Guar Gum-Based Hydrogels as Potent Green Polymers for Enhanced Oil Recovery in High-Salinity Reservoirs

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ABSTRACT: Improving oil production for high-salinity reservoirs using polymer flooding is challenging due to chemical and mechanical degradations. This study developed two biodegradable biopolymers based on graft copolymerization of guar gum (GG) with two different co-monomers, which are acrylamide (Am) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and cross-linked by N,N′-methylene bisacrylamide (MBA) to face these challenges. The newly synthesized guar gum-based hydrogels, GG-g-poly(Am-AMPS) (GH) and GG-g-poly(Am-AMPS)/Biochar (GHB composite), were evaluated as potential candidates for enhanced oil recovery (EOR) under high-salinity conditions. Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) of the synthesized hydrogels were investigated, and their rheological properties were measured at room temperature. Both GH and GHB display a shear-thinning performance. In polymer flooding experiments, guar gum hydrogel (GH) and guar gum/biochar composite hydrogel (GHB) showed a remarkable influence on delaying the water breakthrough and proved to be effective biopolymers for enhanced oil recovery in high-salinity reservoirs. At the optimum concentration of 5 g/L, GH flooding achieved maximum oil recoveries of 70.53 and 72.11% in secondary and tertiary recovery processes, respectively. Meanwhile, the waterflooding process achieved an ultimate oil recovery of 58.42%. GHB flooding at optimum concentration, 2 g/L, increased the amount of oil recovery by 8.95% in tertiary recovery compared to waterflooding. Furthermore, GH (5 g/L) and GHB (2 g/L) slightly enhanced the rock water wettability as confirmed by contact angle measurements for GH and the relative permeability saturation curves for GH and GHB.

1. INTRODUCTION

Water production from oil wells is a problem that needs to be tackled in the process of oil field development. Such a problem depletes the energy of formation, decreases the efficiency of the pump, decreases the oil recovery, and increases corrosion. The produced water leads to environmental contamination, and its treatment increases the dehydration unit load.1–7

Different enhanced oil recovery (EOR) methods have been employed to obtain the maximum amount of recoverable oil. Recently, research groups applied surfactants,8 alkalines,9 nanoparticles,10–13 and synthetic polymers14,15 flooding in the EOR. Despite their remarkable efficiency, their high cost and undesired environmental impact made the synthetic polymers and surfactant flooding less popular.16 Consequently, exploring alternative low-cost and environmentally friendly materials for the EOR has become an urge in the petroleum industry.17

Polymer flooding was successfully employed in both secondary and tertiary recovery processes and in carbonate and sandstone reservoir as well.16,19 The key action of polymer flooding in oil recovery is to increase the viscosity of the injected water and hence increase the reservoir sweep efficiency.14 Despite the successful application of polymers in chemical flooding for enhanced oil recovery, instability of the polymer chemical composition in high-salinity reservoirs is still a challenge.20 Biopolymers are preferred over synthetic polymers due to their favorable properties. Biopolymers are natural, cost-effective, and have rheological properties that are compatible with the conditions found in reservoirs, such as high temperature, high salinity, bacteria, and salinity of connate water.16,21

Guar gum biopolymer is a biodegradable, nontoxic, low-cost, and renewable raw material that has been used potentially as a fracturing fluid component during the extraction of oil deposits from reservoirs22–25 but still not fully investigated as biopolymer for enhanced oil recovery.26 However, it has been reported that guar gum is very sensitive to salt concentration and temperature because the viscosity of its solutions decreases tremendously in seawater and in high-
temperature solutions. Tuning the physical and chemical properties of guar gum can be achieved by incorporating appropriate groups in its matrix through grafting and/or cross-linking.

