the AS surfactant at the CMC point (4,000 ppm), followed by NaCl and then Na_2SO_4 . The IFT values at the optimum salinity point (10,000 ppm) of Na_2SO_4 , NaCl, and Na_2CO_3 were 3.18, 3.05, and 2.87 mN/m, respectively. Moreover, the contact angles at the optimum salinity point of 10,000 ppm after 150 hr and at the reservoir temperature (80°C) were 36.58°, 40.76°, and 44.18° with Na_2CO_3 , NaCl, and Na_2SO_4 , respectively. Furthermore, the addition of NaOH improved the efficiency of the green surfactant in terms of maximizing the recovery factor by decreasing the IFT values and changing the wettability of the rock toward a more water-wet state. The final recovery factors of 88.45%, 80.87%, and 7.98% were attained using Na_2CO_3 , NaCl, and Na_2SO_4 , respectively, when 1 PV of NaOH was injected as the preflush, followed by 4 PVs of natural AS surfactant.

1. Introduction

Increasing energy demand and the necessity to produce more crude oil have led researchers to look into a new method to maximize recovery factor (RF) from the reservoirs. Chemically enhanced oil recovery (CEOR) is one of those methods that has received significant attention over the past few years. Surfactant flooding is one of the CEOR methods that results in significant oil recovery from reservoirs. Regardless of their effectiveness in increasing the RF, their toxicity and environmental drawbacks are the major obstacles to large-scale implementation nowadays. Therefore, using green chemicals to reduce this problem is critical [1–3]. Recently, the use of green surfactants derived from sustainable resources has gained substantial attention to be

used for EOR applications. These surfactants are usually derived from different plants and animals. The efficiency of the extracted saponin from sustainable resources is comparable with the conventional chemical-based surfactants. In addition, they overcome the negative impacts of using commercial surfactants from an environmental point of view [4, 5]. One of the earliest investigations that used a green surfactant for EOR purpose was performed by Chhetri et al. [6]. These researchers extracted a natural surfactant from soapnut fruit pericarp shells. They concluded that the extracted saponin was very effective in reducing interfacial tension (IFT), wettability alteration from oil-wet to water-wet states, and increasing the recovery factor from the reservoir. After proving the efficiency of the green surfactants for EOR purposes, the research started to gain more attention [6].

TABLE 1: Properties of the carbonate core samples utilized in this investigation.

Sample name	Diameter (cm)	Length (cm)	Pore volume (cm ³)	Bulk volume (cm ³)	Permeability (mD)	Porosity (%)
D1	3.81	7.58	9.73	86.38	14.86	11.27
D2	3.81	7.56	9.69	86.15	14.82	11.25
D3	3.81	7.58	9.73	86.38	14.85	11.26
D4	3.81	7.55	9.65	86.03	14.89	11.22
D5	3.81	7.61	9.79	86.72	14.85	11.29
D6	3.81	7.58	9.73	86.38	14.86	11.27

In a study performed by Moradi et al. [7], the effectiveness of the green surfactant derived from *Tribulus terrestris* was investigated. They performed different experiments, including IFT, contact angle, and oil recovery measurements. Moreover, the efficiency of the green surfactant in the presence of smart water was also examined. The obtained results from their experiments revealed that the *T. terrestris* surfactant is highly compatible with the ions present in smart water. In addition, the contact angle and IFT values were reduced to 54.4° and 13.5 mN/m, respectively. In addition, the maximum oil RF of 72% was achieved with tertiary recovery using the injection of smart natural surfactant [7]. A nonionic surfactant derived from linseed oil was used for EOR in another investigation conducted by Nafisifar et al. [8]. The efficiency of the green surfactant was evaluated when NaCl, the most prevalent salt, was present. The obtained results demonstrated that NaCl salt and the surfactant were compatible. In addition, ultra-low IFT values were achieved using low concentrations. At the CMC point, the IFT value was found to be 0.99 mN/m, and the value was further lowered to 0.26 mN/m when NaCl was added to the solution. They concluded that the green surfactant extracted from linseed's oil is very effective to be used for EOR applications [8].

Norouzpour et al. [9] extracted a nonionic surfactant from the red beet (RB) plant and utilized it for EOR application in different solutions, including fresh water and NaCl. They conducted various experiments, including contact angle and IFT experiments as well as core flooding tests. Their findings revealed that the derived saponin was highly effective in increasing the RF as the tertiary recovery, where an additional 26.29% was achieved in RF. In addition, at the CMC point of 2,500 ppm, the IFT value of 9.92 mN/m was achieved, and the contact angle changed from 151.4° to 42.14° [9]. Sami et al. [10] also investigated the feasibility of deriving a natural surfactant from *Avena sativa* (AS) plant for EOR purposes. They used nine various salts, like Na₂SO₄, NaCl, MgSO₄, CaCl₂, K₂SO₄, MgCl₂, KCl, NaHCO₃, and Na₂CO₃ with constant ionic strength of 40.517×10^{-3} . The concentrations of these salts were in a low salinity range of 1,219–3,403 ppm, respectively. They deduced that the extracted AS surfactant is very effective in low salinity conditions. In addition, Na₂CO₃ was the most compatible salt with the AS surfactant in terms of decreasing IFT and contact angle values and raising the oil recovery factor [10]. Other researchers investigated the applicability of various natural surfactants extracted from different plants. These plants are soapnut, soapwort plant, *Zizyphus spina-christi* trees (cedar), quinoa, mulberry leaves,

Vernonia amygdalina, Chuback, setifera plant, and soapnut fruit [11–19].

NaCl salt has been employed in the majority of the published papers as the most prevalent salt type present in the formation brine, whereas the application of natural surfactants in low salinity conditions has been the subject of several others. Therefore, the primary objective of this work was to examine the influence of various ions and salt types present in the formation brine on the effectiveness of the AS surfactant in a large variety of salinities, which has not before been studied. In addition, the investigation of the role of chemical additives in improving the efficiency of AS surfactant under reservoir conditions was the other purpose of this study. Therefore, the effectiveness of the AS surfactant was investigated in the presence of three various salts, including NaCl, Na₂CO₃, and Na₂SO₄, in a wide range of salinity (1,000–97,000 ppm). In addition, the effect of NaOH as a chemical supplement on the efficiency of the AS surfactant was examined. The experimental study of these parameters was performed using various tests, including IFT and contact angle measurements, zeta potential measurements, and oil recovery factor experiments. The results of this investigation will offer a better knowledge of the synergism between the AS surfactant and various salts under reservoir conditions during tertiary oil recovery in carbonate reservoirs.

2. Materials and Methods

2.1. Materials. In this investigation, the extraction of saponin compound as the natural surfactant was performed from the dry powder of AS plant, which was purchased from a local shop, to conduct the experiments. A sample of dead crude oil with an API of 31.56°, asphaltene content of 4.59%, resin content of 9.78%, and acid number of 1.63 was used in this investigation. The carbonate rock samples were collected from an outcrop of one of the Iranian carbonate oil fields. The physical and petrophysical characteristics of the core samples used in this investigation are also displayed in Table 1. The formation brine (FB) with a total dissolved salinity (TDS) of 97,645 ppm was used in this study.

