Application of Water-Soluble Polymer/Biopolymer Combined with a Biosurfactant in Oil-Wet Fractured Carbonate Reservoirs

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ABSTRACT: Most fractured carbonate reservoirs are characterized by a highly permeable fracture zone surrounded by a low-permeability oil-wet matrix. These features make the displacement of oil from the matrix into the fracture zone almost impossible during water flooding. This paper presents the results of flooding with the polymer polyacrylamide (PAM) and the biopolymer xanthan gum (XG) in combination with a biosurfactant to enhance water imbibition into oil-wet fractured carbonate rocks. Core flooding experiments were conducted on induced horizontally fractured (at 180°) carbonate cores in room conditions (20 ± 2 °C). The polymer or biopolymer was used to plug the fracture zones, while the biosurfactant was added to the system to alter the wettability state of the rock matrix from oil-wet to water-wet. Rock surface characterization before and after core flooding was conducted using scanning electron microscopy (SEM). The results indicate that PAM flooding led to a higher reduction of 35.6% in fracture-matrix permeability than that with XG at 18.3%. The monitoring of oil production also showed that ultimate oil recovery levels from oil-wet fractured carbonate cores for the aforementioned systems were 16 and 8.7%, respectively, which can be attributed to the drive mechanisms of temporary fracture plugging as well as mobility ratio improvement due to the polymer and wettability alteration by the biosurfactant. SEM images confirm the proposed mechanisms, where the presence of the polymer/biopolymer followed by the biosurfactant can be detected at the rock surface as a result of chemical flow through the system.
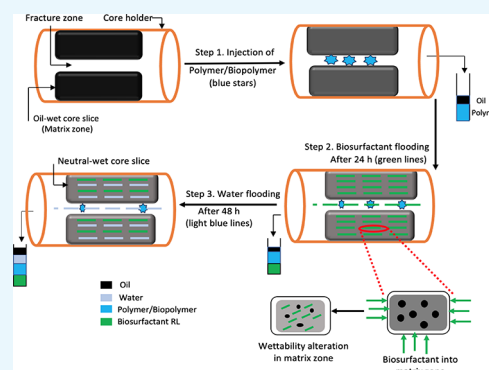
1. INTRODUCTION

Enhanced oil recovery (EOR), also known as tertiary recovery, will play an important role in the oil industry for decades to come.[1,2] This is due to the low oil recovery rates of the primary and secondary approaches, through which only 30−40% of the original oil in place (OOIP) can be recovered.[3,4] Over 50% of total hydrocarbon reservoirs in the world are of the carbonate type,[5,6] and the majority of carbonate reservoirs are naturally fractured formations located mostly in the Middle East.[7] Oil recovery from such reservoirs is a substantial challenge for the oil industry due to their complexity.[8]

There are two flow regimes in a naturally fractured carbonate reservoir, which can be characterized by a highly permeable fracture zone surrounding a low-permeability matrix zone.[9−11] Water flooding is the easiest and cheapest approach used to enhance the production of oil from water-wet reservoirs. However, most fractured carbonate reservoirs are oil-wet, which makes conditions complex and critical, resulting in poor rates of oil recovery.[12,13] In fractured carbonate reservoirs, oil production mainly depends on the water imbibition process to extract the oil present from the matrix network toward the fracture zone. There are several parameters that can affect the imbibition process, such as boundary conditions and the size and shape, matrix permeability, and

heterogeneity of the reservoirs. To improve recovery performance and enhancing the water imbibition process, chemical EOR and bio-EOR methods such as polymer, biopolymer, and biosurfactant flooding are highly recommended.[14]

Polymer injection has been used in the oil industry since the 1960s to improve sweep efficiency by increasing water viscosity.[15−18] For example, Cheraghian et al.[19] conducted experiments on the development of the thermal stability of the PAM system as a nanofluid in the EOR process. The results showed that oil recovery can be improved by adding nanoparticles to PAM solutions under reservoir conditions. Khalili Nezhad and Cheraghian[20] carried out another experiment to improve oil recovery, and the results showed a positive effect in the EOR process using PAM solutions in the presence of clay nanoparticles. Polymeric systems can also be used as a temporary plugging agent in fractured carbonate reservoirs to
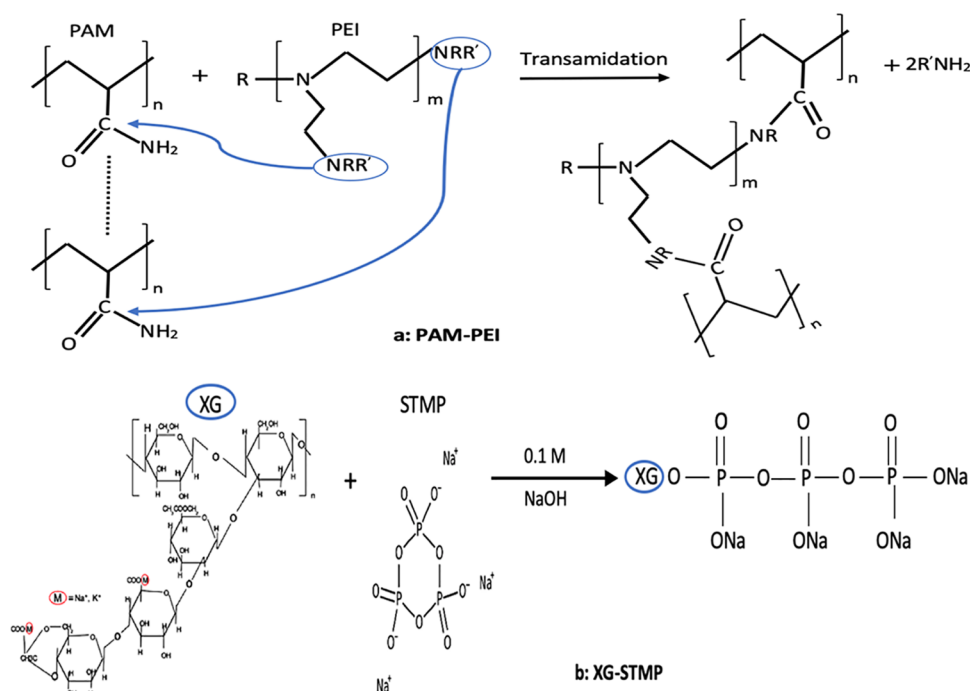
Figure 1. Cross-linking reaction: (a) PAM-PEI and (b) XG-STMP.

reduce permeability in the fracture zones.[21] The results of a study by Shedid[22] on the effect of water and polymer injection in fractured carbonate reservoirs revealed that the highest oil production was observed when polymer flooding was used rather than water flooding. Zhang et al.[23] conducted an experiment to determine the effect of gel particles and the HPAM/Cr^{3+} system on plugging in a fractured oil reservoir. Their results indicated that oil recovery could be increased to 18.5% by using gel particles, and then adding HPAM/Cr^{3+} to the system led to oil recovery up to 29%. Similar observations have been reported for the plugging of fracture zones to improve oil production in fractured carbonate reservoirs when polymer gel is used.[24−26]

Biosurfactant flooding is another important bio-EOR technique. Biosurfactants can reduce the interfacial tension (IFT) between the oil and water phases and also change the wettability state of the matrix from oil-wet to water-wet; hence, water can move easily through the rock pores due to reductions in capillary forces.[27−29] Recently, Cheng et al.[30] have studied the effect of surfactant flooding in a fractured core, and their results indicated that the movement of the surfactant through the matrix depends strongly on diffusion so that increasing the injection rate led to increased oil recovery. Spinler et al.[31] carried out an experiment using a surfactant in chalk cores to enhance forced and spontaneous imbibition. Their results indicated that, even with a low concentration of the surfactant, oil recovery can be improved.