The viscosity and hydrophilic–hydrophobic nature of the modified GG were found to be of great significance in the petroleum industry. Torres et al. reported guar gum derivatives with excellent surfactant characteristics under harsh conditions of salinity and temperature. For fracturing fluid formulations, a new class of guar derivatives has been developed, which is known as hydrophobically modified guar gum (HMGG). This development gave a class of guar gum-based polymers possessing both hydrophilic and hydrophobic characters.

Amundarain et al. Combined guar with xanthan gum solutions to get fluids with enhanced viscosity for EOR. During the chemical modification of guar gum for enhanced oil recovery application, it is important to keep certain hydrophilic–lipophilic balance, which enables the molecules to be arranged on the water–oil interface and alter its properties. Guar gum functionalization with nonionic monomers such as acrylates can increase its salt tolerance and lipophobicity, as well as decrease its biodegradability, while the incorporation of an ionic monomer in the polymer matrix such as AMPS can increase its solubility in water and enhance the thermal stability. Polymerization reaction is usually carried out by a free-radical-induced mechanism in which persulfate salt (KPS) acted as the initiator.

Hydrogels are cross-linked hydrophilic polymers that are capable of retaining an amount of water or fluids into their three-dimensional (3D) network. This unique versatility enables hydrogels to be utilized in a broad range of applications. They have received common interest in oil/water separation and as oil-repellent materials because they combined hydrophilic compositions and surface micro/nano-hierarchical structures.

Acrylamide (Am) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) are important monomers that are widely used in polymerization reactions. The general mechanism for radical graft polymerization of acrylamide (Am) and AMPS onto guar gum in the presence of MBA as a cross-linker is shown in Figure 1.

![Figure 1. General mechanism for radical graft polymerization of acrylamide (Am) and AMPS onto guar gum in the presence of MBA as a cross-linker.](https://doi.org/10.1021/acsomega.1c03352)
used for the preparation of functional hydrogels. Acrylamide is nonionic monomer, while AMPS is a hydrophilic monomer that contains both nonionic and anionic groups. The incorporation of ionic groups in the superabsorbent is to increase their swelling capacity, while the nonionic groups can improve their salt tolerance.

Biochar is an eco-friendly carbonic material with high stability and resistance to degradation. It has been used as a filler that could improve the physical and mechanical properties of composites due to its high surface area, high carbon content, and hydrophobic nature.

In this work, a guar gum-based hydrogel (GH) has been synthesized by graft copolymerization of the monomers acrylamido-2-methylpropane sulfonic acid (AMPS) and acrylamide (Am) on chains of guar gum (GG) and cross-linked with MBA. A hydrogel composite (GHB) has been also synthesized by incorporation biochar into the network of the guar gum hydrogel to produce a guar gum-based biocomposite (GHB) with enhanced physical and mechanical properties. The hydrogel formation was confirmed by Fourier transform infrared (FTIR) spectroscopy, and their thermal properties were investigated by thermogravimetric analysis (TGA). The rheological properties of the newly synthesized biopolymer hydrogels were investigated, and their efficiency in polymer flooding for enhanced oil recovery was evaluated.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. 2.1.1. Synthesis of Guar Gum-Based Hydrogels. The sulfate radical anion generated from the thermal decomposition of the KPS abstracted the hydrogen from the hydroxyl group in the guar gum (GG) backbone creating a GG macroradical. Acrylamide (Am) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomers were then successfully grafted onto the GG active radicals. N,N'-methylene bisacrylamide (MBA) was used as the cross-linker to form a three-dimensional network (3D) structure of the hydrogel GG-g-poly(Am-co-AMPS), GH. The synthesis route of the newly synthesized guar gum-based hydrogel (GH) is illustrated in Figure 1.

The synthesis of GG-g-poly(Am-co-AMPS)/biochar (GHB) took place by dispersing the biochar consistently in the GH network (eq 1).

\[
\text{GG-g-poly(Am-co-AMPS)} \quad \xrightarrow{\text{biochar}} \quad \text{GG-g-poly(Am-co-AMPS)/biochar hydrogel (GHB)}
\]

Equation 1 shows the formation of GHB by dispersing biochar in GH.