2.2. Methods. To extract saponin from AS powder, the procedure explained in our previous work by Sami et al. [10] was carefully followed. In order to measure IFT values, the IFT400 (Fars EOR Tech. Co, Iran) apparatus was used, as shown in Figure 1. This apparatus uses the Axisymmetric Drop Shape Analysis (ADSA) technique. In this method, the shape of each drop is recorded then the IFT of each drop is calculated using

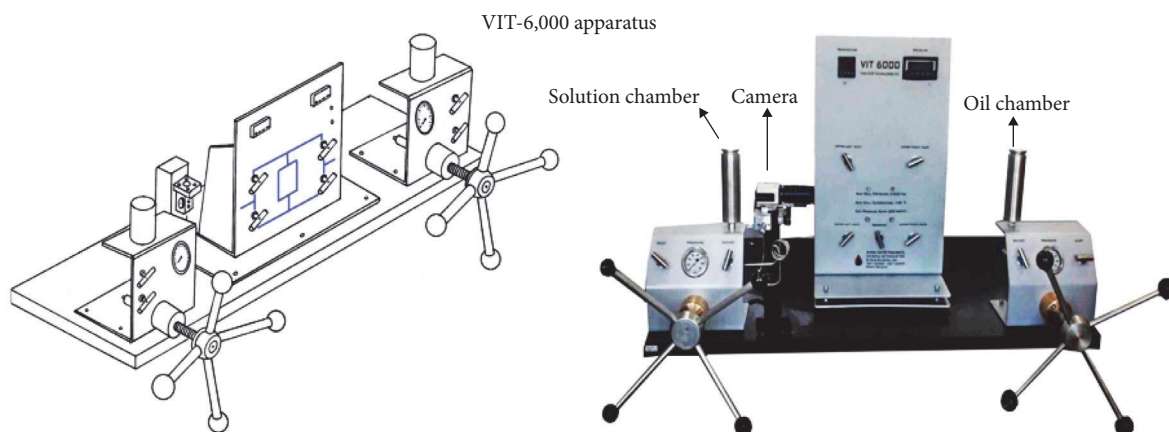


FIGURE 1: IFT400 schematic utilized in this investigation [9].

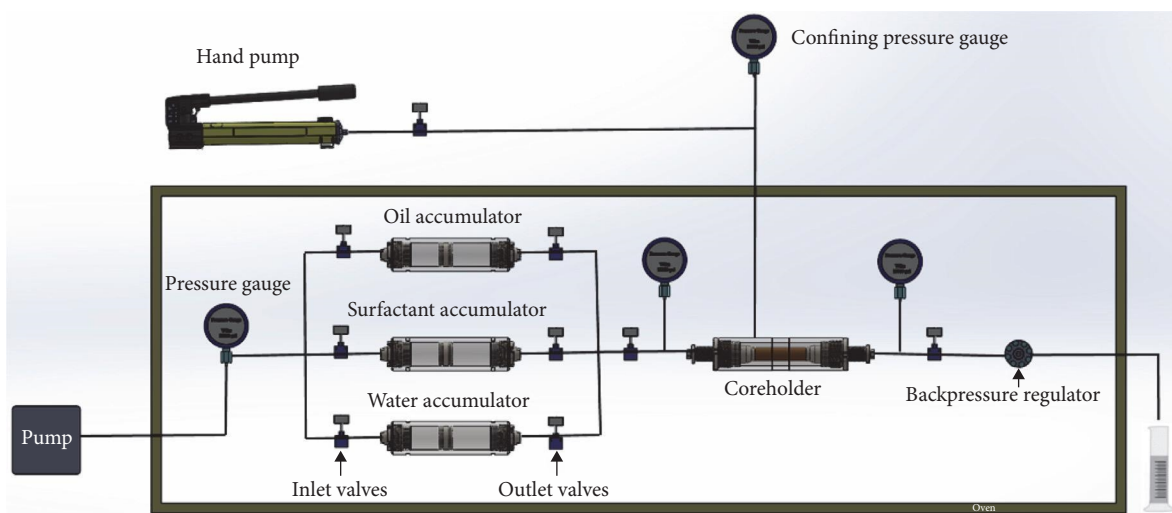


FIGURE 2: Schematic illustration of the core flooding setup employed in this research [10].

the ADSA technique. In this investigation, first, a variety of solutions were made, and the IFT value between various solutions and crude oil was evaluated at a temperature of 80°C (reservoir temperature). An inaccuracy of $\pm 5\%$ was chosen to be reported for the IFT values.

The contact angle measurement was performed using the IFT400 instrument. Prior to the measurement, rock samples were cut, sliced, and immersed in an oil phase for a period of 40 days at 80°C. This was done to make sure that the wettability of the rock samples changed to the original oil-wet state. The sessile drop method was then used to measure the contact angle of each drop in a variety of solutions at atmospheric pressure and 80°C. Each recording was performed after 150 hr. The contact angle value was determined by measuring the average of three separate measurements.

The zeta potential measurement was carried out using a zeta potentiometer (Horiba SZ100, Japan). This method involved adding 0.125 g of crushed rock sample to 20 ml of each solution and then each solution was agitated for 72 hr. Afterward, each suspension was settled for nearly 1 hr until a

clear suspension was produced. Then, the extraction of fine particles suspended in the solution was carried out using a spinal needle, followed by filtration. Finally, the samples were analyzed using the zeta potentiometer.

The core flooding apparatus depicted in Figure 2 was used to conduct the core flooding tests. Initially, acetone and toluene were used to wash all the core samples, followed by drying in an oven at 70°C. Then, each core sample was saturated with FB at a pressure of 3,500 psi for 24 hr. In the next step, each saturated core sample was flooded with 5 PVs of FB under the confining pressure of 4,500 psi and temperature of 80°C (representing reservoir pressure and temperature). Following the injection of 5 PVs of dead crude oil into the core, each sample was aged in crude oil at 80°C for 30 days to restore the rock sample's original wettability. Afterward, 5 PVs of FB was injected as secondary recovery after the aged core samples were placed inside the core holder. For the tertiary recovery, 5 PVs of AS surfactant prepared at 10,000 ppm of each salt was injected into the core samples. Another series of tertiary tests began with the injection of 1 PV of NaOH

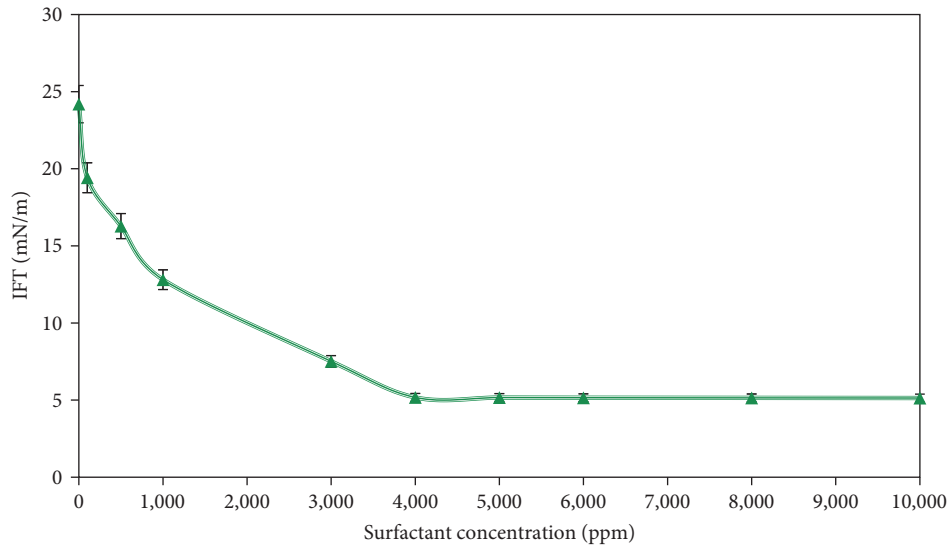


FIGURE 3: CMC measurement of AS surfactant at 80°C.