It is suggested that flooding with both the surfactant and polymer (SP flooding) can be used as an effective approach in the EOR process to change the wettability of reservoir rocks as well as plugging high-permeability zones.[32] Sayed Akram and Mamora[33] conducted a simulation study of polymer-surfactant injection in fractured carbonate reservoirs, and the results showed that such flooding can improve oil recovery. Since various chemicals for EOR are available to increase oil production in fractured carbonate reservoirs, where each has specific advantages and disadvantages, it is challenging to

determine the best chemical EOR methods in the most ideal approaches to fulfill all requirements.[34,35]

In this study, PAM and XG were selected to represent the polymer and biopolymer, respectively, as potential chemicals for EOR and bio-EOR due to their low cost and ability to decrease water mobility and increase its viscosity.[36] On the other hand, environmentally friendly biosurfactant rhamnolipid was also combined with those chemicals to enhance the water wetness of oil-wet carbonate as well as the interfacial activities of rock/water/oil interfaces.[37]

Although a significant volume of research has been carried out on the effects of chemical EOR in production from sandstone reservoirs, there have been few publications relating to chemical EOR in fractured carbonate reservoirs. Water flooding alone cannot be performed in fractured carbonate reservoirs due to a large contrast between fracture and matrix permeability as well as the rock matrix being in a strongly oil-wet state. This research proposes a new approach to solve this problem and reap the benefits of water flooding, where the fractured zones are temporarily plugged with the polymer PAM and biopolymer XG to divert the water into the matrix zones. After that, the wettability state of the strongly oil-wet rock matrix is modified toward a water-wet state using biosurfactant RL following the injection of polymeric solutions. Furthermore, a comparison of the performance of polymer PAM and biopolymer XG is conducted.

2. RESULTS AND DISCUSSION

Before starting core flooding, the polymeric solutions were prepared by mixing the polymer with an appropriate cross-linker. Figure 1 illustrates the cross-linking reactions of PAM-PEI and XG-STMP. The PAM-PEI system produces gels through the transamidation mechanism,[38] in which the amine nitrogen in the PEI structure reacts with the amide group within the structure of PAM to produce PAM-PEI gelation (Figure 1a).

In the cross-linked biopolymer reaction presented in Figure 1b, the structure of STMP is that of a cyclic triphosphate, which makes it difficult for it to react with XG. Therefore, NaOH was added to break down the cyclic triphosphate within the STMP. After that, the hydroxyl group on the XG chains reacts with the STMP to produce PAM-STMP gelation.[39]

After preparation of the cross-linked polymer/biopolymer solutions, their values of viscosity against the shear rate were measured and are presented in Figure 2. As can be seen in this
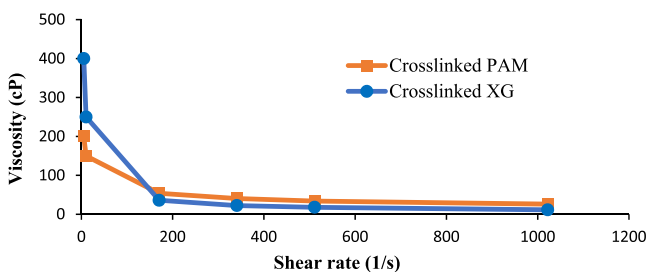
Figure 2. Viscosities of the cross-linked polymer and biopolymer at 20 ± 2 °C.

figure, both solutions behave similarly at higher shear rates, while the biopolymer is more viscous at lower shear rates. If we translate this behavior into flow regimes near to and far from the wellbore, it could be concluded that both polymeric solutions would behave similarly near the wellbore with higher shear rates. However, far from the wellbore, the biopolymer would retain more of its gelation properties compared to the polymer, and hence, better performance would be expected from the biopolymer. The impact of temperature on the rheological properties of the chemicals used in this study was reported in previous research by Elyasi Gomari et al.[16] It is interesting to note that the viscosities of both polymer and biopolymer decrease with temperature; however, a greater reduction was reported for XG compared to PAM solutions at higher temperature.

2.1. Effect of Chemical EOR and Bio-EOR on the Permeability of the Fractured-Matrix System.

Figure 3 shows the effect of the chemical EOR and bio-EOR on the permeability of fractured-matrix systems for PAM (Figure 3a) and XG (Figure 3b). It should be noted that the average water permeability (K_w) of the core samples before fracturing was measured between 12 and 15 mD (see Table 7), while after fracturing it increased to the 100−200 mD range, which can be termed the fracture-matrix permeability to water (K_{fmw}).