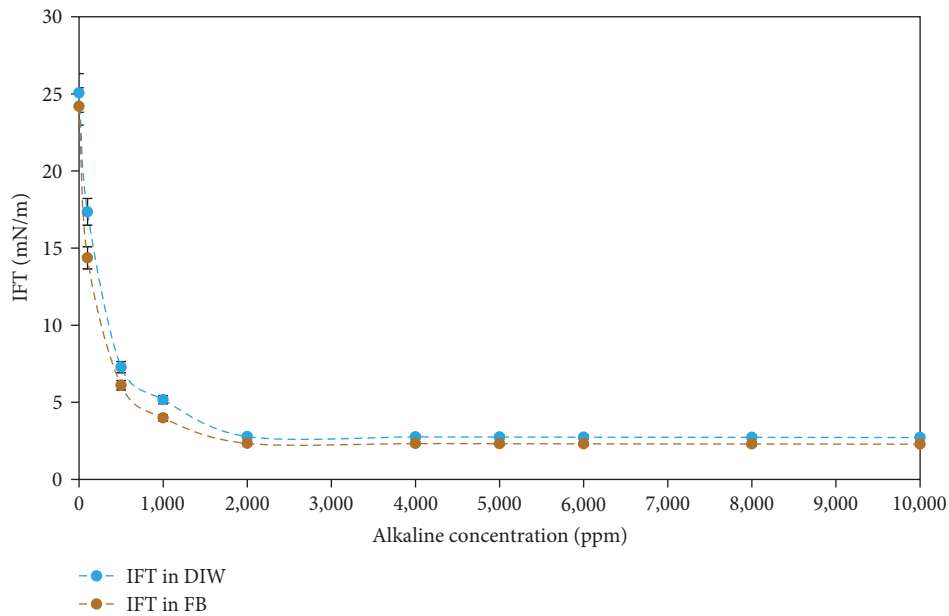


FIGURE 4: IFT value of NaOH and crude oil at 80°C.

solution as a preflush, followed by the injection of 4 PVs of AS surfactant. Finally, the recovery factor of each core flooding experiment was determined accordingly.

3. Results and Discussion

3.1. CMC Measurement. The CMC measurement in this investigation involves the CMC measurement of natural surfactant and alkaline. In this regard, natural surfactant and alkaline solutions were prepared in deionized water (DIW) and FB. The IFT of each solution was determined by the different surfactant and alkaline concentrations (100–10,000 ppm).

The IFT values for crude oil and surfactants are shown in Figure 3. This figure illustrates how the IFT of the surfactant

and crude oil is strongly influenced by the concentration of the surfactant, with negligible changes occurring when the concentration was increased to 10,000 ppm after a drastic decline to 4,000 ppm. Surfactant's IFT values were 5.17 and 5.13 mN/m at 4,000 and 10,000 ppm, respectively. These results imply the CMC point of the AS surfactant is 4,000 ppm.

Figure 4 also represents the IFT values of alkaline and crude oil in both DIW and FB. As shown in this figure, IFT is significantly reduced with increasing alkaline concentration. Two different trends of IFT are observed with increasing the concentration of alkaline. IFT values are initially reduced substantially up to 2,000 ppm, after which raising the concentration has no significant impact on IFT. This trend in IFT values is observed for both solutions prepared in DIW

TABLE 2: IFT values of diluted formation brine and crude oil at 80°C.

Diluted formation brine (ppm)	IFT (mN/m)
1,000	19.64
5,000	16.42
10,000	14.26
20,000	14.78
50,000	15.34
75,000	15.89
97,000	17.02

and FB; however, the IFT values of NaOH solutions prepared in FB are slightly lower than that in DIW. These findings suggest that the optimum point of NaOH is 2,000 ppm, in which the IFT values at the optimum point are 2.34 (solutions in FB) and 2.78 mN/m (solutions in DIW).

3.2. Impact of Various Salts on IFT Measurements. Table 2 presents the IFT values of diluted formation brine (DFB) and crude oil. As shown in this table, there are two different behaviors for IFT with formation brine salinity. From 1,000 to 10,000 ppm salinity, the IFT gradually decreases, and increasing the salinity to 97,000 ppm increases the IFT. In other words, the optimum salt concentration of 10,000 ppm exists, where the minimal IFT value of 14.26 mN/m is obtained. Decreasing the IFT values up to an optimum point is due to the “salting-in” effect, which is due to the increased solubility of organic compounds. On the other hand, at higher concentrations of salt, the solubility of the organic compounds is decreased, resulting in higher IFT values between the salts and crude oil. “Salting-out” impact refers to this phenomenon [18, 20–22].

Figure 5 presents the IFT values of 4,000 ppm of AS surfactant prepared in different concentrations of Na_2SO_4 , NaCl, and Na_2CO_3 . As shown in this figure, there is an optimum point of IFT value for all three tested salts. Increasing the salt concentration has a positive impact on IFT reduction, where this concentration is 10,000 ppm, and further increasing the salt concentration to 97,000 ppm has a negative influence on IFT values and results in an increased IFT. Among these three salts, Na_2CO_3 had the best performance with the natural surfactant, followed by NaCl, and finally Na_2SO_4 . The IFT values at 10,000 ppm of Na_2SO_4 , NaCl, and Na_2CO_3 were 3.18, 3.05, and 2.87 mN/m, respectively.

The IFT can be significantly decreased by adding a surfactant to the solution. Although a similar trend was seen in the IFT of FB and crude oil, the values were significantly lower when the AS surfactant’s CMC was added to the solutions. The optimum point of salinity is at 10,000 ppm for all three tested salts, where the minimum IFT is achieved. At slightly low concentrations of salts in solution, the “salting-in” phenomenon occurs, where the solubility of organic compounds is increased, consequently reducing the IFT. However, exceeding the optimum concentration of salt in solution results in a decreased organic compound solubility and increased IFT, a so-called “salting-out” phenomenon. According to the results, CO_3^{2-} (basic cations and anions) are more compatible with the natural surfactant rather than Cl^- and SO_4^{2-} (acidic anion).

The interaction between the crude oil’s carboxylic acid and the alkaline portion of Na_2CO_3 results in the production of an in situ surfactant. This results in lower IFT values from the solutions of Na_2CO_3 and the natural surfactant. For solutions with NaCl and Na_2SO_4 , the acidic strength of the anions is the controlling parameter for IFT reduction, where the higher the acidic strength of anions the higher the IFT values. This is the reason for having lower IFT values with NaCl rather than Na_2SO_4 [23–26].

Figure 6 displays the IFT values between crude oil and various solutions that were prepared using the AS surfactant’s CMC value and optimum value of alkaline. As the results show, the addition of 2,000 ppm NaOH is highly efficient in decreasing IFT values. The salt concentration of 10,000 ppm is the optimum salt concentration, where the lowest IFT is achieved with all three tested salts. The performance of Na_2CO_3 is better than NaCl, and Na_2SO_4 in all tested concentrations. The minimum IFT values between Na_2CO_3 , NaCl, and Na_2SO_4 in the presence of the CMC value of surfactant and alkaline are 1.52, 1.63, and 1.81 mN/m, respectively. These findings suggest that salting-in and salting-out effects are the reason for having an optimum concentration of salt in terms of IFT reduction, which is 10,000 ppm in this study. Furthermore, the IFT values were successfully decreased by adding the optimal amount of NaOH to the surfactant solutions. Considering the IFT values between various salts and the AS surfactant’s CMC reveals that a reduction of 1.38 mN/m is achieved on average with NaOH addition to the solutions. These findings also imply that the acidic strength of the anions as well as the in situ soap generation between the carboxylic content of the crude oil and natural surfactant are still the main mechanisms for having a lower IFT with Na_2CO_3 , NaCl, and Na_2SO_4 accordingly [17, 27].

3.3. Effect of Different Salts on Wettability Alteration.

Dynamic contact angle measurements between crude oil and various solutions, including FB, the AS surfactant’s CMC and FB, and the optimum value of alkaline and FB, are shown in Figure 7. The tests aimed to identify the optimum time for measuring the contact angle. The experimental findings revealed that the contact angle value decreased sharply from the initial state to some extent, and from that point onward the changes are insignificant. Initially, the contact angle decreased for the first 150 hr, but after that, the changes are insignificant. Considering the time of 150 hr as the optimum time for contact angle measurement results in a contact angle of 128.11°, 90.88°, and 95.36° for solutions of FB, 4,000 ppm of AS surfactant in FB, and 2,000 ppm of NaOH in FB. These results also show that the contact angle is decreased remarkably when the AS surfactant is added to the FB rather than NaOH. The AS surfactant is very compatible with FB in changing the contact angle to an oil-wet state.

Figure 8 illustrates the contact angle after 150 hr at 80°C between crude oil and various salts in the presence of 4,000 ppm AS surfactant. This figure illustrates how the contact angle is considerably changed when the salt concentration rises from 1,000 to 97,000 ppm. Regardless of the salt type, the optimal salt concentration was found to be at

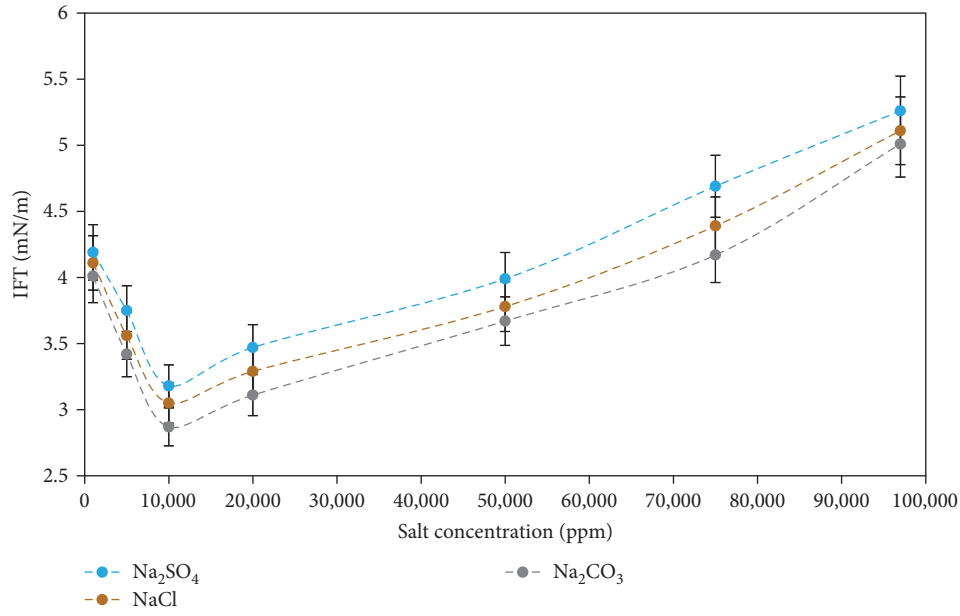


FIGURE 5: IFT values of 4,000 ppm of AS surfactant prepared in different salts with crude oil at 80°C.

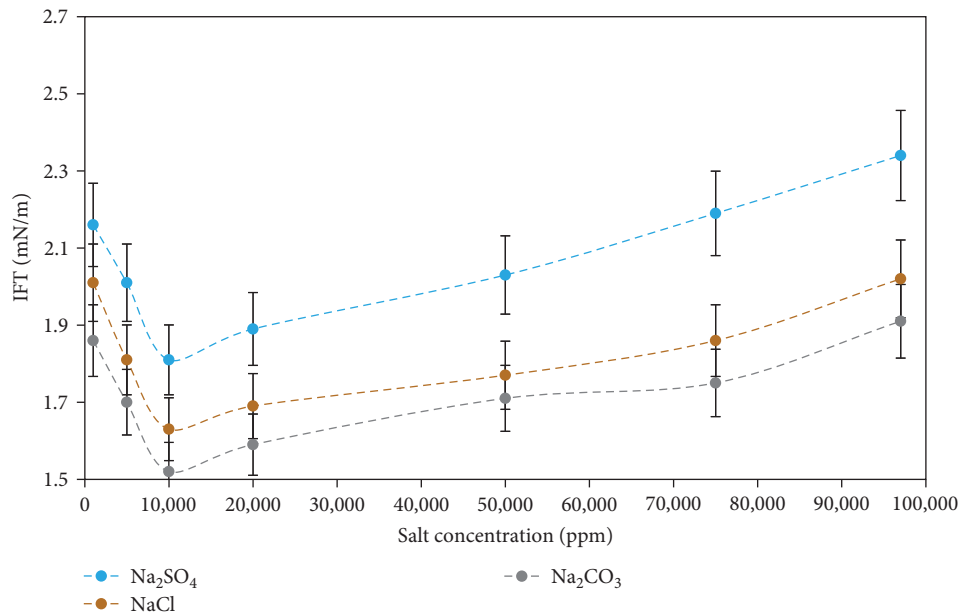


FIGURE 6: IFT values of 4,000 ppm of AS surfactant and 2,000 ppm of NaOH prepared in different salts with crude oil at 80°C.

10,000 ppm, which resulted in the lowest contact angle value. The maximum contact angle is achieved when 1,000 ppm salt is used, and further increasing the salt concentration reduced the contact angle sharply, and further increasing the concentration to 97,000 ppm increased the contact angle. The optimum contact angles at 10,000 ppm salt concentration are 36.58°, 40.76°, and 44.18° with Na₂CO₃, NaCl, and Na₂SO₄, respectively.