The whole injection into fractured plug was performed in four steps. In the first step, 6 pore volumes of distilled water were injected, and no changes were observed in fracture-matrix permeability. This is due to the high contrast between fracture permeability and matrix permeability, and because the sample is oil-wet, all water will pass through the fracture and no change in fracture-matrix permeability was recorded. Therefore, this step is not presented in Figure 3. In the second step, 6 pore volumes of polymeric solutions were injected, and the fracture-matrix permeability to water was decreased due to the plugging of the fracture by the polymeric gels. In the third step, the fracture-matrix permeability to water was increased after injection of 6 pore volumes of the biosurfactant. The reason
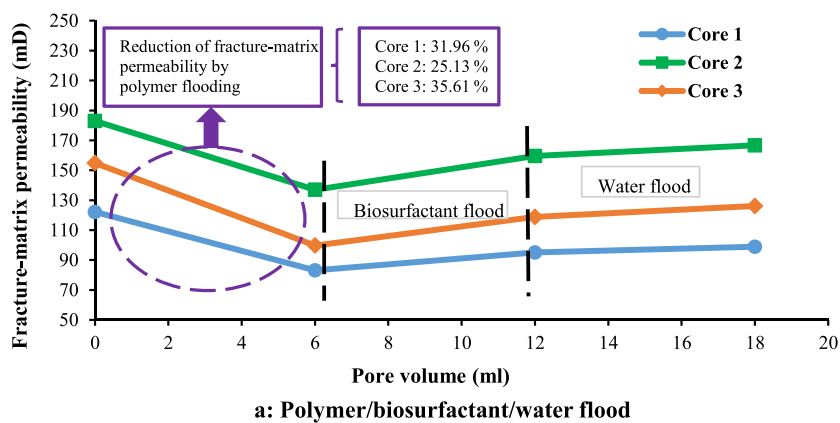
a: Polymer/biosurfactant/water flood
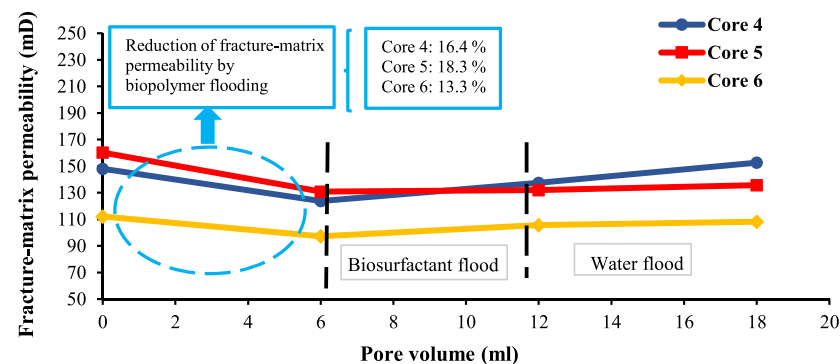
b: Biopolymer/biosurfactant/water flood

Figure 3. Effect of chemical EOR and bio-EOR on the permeability of the fractured-matrix system: (a) polymer; (b) biopolymer.
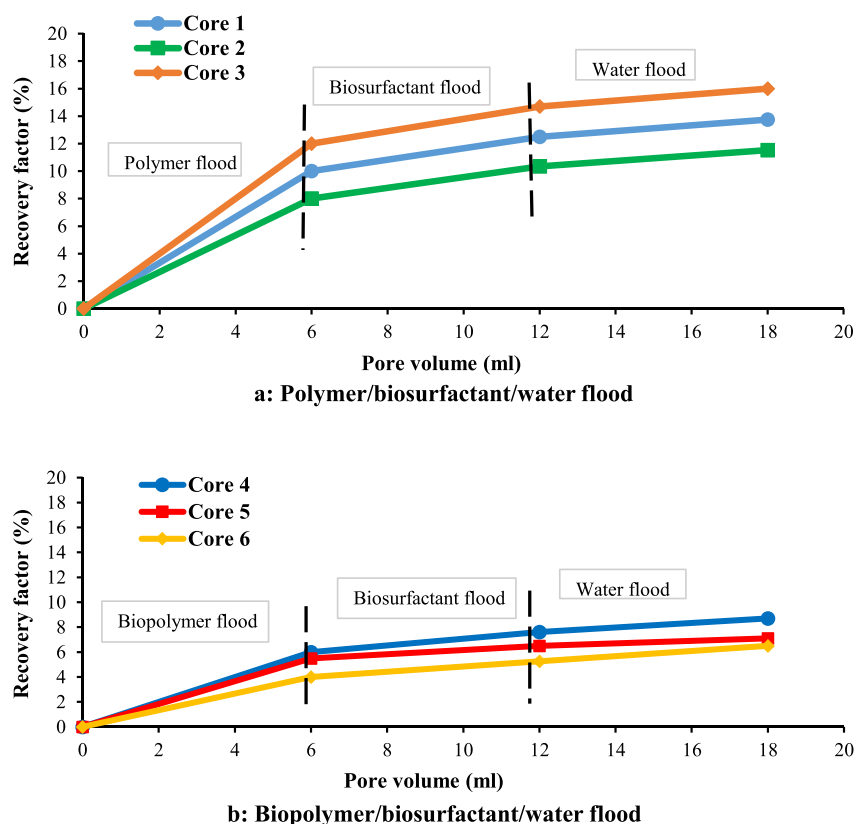
Figure 4. Effect of chemical EOR and bio-EOR on fractured carbonate reservoirs: (a) polymer; (b) biopolymer.

could be due to two main mechanisms that can happen by injection of a biosurfactant. The first mechanism is that the biosurfactant had displaced some of the polymeric gels, and the fluid moves faster in the porous and fracture system, the inference being that the polymer had temporarily plugged the fracture zones. The second mechanism is that the biosurfactant causes a reduction in IFT and wettability alteration through the system. In this scenario, the resistance of the fluid can reduce, and this resulted in the increase of the fracture-matrix permeability to water. Finally, the injection resumed by final 6 pore volumes of water where no significant change in permeability was recorded.

Overall, the fracture-matrix permeability decreased after the injection of the cross-linked polymer/biopolymer into the system. It can be seen from Figure 3a that the highest reduction in fracture-matrix permeability was observed for core 3. In fact, there was a decrease of 55.133 mD (35.61%) in fracture-matrix permeability from 154.823 to 99.69 mD for this core. Meanwhile, values of fracture-matrix permeability for cores 1 and 2 dropped by 39.045 and 45.973 mD, respectively. The reduction in permeability occurs due to the plugging of the fracture by the polymer gel.[40,41] In highly permeable zones, a polymer solution can be injected and leads to greater flow resistance in such reservoirs. Therefore, this process can improve macroscopic sweep efficiency by helping the injected water to be diverted into poorly swept zones of low permeability.[42−44] Canbolata and Parlaktunab's experimental study of the effect of polymer gel on oil recovery in fractured reservoirs showed that the permeability of fractured cores was reduced by the injection of polymer gel, hence increasing sweep efficiency.[45] The same conclusion that the permeability

of fractured carbonate reservoirs could be reduced using polymer gels has also been drawn by other authors.[46,47]

Similar results were observed when XG solutions were used (see Figure 3b), but they were not as effective as PAM. According to Figure 3b, the highest reduction in fracture-matrix permeability was observed for core 5, which was of 29.339 mD (18.3%), followed by cores 4 and 6 at 24.346 and 14.926 mD, respectively. Differences in the effect of the polymer and biopolymer in reducing fracture-matrix permeability may be due to their differences in terms of shear thinning and thickening. The received wisdom in the literature is that, in most cases, polymers and biopolymers display shear thinning behavior at different shear rates.

An example from the biopolymers is XG, which demonstrates shear-thinning flow behavior in porous media that is independent of the flow rate. Meanwhile, some polymers such as PAM can have effects that are dependent on the flow rate and may exhibit shear-thickening flow behavior. The reason for this could be that the carboxylic groups in the PAM structure release their molecular chain stretch in water. The subsequent increase in the hydrodynamic radius of the polymer molecular chain in aqueous solution thus makes the solution more viscous in porous media.[48−50] It should be noted that, after the injection of the biosurfactant and the subsequent injection of water, the fracture-matrix permeability was increased. This may be because the injected fluid had displaced some of the polymer gel, the inference being that the polymer had temporarily plugged the fracture zones.

2.2. Effect of Chemical EOR and Bio-EOR on Oil Recovery in Fractured Carbonate Reservoirs. Figure 4 illustrates the effect of the chemical EOR and bio-EOR on oil recovery versus pore volume injected into the fractured
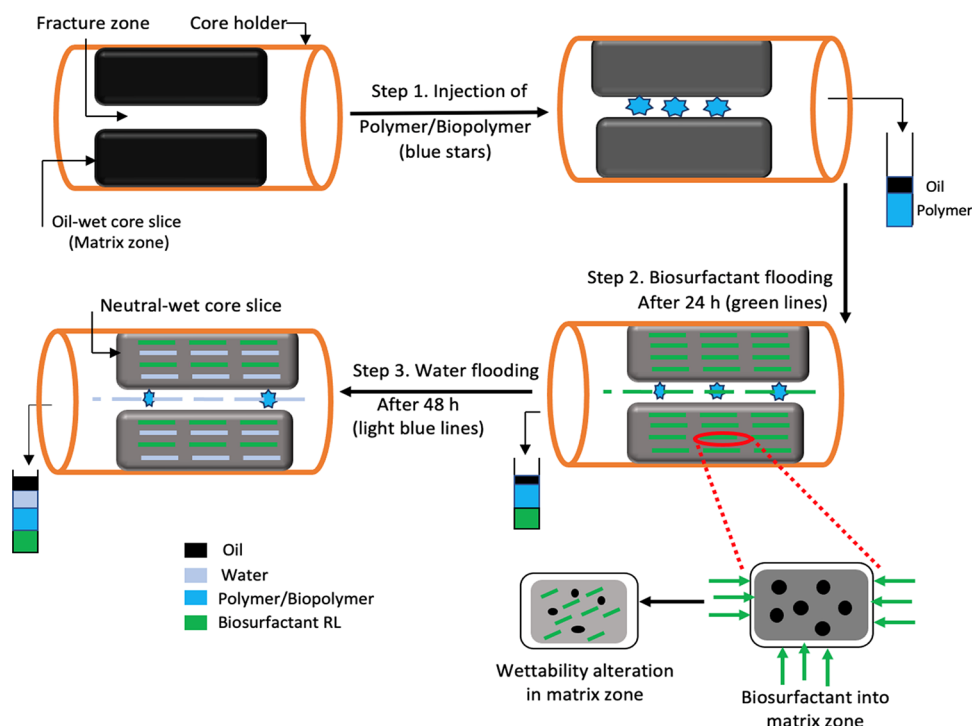
Figure 5. Schematic of the procedure applied for oil recovery measurements.
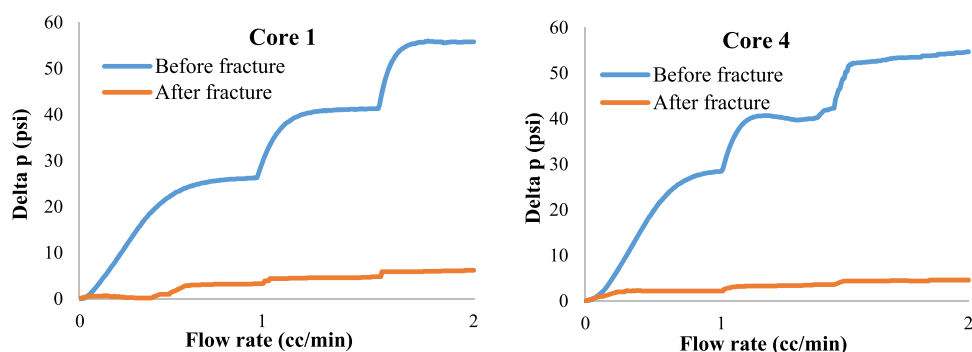

Figure 6. Effect of a fractured system on differential pressure across the core samples.

carbonate reservoirs. It should be noted that, in the first step, no oil was produced after flooding with 6 pore volumes of distilled water. This indicates that the flow mostly occurred via fracture.[12] This step is not presented in Figure 4.

The polymer or biopolymer has started right after ineffective water flooding, where, as shown in Figure 4, the oil recovery was increased by chemical EOR and bio-EOR. The highest level of oil production was obtained by the polymer and biopolymer flooding of the system, at up to 12 and 6%, respectively. Moreover, an extra 3−4% of oil recovery was achieved by employing the biosurfactant followed by the water flooding of the systems. Use of the biosurfactant leads to improved oil recovery due to the alteration in wettability and reduced IFT between the water and oil phases in porous media.[51,52] From Figure 4a, the highest improvement in oil recovery of approximately 16% was obtained in core 3 followed by core 1 at 13.75%, while core 2 exhibited the lowest improvement of 11.53%. However, it is noticeable from Figure 4b that the highest oil production obtained by biopolymer/biosurfactant/water flooding was 8.7%, which was approximately half of that achieved by flooding with the polymer/

biosurfactant/water system, as shown in Figure 4a. This may be due to the fact that the highest reduction in fracture-matrix permeability was observed when using polymer flooding as opposed to the biopolymer system (see Figure 3). Therefore, it can be concluded that there is a link between fracture-matrix permeability and oil recovery. In fact, as fracture-matrix permeability declines, oil recovery increases, which means that the polymer can plug the fracture and then the injected fluid penetrates into the rock matrix and drives the trapped oil out of the core.[53−55] Al-Hattali et al. studied the effect of microbial biomass in fractured carbonate reservoirs, and their results revealed that, by using microbial biomass, oil recovery can be increased to 27−30% due to the plugging of fractures.[56] The influence of microbial and water flooding in fractured carbonate rocks was examined by Zekri and El-Mehaideb.[57] Their results indicated that microbial flooding was capable of improving oil recovery in fractured carbonate rocks and altering the performance of the system by plugging a part of the fracturing. A study by Shedid[22] on the effect of the fracture angle on oil recovery by polymer flooding concluded that polymer injection in a fractured reservoir is strongly

recommended, supporting the present results. His results also showed that the highest oil recovery in water/polymer flooding was obtained from the horizontally fractured formation compared to other fracture orientations. In general, the results indicate that approximately 4−10% of oil recovery can be achieved in fractured carbonate reservoirs by polymer flooding, depending on various factors such as fracture-matrix permeability and orientations. However, based on Figure 4, it can be observed that polymer flooding followed by biosurfactant flooding increases oil production up to 16%, which indicates that biosurfactant flooding had a significant effect on obtaining higher oil production.