These findings suggest that the optimum salt concentration is due to the salting-in and salting-out phenomenon, which occurs at low and high concentrations of salt in

solution, resulting in 10,000 ppm being the optimum salt concentration. Among the three tested salts, Na₂CO₃ performed better than the other two in decreasing the contact angle value. The in situ generation of soap due to the reaction of the carboxylic content of crude oil and the alkaline part of Na₂CO₃ results in favorable conditions for wettability modification in the presence of Na₂CO₃. On the other hand, the synergism between acidic salt and AS surfactant is the determining factor in altering rock wettability. The acidic strength of SO₄²⁻ is higher than Cl⁻, which results in a higher synergism between NaCl and natural surfactant compared with

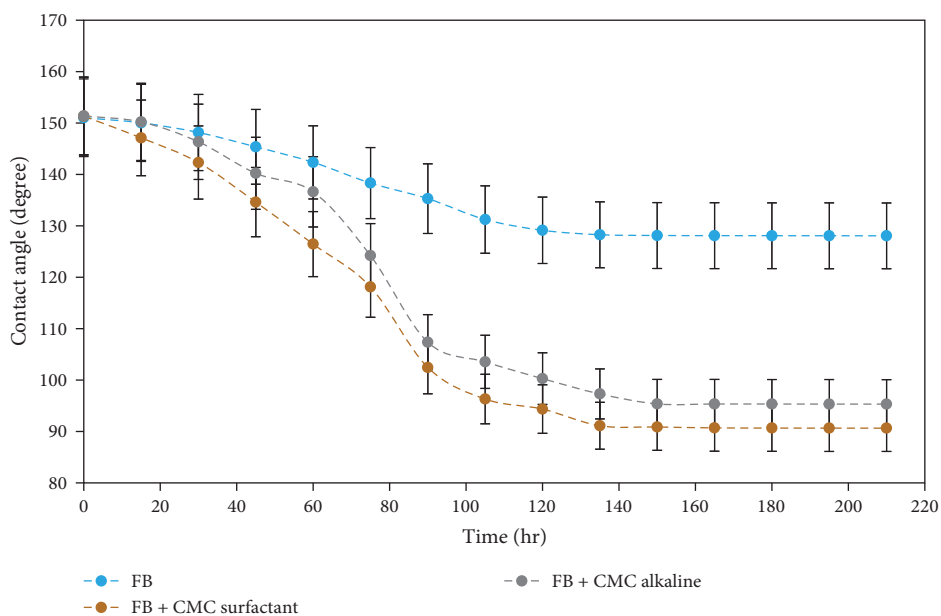


FIGURE 7: Contact angle results of FB prepared in 4,000 ppm of AS surfactant and 2,000 ppm of NaOH with crude oil at 80°C.

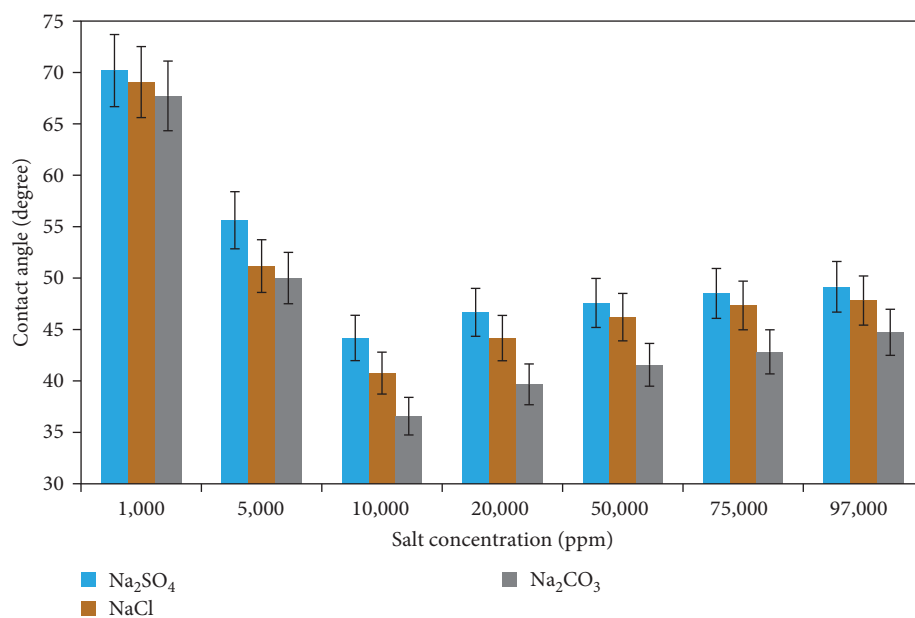


FIGURE 8: Contact angle results of different salts prepared in 4,000 ppm of AS surfactant and crude oil at 80°C after 150 hr.

Na₂SO₄ and natural surfactant in changing the rock wettability [28–31].

The wettability of carbonate rock is a complex phenomenon that can be influenced by various factors. One of the critical factors that affect the wettability of carbonate rock is carbonate rock minerals [9]. In this investigation, the mechanisms that alter the wettability of carbonate rock from oil-wet to water-wet states have been investigated. The first step in the study was to confirm that the original components of the carbonate rocks were magnesium and calcium components. These positively charged sites can decrease the contact angle between the rock surface and

fluids [32]. However, it was observed that the interaction between oil molecules and Mg²⁺ is weaker than that of Ca²⁺ due to the larger hydration energy of Mg²⁺ [33]. Moreover, the link between carboxylate and Ca²⁺ is stronger than the bond between carboxylate and Mg²⁺. This can result in reduced oil component adsorption on the carbonate surface, leading to a change in wettability toward a water-wetting state [34].

Another significant mechanism for the adsorption of surfactants to alter the wettability of carbonate rock is the electrostatic attraction forces between negatively charged hydroxyl groups and positively charged carbonate rock

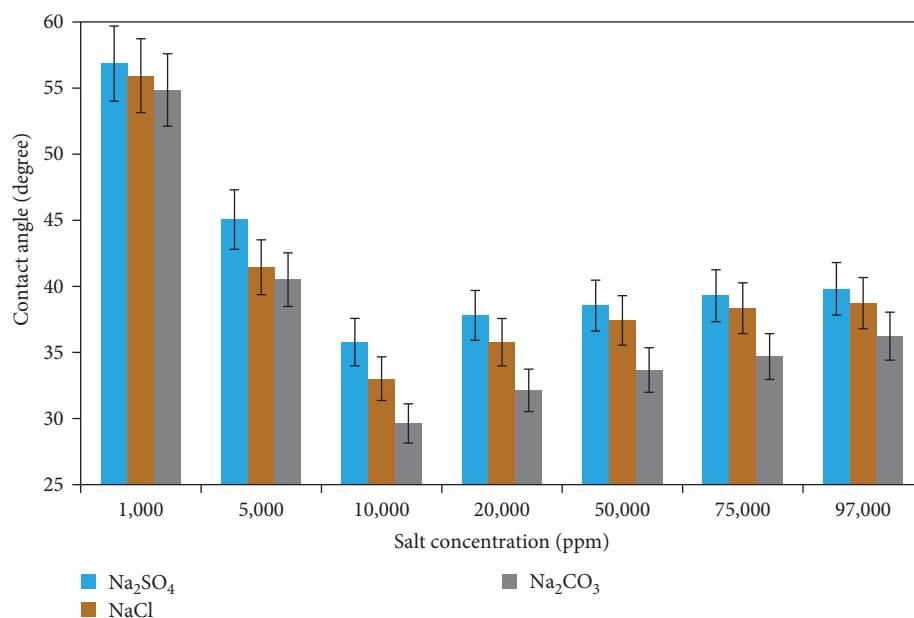


FIGURE 9: Contact angle results of different salts prepared in 2,000 ppm of NaOH and crude oil at 80°C after 150 hr.

surfaces. This mechanism is called the adsorption mechanism, which is further supported by the FT-IR results showing that the extracted saponin from the AS, as the natural surfactant, possesses hydroxyl groups, each having a negative charge. Therefore, these mechanisms can work together to change the wettability of carbonate rock from oil-wetting to water-wetting states. The study findings highlight the importance of understanding the mechanisms that control wettability alteration in carbonate rocks, which can have implications for oil recovery in carbonate reservoirs [9, 35].