Figure 5 presents the details of the procedure applied and oil recovery mechanisms during polymer/biopolymer flooding followed by biosurfactant and water flooding. Temporary plugging of the fracture by gels followed by the alteration of the wettability of the matrix by the biosurfactant directs the oil toward fractures, hence enhancing oil production from an oil-wet fractured carbonate core plug.

2.3. Effect of Chemical EOR and Bio-EOR on the Pressure Drop across the Fractured Systems.

Figure 6 illustrates a plot of differential pressure across the core sample versus flow rate before and after fracture. Cores 1 and 4 were selected for analysis in this section. In general, it is clear that the differential pressure was high in unfractured cores, while there was a significant decline in differential pressure after fracturing. This indicates that the presence of a fracture in the rock system can act as a resistance-free channel to the flow where the injected fluid in porous media moves more easily. For example, when a polymer solution is introduced into a fractured carbonate reservoir, the polymer preferentially penetrates into the highly permeable networks rather than the matrix zones, as shown in Figure 7.
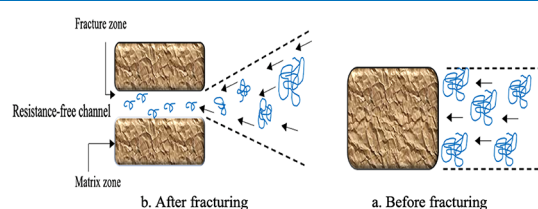

Figure 7. Polymer injection in (a) unfractured and (b) fractured core samples.

The influence of chemical EOR and bio-EOR on differential pressure across the fractured system is shown in Figure 8. As can be seen in this figure, the differential pressure increases as a function of injected chemical EOR and bio-EOR due to the

plugging of some parts of the fracture zones. Similar observations have been reported by several other authors.[58−60] The SEM images of core samples confirm the existence of the biopolymer (Figure 9c) and polymer (Figure 10c) at the surface of the rock slice.

It should be noted that the increase in differential pressure during polymer flooding (Figure 8a) was slightly higher than that for biopolymer flooding (Figure 8b). It can be concluded that there is a direct link between differential pressure and fracture-matrix permeability, with the highest reduction in fracture-matrix permeability being observed during polymer as opposed to biopolymer flooding.

Figure 11 shows the oil recovery and differential pressure for cores 1 and 4. The differential pressures were recorded as DP 1, DP2, and DP3 for three flooding scenarios of PAM or XGAM flooding, biosurfactant flooding, and water flooding, respectively. As can be seen in this figure, the first pressure buildup was conducted for polymer PAM/biopolymer XG flooding, where the highest differential pressure and oil recovery were observed at 6 pore volumes (DP1). In this step, the differential pressure was stabilized at 9.4 and 5.6 psi for polymer PAM (core 1) and biopolymer XG (core 4), respectively. After that, biosurfactant RL was injected into the system, and the results show a lower differential pressure in DP2 than in DP1. It should be noted that, in each step, the pump was started from zero as the solution needs to be changed. Finally, water flooding was conducted to achieve the ultimate oil recovery. The values of final oil recovery were observed to be 16 and 8.7% for cores 1 and 4, with corresponding stabilized differential pressures at 4.3 and 3.1 psi, respectively. The change in recorded differential pressure clearly indicates the positive impact of polymer/biopolymer-biosurfactant on water flooding in carbonate fractured reservoirs.

2.4. Contact Angle Measurement as an Indicator of Alteration in Wettability.

Tables 1 and 2 show the contact angle measurements of aged core slices before contact with chemical EOR or bio-EOR. Cores 3 and 6 were used to analyze the effect of chemical EOR on changes in wettability. As can be seen in the tables, the average contact angles measured on aged cores were 128.7° for core 3 (Table 1) and 122.6° for core 6 (Table 2), indicating oil-wet systems.

The results for the effect of chemical EOR and bio-EOR on the wettability of oil-wet systems are presented in Tables 3 and 4. The use of chemical EOR, and especially the addition of the biosurfactant across the core sample, reduced the contact angle from 128.7 to 94.8° in core 3 (Table 3), altering the wettability of the rock matrix to a neutral-wet state. The same result was observed to a lesser extent for core 6 (Table 4), where the
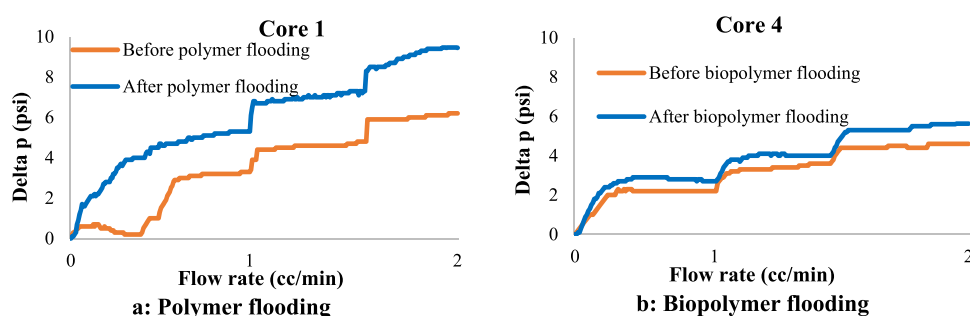

Figure 8. Effect of chemical EOR and bio-EOR on differential pressure across fractured systems: (a) polymer; (b) biopolymer.
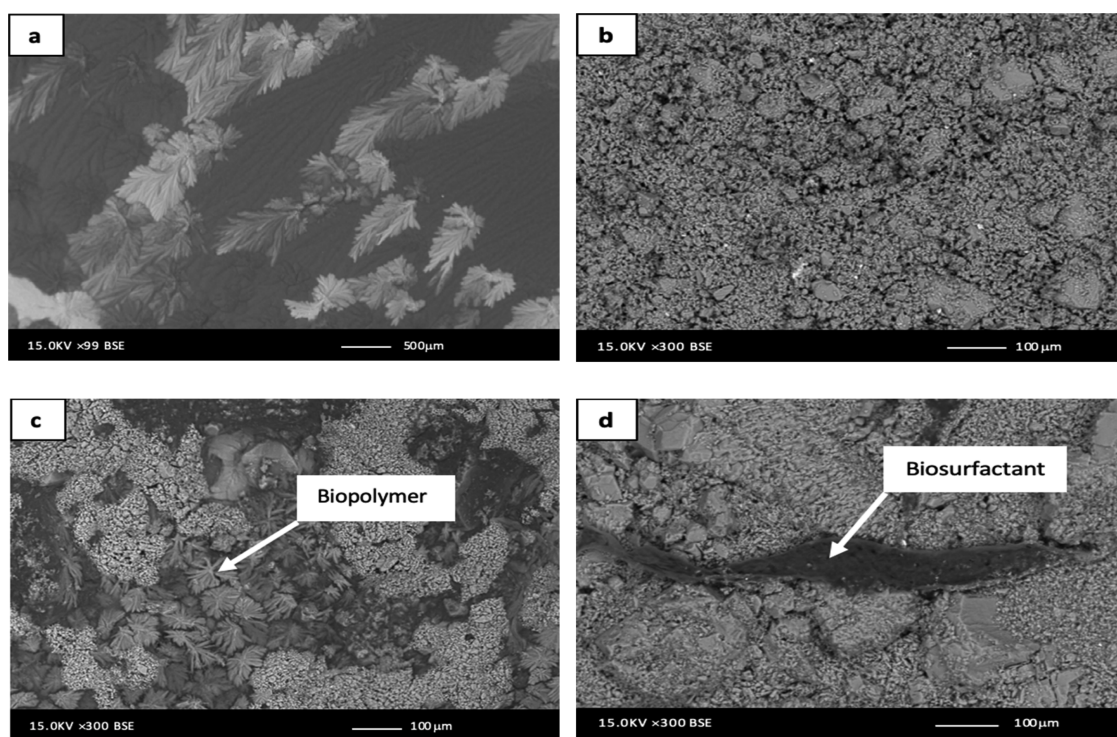
Figure 9. SEM images: (a) XG-STMP; (b) surface of a rock slice without any chemical EOR; (c) surface of a rock slice with XG-STMP; (d) surface of a rock slice with XG-STMP + biosurfactant.
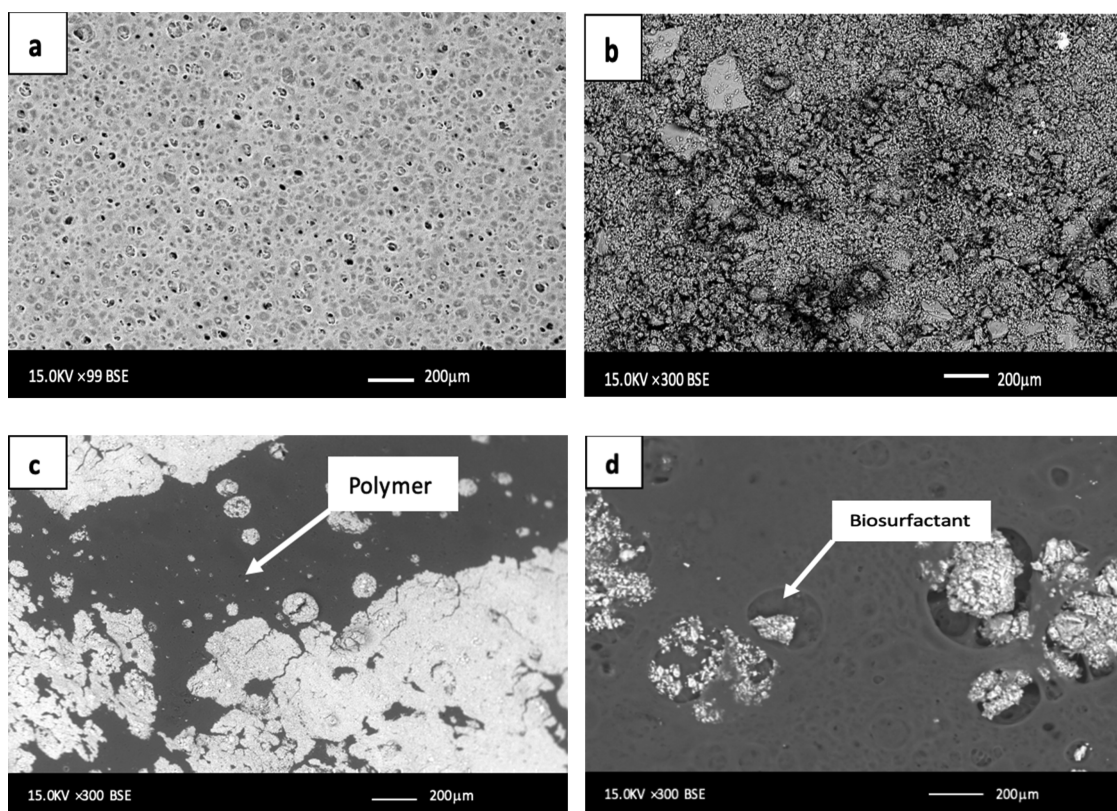
Figure 10. SEM images: (a) PAM-PEI; (b) surface of a rock slice without any chemical EOR; (c) surface of a rock slice with PAM-PEI; (d) surface of a rock slice with PAM-PEI + biosurfactant.

contact angle dropped from 122.6 (oil-wet) to 97.9° (neutral-wet). Based on the SEM images presented in Figures 9d and 10d, some dense deposits of biosurfactant layers have built up

at the surface of the rock, and this is responsible for the change in wettability of the oil-wet rock. Several researchers have carried out experiments to alter the wettability of carbonate
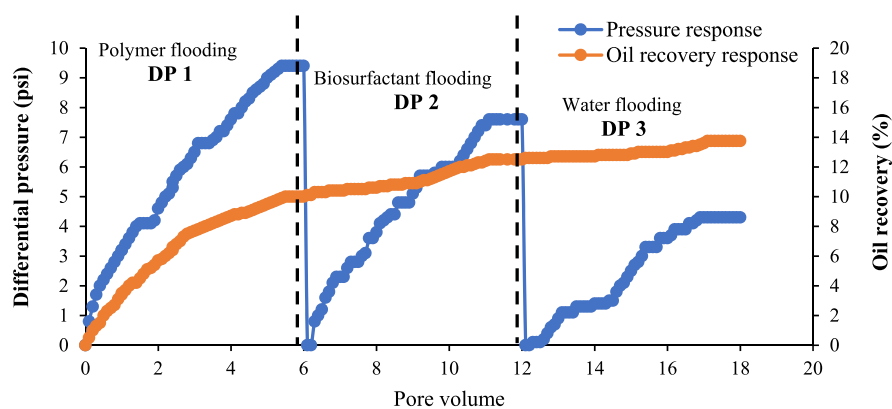
11a. Core 1
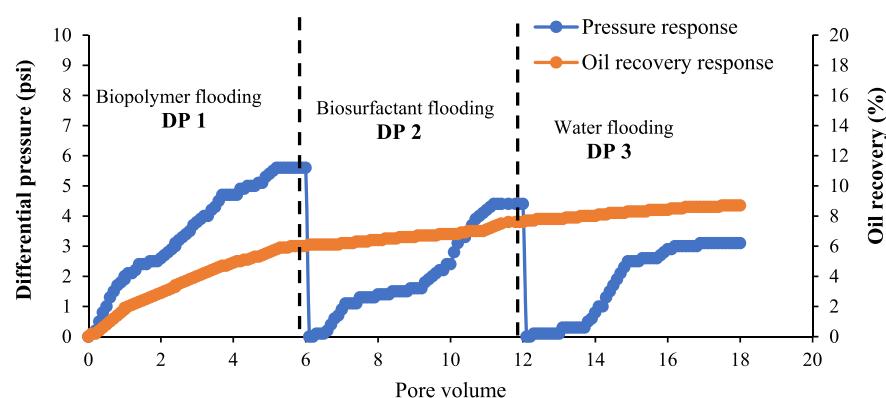
11b. Core 4

Figure 11. Oil recovery and differential pressure for cores 1 (a) and 4 (b).