Figure 9 presents the contact angle measurements when different salts were prepared in 2,000 ppm NaOH and 4,000 ppm of AS surfactant. The gained contact angle results showed that the lowest contact angle values were achieved at the optimum salt concentration of 10,000 ppm. At any concentration above this point, the contact angle increased slightly, which was due to the salting-out effect. The minimum contact angles of 35.79°, 33.02°, and 29.63° were achieved at 10,000 ppm salt concentration when the optimum amount of alkaline and AS surfactant was utilized in the sample solution. This finding suggests that NaOH is highly compatible with the AS surfactant and salts for wettability modification toward a water-wet state. However, the synergism of NaOH and AS surfactant was higher with salts in the order of Na₂CO₃, NaCl, and Na₂SO₄. Moreover, the addition of NaOH to the surfactant solution and different salts resulted in an average 9° further reduction in the contact angle compared with the solution without alkaline. Based on the obtained results, it is clear that adding NaOH to the natural surfactant and salts was very effective in reducing contact angle values.

3.4. Effect of AS Surfactant and Alkaline on Zeta Potential Measurements. Figure 10 presents the zeta potential results of various solutions made with 4,000 ppm of AS surfactant, 1,500 ppm NaOH, and 10,000 ppm of various salts with rock

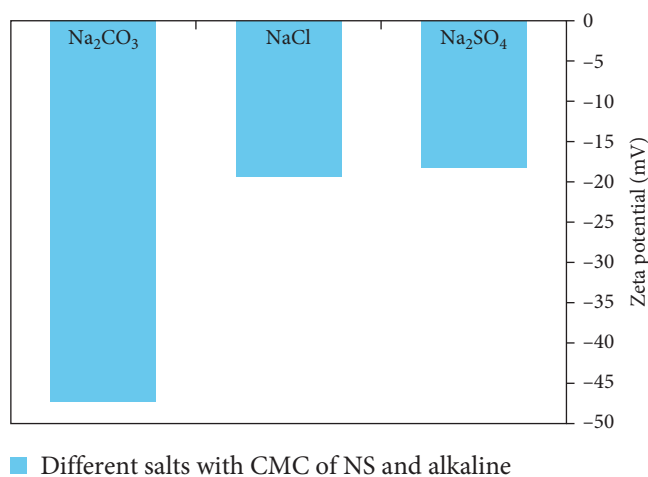


FIGURE 10: Zeta potential measurements of various solutions at 80°C.

powder. As shown in this figure, the zeta potential results are negative for all three solutions; however, the values are different. For the solution prepared in Na₂SO₄, the zeta potential value is -18.21 mV, and it is -19.34 mV for the NaCl and 47.36 mV for NaCl and Na₂CO₃, respectively.

In order to investigate the impact of the natural green surfactant on the electrostatic charge of various solutions at the carbonate rock interface, zeta potential measurements were conducted. A direct correlation was found between the zeta potential and contact angle values, with a lower contact angle corresponding to a lower (more negative) zeta potential. The thick electrical double-layer expansion at the brine, rock, and crude oil interface resulted in a higher negative value of the zeta potential, leading to a more water-wetting state by increasing the repulsive forces at the rock-brine interface.

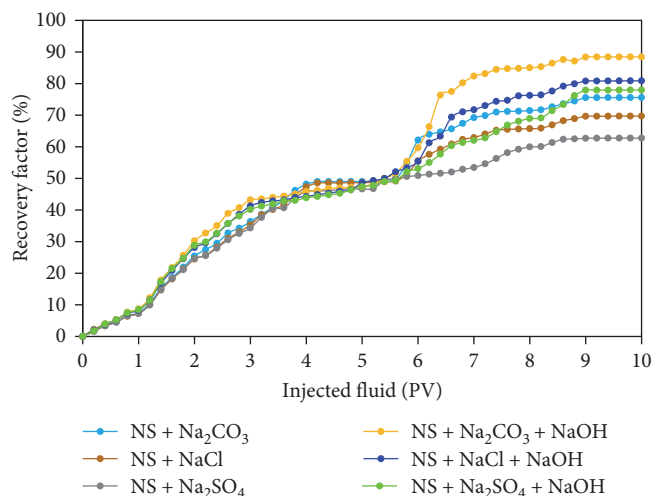


FIGURE 11: Oil recovery factor using different fluids as the tertiary recovery.

The AS surfactant was found to be responsible for altering the surface charge, resulting in this phenomenon. When the CMC value of the AS green surfactant is added to the solution, a condition is formed for more negativity to be achieved with the surface charge, leading to a higher negative zeta potential value with the surfactant. Moreover, adding NaOH to the solution also resulted in further negativity for all three tested salts. In other words, increasing the repulsive force of salt and carbonate rock results in the creation of a thicker water film around the rock surface and makes the rock surface more water-wet [9, 10, 25, 36, 37].

3.5. Oil Recovery Measurements. Figure 11 shows the oil recovery measurements during six different fluid injections as the tertiary recovery. The first three fluids were composed of 5 PVs of AS surfactant prepared in various salts, and the other three fluids were 1 PV of NaOH injection followed by 4 PVs of natural green surfactant prepared in different salts. Table 3 also presents the final recovery factor during tertiary recovery with different fluids.

The recovery factor measurement results showed that the recovery factor increased significantly during tertiary recovery, regardless of the fluid type injected. As the results show, when only the natural surfactant was injected for the tertiary recovery, the maximum recovery factors of 75.60%, 69.72%, and 62.75% were achieved with 4,000 ppm of AS surfactant prepared in Na_2CO_3 , NaCl, and Na_2SO_4 , respectively. These findings also confirm the IFT and contact angle measurement results showing that Na_2CO_3 was most compatible with the AS surfactant, followed by NaCl and Na_2SO_4 . In addition, when 1 PV of NaOH was injected as the pre-flush, followed by 4 PVs of natural surfactant, the recovery factor was significantly increased. The final recovery factors of 88.45%, 80.87%, and 77.98% were achieved using Na_2CO_3 , NaCl, and Na_2SO_4 , respectively. The recovery factor measurement results showed that the injection of NaOH as pre-flush resulted in an increase of 12.85%, 11.15%, and 15.23% with Na_2CO_3 , NaCl, and Na_2SO_4 , respectively.

TABLE 3: Final recovery factors using different fluids as the tertiary recovery.

Injected fluid as the tertiary recovery	Maximum recovery factor (%)
$\text{Na}_2\text{CO}_3 + \text{NS}$	75.60
$\text{NaCl} + \text{NS}$	69.72
$\text{Na}_2\text{SO}_4 + \text{NS}$	62.75
$\text{Na}_2\text{CO}_3 + \text{NaOH} + \text{NS}$	88.45
$\text{NaCl} + \text{NaOH} + \text{NS}$	80.87
$\text{Na}_2\text{SO}_4 + \text{NaOH} + \text{NS}$	77.98

In this study, it has been concluded that the use of AS green surfactant can increase oil recovery through two dominant mechanisms. The first mechanism is the IFT reduction, which is discussed in Section 3.2. The second mechanism is changing the wettability of the carbonate rock from hydrophobic to hydrophilic states, which is discussed in Section 3.3. These two mechanisms have proven to be effective in increasing oil recovery using AS green surfactant. The results of this study from core flooding experiments are in agreement with similar studies that have also used natural surfactants. The findings of this study are in good agreement with the literature [10, 11, 36–39].