Table 1. Contact Angle Measurements for Aged Core 3 before Contact with Chemical EOR

droplet	reading 1 (°)	reading 2 (°)	reading 3 (°)	average contact angle (°)	wettability
DW droplet 1	128.3	129.1	128.1	128.5	oil-wet
DW droplet 2	126.4	126.1	126.8	126.4	oil-wet
DW droplet 3	131.1	130.8	131.3	131.1	oil-wet
average contact angle for core 3 (°)				128.7	oil-wet

Table 2. Contact Angle Measurements for Aged Core 6 before Contact with Chemical EOR

droplet	reading 1 (°)	reading 2 (°)	reading 3 (°)	average contact angle (°)	wettability
DW droplet 1	120.5	120.6	120.1	120.4	oil-wet
DW droplet 2	123.9	124.8	124.2	124.3	oil-wet
DW droplet 3	123.2	123.1	122.9	123.1	oil-wet
average contact angle for core 6 (°)				122.6	oil-wet

Table 3. Contact Angle Measurements for Aged Core 3 after Contact with Chemical EOR

droplet	reading 1 (°)	reading 2 (°)	reading 3 (°)	average contact angle (°)	wettability
DW droplet 1	95.0	94.6	95.1	94.9	neutral-wet
DW droplet 2	99.1	98.3	98.4	98.6	neutral-wet
DW droplet 3	91.3	90.6	90.6	90.8	neutral-wet
average contact angle for core 3 (°)				94.8	neutral-wet

Table 4. Contact Angle Measurements for Aged Core 6 after Contact with Chemical EOR

droplet	reading 1 (°)	reading 2 (°)	reading 3 (°)	average contact angle (°)	wettability
DW droplet 1	98.7	98.5	97.9	98.4	neutral-wet
DW droplet 2	99.2	98.8	99.0	99.0	neutral-wet
DW droplet 3	95.8	96.5	96.9	96.4	neutral-wet
average contact angle for core 6 (°)				97.9	neutral-wet

rocks using surfactants, and they have concluded that biosurfactants such as rhamnolipids are capable of effecting this change. Some biosurfactants have a stronger effect on wettability than others because of their different hydrophilic–hydrophobic balance (HLB). For instance, the HLB of rhamnolipid has been reported to be 9.5 (low HLB), which can alter wettability to a neutral-wet system. However, surfactants with an HLB of 21.27 (representing high HLB) can change the wettability of an oil-wet system toward the water-wet state. Modifications of the wettability of the rock

Table 5. Chemical Properties and Sources of the Materials Used

material	structural formula	supplier	molecular weight	purity
polyacrylamide (polymer)	$(C_3H_5NO)_n$	Sigma-Aldrich	2 million g/mol	
xanthan gum (biopolymer)	$(C_{35}H_{49}O_{29})_n$	Sigma-Aldrich	$5-6 \times 10^6$ g/mol	
polyethylenimine (PEI)	$(C_2H_5N)_n$	Sigma-Aldrich	~25,000 by LS	
trisodium trimetaphosphate (STMP)	$Na_3P_3O_9$	Sigma-Aldrich	305.89 g/mol	≥95%
sodium hydroxide	NaOH	Sigma-Aldrich	39.997 g/mol	≥98%
rhamnolipids	$C_{32}H_{58}O_{13}$	AGAE	650.8 g/mol	≥90%
stearic acid (acid)	$C_{18}H_{36}O_2$	Sigma-Aldrich	284.48 g/mol	≥98.5%
n-decane	$CH_3(CH_2)_8CH_3$	Sigma-Aldrich	142.28 g/mol	≥94%

Table 6. Specifications of Core Samples

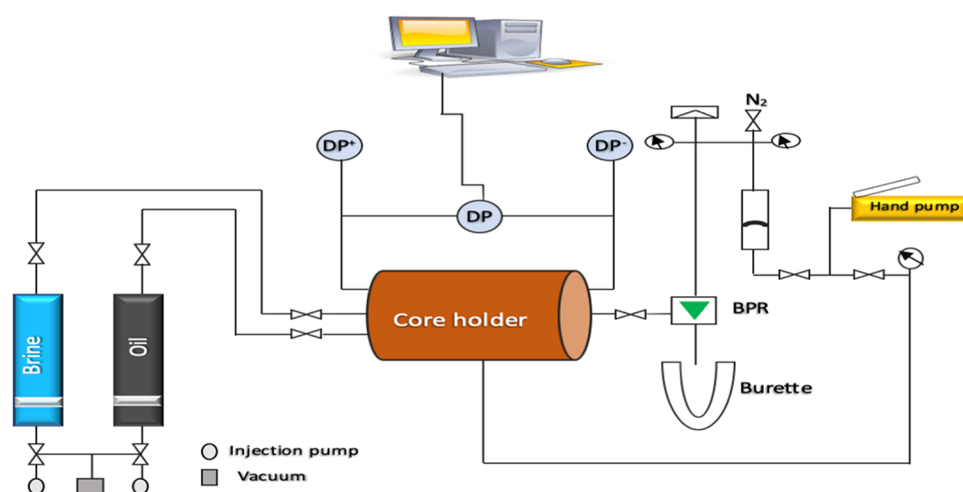| core sample	length (cm)	diameter (cm)	dry weight (gr)	wet weight (gr)	porosity (%)	pore volume (mL)
1. Polymer	6.99	2.51	66.17	76.50	29.86	10.33
2. Polymer	6.98	2.47	61.62	72.01	31.08	10.39
3. Polymer	6.98	2.48	62.61	73.85	33.34	11.24
4. Biopolymer	6.98	2.45	62.68	72.80	30.78	10.12
5. Biopolymer	6.98	2.49	67.69	82.08	42.34	14.39
6. Biopolymer	6.97	2.50	65.54	76.74	32.73	11.20

Figure 12. Schematic diagram of core flooding apparatus.

matrix may be due to interactions between the carbon components attached to the carbonate surface and the hydrophobic heads of the surfactant.[61−65]

3. CONCLUSIONS

This study has presented an analysis of the effect of polymer, biopolymer, and biosurfactant elements of chemical EOR and bio-EOR on oil recovery performance in fractured carbonate reservoirs. The results show that chemical EOR and bio-EOR flooding can be considered as potentially effective approaches to the improvement of sweep efficiency in fractured carbonate reservoirs. The results indicate that the proposed technique can improve oil recovery, with the highest rates up to 16% being observed using polymer/biosurfactant/water flooding. SEM images show that the polymer and biopolymer were adsorbed physically onto the surface, whereas after bio-surfactant flooding no polymer/biopolymer remained on the surface. The images prove that the gels were temporarily plugging the fracture zones, hence reducing fracture-matrix permeability by 18.3−35.61% in porous media and diverting the biosurfactant slug toward matrix zones. The addition of the biosurfactant to the system has been identified as modifying the wettability of the rock matrix from oil-wet to neutral-wet, hence easing the oil flow toward fractures.