4. Conclusion

This investigation aimed to evaluate the performance of a natural surfactant derived from AS in combination with three different salts and the addition of NaOH as a supplementary chemical. Various experiments, including IFT, contact angle, zeta potential, and recovery factor measurements, were conducted. The positive results of this investigation can have a significant impact on sustainable crude oil production from carbonate reservoirs. The successful use of AS as a natural surfactant in this study can lead to further research and development in this area. Moreover, it can help reduce the dependence on synthetic surfactants, which can have negative environmental impacts. The findings of the research could be summarized as follows:

- (i) According to the results, it was found that the optimum salt concentration for minimum IFT and contact angle values for all three tested salts was 10,000 ppm. These results suggest that salting-in and salting-out impacts are the reasons for having an optimum concentration of salt in terms of IFT and contact angle reduction.
- (ii) Based on the findings, the different ions present in the salts affected the maximum compatibility of the natural surfactant with Na_2CO_3 , followed by NaCl and Na_2SO_4 , in terms of contact angle and IFT reduction.
- (iii) The addition of NaOH as a chemical supplement was proven to be effective in enhancing the performance of the natural surfactant under reservoir conditions. The minimum IFT values between Na_2CO_3 , NaCl, and Na_2SO_4 in the presence of the CMC value

of surfactant and alkaline were 1.52, 1.63, and 1.81 mN/m, respectively.

- (iv) The results showed that NaOH is highly compatible with the AS surfactant and salts for wettability modification toward a water-wet condition. The minimum contact angles of 35.79°, 33.02°, and 29.63° were achieved at 10,000 ppm salt concentration when the optimum amount of alkaline and AS surfactant was utilized in the sample solution.
- (v) The highest oil recovery factor of 88.45% was obtained when the AS natural surfactant and NaOH were combined at their CMC points with Na₂CO₃ and injected as tertiary recovery.
- (vi) Based on the obtained results, it was confirmed that the IFT reduction and wettability alteration of carbonate rock were the primary mechanisms in improving oil recovery.

Data Availability

Data will be available on request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors would like to express their appreciation to the Department of Petroleum Engineering, Faculty of Engineering, Marvdasht Islamic Azad University, Marvdasht, Iran, for providing the lab space needed to conduct the tests.

References

- [1] M. Norouzpour, M. Nabipour, A. Azdarpour, and R. M. Santos, "Isolating the effect of asphaltene content on enhanced oil recovery during low salinity water flooding of carbonate reservoirs," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, pp. 1–14, 2020.
- [2] A. N. Haghghi, M. Nabipour, A. Azdarpour, and B. Honarvar, "Mechanistic investigation of using optimum saline water in carbonate reservoirs low asphaltenic crude oil with high resin content: a carbonate-coated microfluidic study," *Journal of Molecular Liquids*, vol. 368, Part B, Article ID 120806, 2022.
- [3] A. Azdarpour, O. Rahmani, E. Mohammadian, M. Parak, A. R. M. Daud, and R. Junin, "The effects of polymer and surfactant on polymer enhanced foam stability," in *2013 IEEE Business Engineering and Industrial Applications Colloquium (BEIAC)*, pp. 97–102, Langkawi, Malaysia, 2013.
- [4] S. Qazvini, A. Golkari, A. Azdarpour, R. M. Santos, M. S. Safavi, and M. Norouzpour, "Experimental and modelling approach to investigate the mechanisms of formation damage due to calcium carbonate precipitation in carbonate reservoirs," *Journal of Petroleum Science and Engineering*, vol. 205, Article ID 108801, 2021.
- [5] A. Esfandiarian, A. Azdarpour, R. M. Santos et al., "Mechanistic investigation of LSW/Surfactant/Alkali synergism for enhanced oil recovery: fluid–fluid interactions," *ACS Omega*, vol. 5, no. 46, pp. 30059–30072, 2020.
- [6] A. B. Chhetri, K. C. Watts, M. S. Rahman, and M. R. Islam, "Soapnut extract as a natural surfactant for enhanced oil recovery," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 31, no. 20, pp. 1893–1903, 2009.
- [7] S. Moradi, A. A. Isari, Z. Bachari, and H. Mahmoodi, "Combination of a new natural surfactant and smart water injection for enhanced oil recovery in carbonate rock: synergic impacts of active ions and natural surfactant concentration," *Journal of Petroleum Science and Engineering*, vol. 176, pp. 1–10, 2019.
- [8] A. Nafisifar, A. K. Manshad, and S. R. Shadizadeh, "Evaluation of a new green synthesized surfactant from linseeds-chemical EOR implications from sandstone petroleum reservoirs," *Journal of Molecular Liquids*, vol. 342, Article ID 117263, 2021.
- [9] M. Norouzpour, A. Azdarpour, M. Nabipour et al., "Red beet plant as a novel source of natural surfactant combined with 'Smart Water' for EOR purposes in carbonate reservoirs," *Journal of Molecular Liquids*, vol. 370, Article ID 121051, 2023.
- [10] B. Sami, A. Azdarpour, B. Honarvar, M. Nabipour, and A. Keshavarz, "Application of a novel natural surfactant extracted from *Avena sativa* for enhanced oil recovery during low salinity water flooding: synergism of natural surfactant with different salts," *Journal of Molecular Liquids*, vol. 362, Article ID 119693, 2022.
- [11] M. Norouzpour, M. Nabipour, A. Azdarpour, H. Akhondzadeh, R. M. Santos, and A. Keshavarz, "Experimental investigation of the effect of a quinoa-derived saponin-based green natural surfactant on enhanced oil recovery," *Fuel*, vol. 318, Article ID 123652, 2022.
- [12] I. Nowrouzi, A. H. Mohammadi, and A. K. Manshad, "Double-chain single-head modification of extracted saponin from *Anabasis Setifera* plant and its effects on chemical enhanced oil recovery process by surfactant-alkali slug injection into carbonate oil reservoirs," *Journal of Petroleum Science and Engineering*, vol. 201, Article ID 108438, 2021.
- [13] I. Nowrouzi, A. H. Mohammadi, and A. K. Manshad, "Characterization and likelihood application of extracted mucilage from *Hollyhocks* plant as a natural polymer in enhanced oil recovery process by alkali-surfactant-polymer (ASP) slug injection into sandstone oil reservoirs," *Journal of Molecular Liquids*, vol. 320, Article ID 114445, 2020.
- [14] M. A. Ahmadi, Y. Arabsahebi, S. R. Shadizadeh, and S. S. Behbahani, "Preliminary evaluation of mulberry leaf-derived surfactant on interfacial tension in an oil-aqueous system: EOR application," *Fuel*, vol. 117, Part A, pp. 749–755, 2014.
- [15] N. Yekeen, A. A. Malik, A. K. Idris, N. I. Reepei, and K. Ganie, "Foaming properties, wettability alteration and interfacial tension reduction by saponin extracted from soapnut (*Sapindus mukorossi*) at room and reservoir conditions," *Journal of Petroleum Science and Engineering*, vol. 195, Article ID 107591, 2020.
- [16] S. Emadi, S. R. Shadizadeh, A. K. Manshad, A. M. Rahimi, I. Nowrouzi, and A. H. Mohammadi, "Effect of using *Zyziphus Spina Christi* or *Cedr Extract* (CE) as a natural surfactant on oil mobility control by foam flooding," *Journal of Molecular Liquids*, vol. 293, Article ID 111573, 2019.
- [17] N. Saxena, A. Goswami, P. K. Dhodapkar, M. C. Nihalani, and A. Mandal, "Bio-based surfactant for enhanced oil recovery: interfacial properties, emulsification and rock–fluid interactions," *Journal of Petroleum Science and Engineering*, vol. 176, pp. 299–311, 2019.

- [18] N. Saxena, N. Pal, S. Dey, and A. Mandal, "Characterizations of surfactant synthesized from palm oil and its application in enhanced oil recovery," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 81, pp. 343–355, 2017.
- [19] S. Kumar, N. Saxena, and A. Mandal, "Synthesis and evaluation of physicochemical properties of anionic polymeric surfactant derived from Jatropha oil for application in enhanced oil recovery," *Journal of Industrial and Engineering Chemistry*, vol. 43, pp. 106–116, 2016.
- [20] H. Imuetinyan, A. Agi, A. Gbadamosi, R. Junin, and J. Oseh, "Oil–water interfacial tension, wettability alteration and foaming studies of natural surfactant extracted from *Vernonia amygdalina*," *Petroleum Research*, vol. 7, no. 3, pp. 350–356, 2022.
- [21] W. Chen and D. S. Schechter, "Surfactant selection for enhanced oil recovery based on surfactant molecular structure in unconventional liquid reservoirs," *Journal of Petroleum Science and Engineering*, vol. 196, Article ID 107702, 2021.
- [22] H. Deymeh, S. R. Shadizadeh, and R. Motafakkerfard, "Experimental investigation of *Seidlitzia rosmarinus* effect on oil–water interfacial tension: usable for chemical enhanced oil recovery," *Scientia Iranica*, vol. 19, no. 6, pp. 1661–1664, 2012.
- [23] P. Mehrabianfar, H. Bahraminejad, and A. K. Manshad, "An introductory investigation of a polymeric surfactant from a new natural source in chemical enhanced oil recovery (CEOR)," *Journal of Petroleum Science and Engineering*, vol. 198, Article ID 108172, 2021.
- [24] A. Maghsoudian, A. Esfandiarian, S. Kord, Y. Tamsilian, and B. Soltani Soulgani, "Direct insights into the micro and macro scale mechanisms of symbiotic effect of SO_4^{2-} , Mg^{2+} , and Ca^{2+} ions concentration for smart waterflooding in the carbonated coated micromodel system," *Journal of Molecular Liquids*, vol. 315, Article ID 113700, 2020.
- [25] M. Lashkarbolooki, S. Ayatollahi, and M. Riazi, "Mechanistic study of effect of ions in smart water injection into carbonate oil reservoir," *Process Safety and Environmental Protection*, vol. 105, pp. 361–372, 2017.
- [26] A. Goyal, P. Singh, P. Chamoli, K. K. Raina, and R. K. Shukla, "Eco-friendly biowaste-based natural surfactant for lyotropic assemblies and bio-adsorbent for dye removal," *Inorganic Chemistry Communications*, vol. 133, Article ID 108871, 2021.
- [27] N. Pal, N. Saxena, and A. Mandal, "Characterization of alkali-surfactant-polymer slugs using synthesized gemini surfactant for potential application in enhanced oil recovery," *Journal of Petroleum Science and Engineering*, vol. 168, pp. 283–300, 2018.
- [28] I. Nowrouzi, A. H. Mohammadi, and A. K. Manshad, "Water–oil interfacial tension (IFT) reduction and wettability alteration in surfactant flooding process using extracted saponin from *Anabasis Setifera* plant," *Journal of Petroleum Science and Engineering*, vol. 189, Article ID 106901, 2020.
- [29] N. Saxena, A. Kumar, and A. Mandal, "Adsorption analysis of natural anionic surfactant for enhanced oil recovery: the role of mineralogy, salinity, alkalinity and nanoparticles," *Journal of Petroleum Science and Engineering*, vol. 173, pp. 1264–1283, 2019.
- [30] H. R. Afifi, S. Mohammadi, A. M. Derazi et al., "A comprehensive review on critical affecting parameters on foam stability and recent advancements for foam-based EOR scenario," *Journal of Molecular Liquids*, Article ID 116808, 2021.
- [31] H. Khayati, A. Moslemizadeh, K. Shahbazi, M. K. Moraveji, and S. H. Riazi, "An experimental investigation on the use of saponin as a non-ionic surfactant for chemical enhanced oil recovery (EOR) in sandstone and carbonate oil reservoirs: IFT, wettability alteration, and oil recovery," *Chemical Engineering Research and Design*, vol. 160, pp. 417–425, 2020.
- [32] S.-P. Mousavi, A. Hemmati-Sarapardeh, S. Norouzi-Apourvari, M. Jalalvand, M. Schaffie, and M. Ranjbar, "Toward mechanistic understanding of wettability alteration in calcite and dolomite rocks: the effects of resin, asphaltene, anionic surfactant, and hydrophilic nano particles," *Journal of Molecular Liquids*, vol. 321, Article ID 114672, 2021.
- [33] A. Aminian and B. ZareNezhad, "Wettability alteration in carbonate and sandstone rocks due to low salinity surfactant flooding," *Journal of Molecular Liquids*, vol. 275, pp. 265–280, 2019.
- [34] M. Karimi, R. S. Al-Maamari, S. Ayatollahi, and N. Mehranbod, "Mechanistic study of wettability alteration of oil-wet calcite: the effect of magnesium ions in the presence and absence of cationic surfactant," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 482, pp. 403–415, 2015.
- [35] M. A. Ahmadi and S. R. Shadizadeh, "Spotlight on the new natural surfactant flooding in carbonate rock samples in low salinity condition," *Scientific Reports*, vol. 8, Article ID 10985, 2018.
- [36] P. Ahmadi, H. Asaadian, A. Khadivi, and S. Kord, "A new approach for determination of carbonate rock electrostatic double layer variation towards wettability alteration," *Journal of Molecular Liquids*, vol. 275, pp. 682–698, 2019.
- [37] I. Nowrouzi, A. K. Manshad, and A. H. Mohammadi, "Effects of TiO_2 , MgO , and $\gamma\text{-Al}_2\text{O}_3$ nano-particles in carbonated water on water–oil interfacial tension (IFT) reduction in chemical enhanced oil recovery (CEOR) process," *Journal of Molecular Liquids*, vol. 292, Article ID 111348, 2019.
- [38] A. K. Manshad, I. Nowrouzi, and A. H. Mohammadi, "Effects of water soluble ions on wettability alteration and contact angle in smart and carbonated smart water injection process in oil reservoirs," *Journal of Molecular Liquids*, vol. 244, pp. 440–452, 2017.
- [39] A. K. Manshad, M. Olad, S. A. Taghipour, I. Nowrouzi, and A. H. Mohammadi, "Effects of water soluble ions on interfacial tension (IFT) between oil and brine in smart and carbonated smart water injection process in oil reservoirs," *Journal of Molecular Liquids*, vol. 223, pp. 987–993, 2016.