4. MATERIALS AND METHODS

4.1. Materials. In this study, two types of polymeric solutions, namely, xanthan gum (XG) and polyacrylamide (PAM), were used. Trisodium trimetaphosphate (STMP) and polyethylenimine (PEI) were utilized as cross-linking agents for the biopolymer and polymer, respectively. Water-soluble rhamnolipid was selected as a biosurfactant to study its application in EOR. Stearic acid (0.01 M) dissolved in n-decane was used to represent a model oil resembling crude oil. Table 5 gives information concerning the materials used.

4.2. Methods. *4.2.1. Preparation of Solutions.* *4.2.1.1. Cross-Linked Polymer.* 10000 ppm PAM and 5000 ppm PEI were mixed with distilled water for 2 h at a speed of 1000 rpm.

4.2.1.2. Cross-Linked Biopolymer. 3000 ppm XG was added to a 0.1 M solution of sodium hydroxide and then mixed with 3000 ppm STMP and distilled water for 1 h.

4.2.1.3. Biosurfactant. 500 mg/L rhamnolipid was used. This concentration was considered to be a suitable CMC measurement for applications in EOR by Li et al.[66]

4.2.2. Viscosity Measurement. The viscosities of cross-linked polymer and biopolymer under different shear rates in the range of 5.109 to 1021.8 s^{-1} were measured using a Fann model 35 viscometer.

4.2.3. Core Sample Preparation. Six carbonate cores (Austin Chalk) were washed with toluene for 48 h and then dried in a vacuum desiccator at 70 °C for 24 h. The specifications of the core samples are given in Table 6. After that, a vacuum saturator was used for 48 h to saturate the cores with distilled water to remove air between the grains. Then, the wet weights of the cores were measured to establish the porosities and pore volumes of the samples.

4.2.3.1. Core Flooding Apparatus. Figure 12 illustrates a diagram of the core flooding device. Brine and oil accumulators are attached to an injection pump, which can be set at different flow rates. Inlet and outlet pressures across the core sample are joined at both sides of the core holder. The core sample is held within the core holder, and then overburden pressure can be applied by confining pressure through the cores. Inlet and outlet end plugs allow fluids to be flooded through the core sample.

4.2.3.2. Core Flooding Experiment before Aging of Core Samples. The unfractured water-wet core was inserted in the core holder, and then distilled water was injected at flow rates of 1, 1.5, and 2 cc/min to establish the permeability to water (K_w). After that, the core was flooded with sample oil to obtain a value of initial water saturation (S_{wi}). At this stage, the oil was injected into the core sample until no distilled water was produced. Then, the permeability to oil (K_o) was determined at flow rates of 0.5, 0.75, and 1 cc/min. Finally, distilled water was injected to establish residual oil saturation (S_{or}). The results are presented in Table 7.

Table 7. Petrophysical Properties of Core Samples before Fracturing

core sample	K_w	K_o	S_{wi}	S_{or}
1	13.032	2.031	29.33	38.72
2	14.255	2.372	24.93	38.50
3	15.308	2.897	39.50	31.14
4	13.826	4.692	17.98	44.47
5	13.146	3.329	45.80	31.27
6	12.430	4.901	34.82	35.71

4.2.3.3. Core Flooding Experiment after Aging of Core Samples. After the evaluation of K_w, S_{wi}, K_o, and S_{or} as described above, the core was cut horizontally as a fractured core at an angle of 180°. Images of unfractured and fractured cores are shown in Figure 13. The core sample was then placed in a cylindrical box that was filled with the model oil for 30 days. The core was placed in the core holder, and the following steps were applied.

First, 6 pore volumes of distilled water were injected. Then, 6 pore volumes of the cross-linked polymer/biopolymer were flooded under a confining pressure of 300 psi and left for 24 h. The reason for the injection of 6 pore volumes is that the pump was stopped after injection of 6−7 pore volumes due to experimental conditions such as the application of confining pressure. Therefore, it was decided to inject only 6 pore volumes for consistency across each chemical flooding during
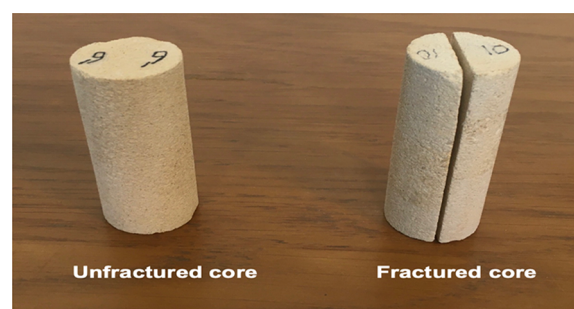

Figure 13. Images of an unfractured core and a core fractured at an angle of 180°.

the experiments. It should be noted that an Enerpac hand pump filled with hydraulic oil allows the confining pressure to build up in the core holder. The operation of the system was controlled through a computer interface. No significant changes in overburden stress occurred during the experiment, and its values remained mostly stable. Subsequently, the biosurfactant was injected at the same confining pressure and left for a further 48 h. Finally, the ultimate oil recovery factor was measured after the injection of distilled water.

4.2.4. Contact Angle Measurements. Contact angle measurements were conducted using a Kruss DSA 100 goniometer analyzer at room temperature (20 ± 2 °C) at two time points. The first point followed the 30 day aging of the core sample, and the second was immediately after the final bio-EOR procedure when the core slices had been further aged in the core holder for 48 h after the injection of the biosurfactant and distilled water flooding. These steps were repeated three times for each core sample, and then the average was given as the final contact angle measurement.

4.2.5. Scanning Electron Microscopy (SEM). To carry out the required experiments and to gather SEM images of the rock surface for characterization with and without chemical EOR, a Hitachi S-3400 N SEM was used. This device was operated with a BSE detector and an accelerating voltage of 15 kV to achieve high-resolution imaging.

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Notes

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