2.1.2. FTIR Spectra for New Hydrogels. FTIR spectra were used to confirm the successful formation of hydrogels, GH and GHB. The successful copolymerization, cross-linking, and biochar incorporation into the network were confirmed by comparing the FTIR spectra of the native guar gum (GG) and the newly synthesized hydrogels GH and GHB as shown in Figure 2.
Figure 2a shows the FTIR spectra of the native GG. The chart showed a broad peak at 3444 cm$^{-1}$ corresponding to the stretching vibration of $\text{O-H}$ and water involved in hydrogen bonding. A small peak at 2925 cm$^{-1}$ is attributed to the $-\text{CH}_2$ stretching vibration. The peaks observed in the spectrum between 800 and 1200 cm$^{-1}$ represented the highly coupled $\text{C-C-O}$, $\text{C-OH}$, and $\text{C-O-C}$ stretching modes of polymer backbone. The bands around 1650 cm$^{-1}$ can be attributed to the ring stretching and bending of water molecules (due to the hydrophilic nature of GG). The peaks around 1420 cm$^{-1}$ are due to $\text{CH}_2$ bending. The band at 1157 cm$^{-1}$ is attributed to the glycosidic linkage $\text{C-O-C}$ of GG. At 1022 cm$^{-1}$, a band corresponding to $\text{CH}_2$ twisting was also observed. At 871 cm$^{-1}$, a band for galactose and mannose appeared. After grafting, the IR spectra of the GH (Figure 2b) showed additional bands that confirm the successful grafting. The new characteristic band at 3648 cm$^{-1}$ is due to overlapping of $\text{O-H}$ stretching of the $\text{O-H}$ group of GG, $\text{N-H}$ stretching of the amide group, and $\text{SO}_3\text{H}$ stretching of the grafted AMPS. At 3159 cm$^{-1}$, a peak characteristic for $\text{OH}$ stretching appeared. The peak at 2928 cm$^{-1}$ in GH is due to $\text{C-H}$ stretching vibrations, whereas the appearance of peaks at 1683 and 1561 cm$^{-1}$ of grafted GG has been assigned as $\text{C=O}$ and $\text{N-H}$ stretching vibration bands, respectively. The peak at 1410 cm$^{-1}$ is assigned to the $\text{C-N}$ stretching bands. The peaks at 1318 and 1411 cm$^{-1}$ correspond to $\text{S=O}$ stretching of the sulfonate group. For the biochar IR spectrum (Figure 3c), the band at 3428 cm$^{-1}$ is for the $-\text{OH}$ group stretching of alcohols and phenols. The band at 1634 cm$^{-1}$ is attributed to $\text{C=O}$ corresponding to acid, aldehyde, and ketone contents.

The band at 1384 cm$^{-1}$ is for the $\text{C-H}$ bending of $\text{CH}_2$ groups, while the band at 1045 cm$^{-1}$ corresponds to $\text{C-O}$ for alcohols and phenols and that at 874 cm$^{-1}$ confirmed the $\text{C=C}$ aromatic bending.$^{39}$ For the new derivative GHB, the IR spectrum (Figure 3d) showed a band at 3664 corresponding to the overlapping of $\text{O-H}$ stretching of the $\text{O-H}$ group of GG, $\text{N-H}$ stretching of the amide group, and $\text{SO}_3\text{H}$ stretching of the grafted AMPS. The band at 3435 cm$^{-1}$ is from the hydroxyl group stretching in biochar. The band at 2946 cm$^{-1}$ is for the $\text{C-H}$ stretching of the polymer. The bands at 1636 and 1665 cm$^{-1}$ are attributed to the $\text{C=O}$ from the biochar and grafted polymer, respectively. The appearance of the bands from the GH and biochar indicates the successful formation of the composite GHB.

2.1.3. Thermogravimetric Analysis (TGA). TGA for the new hydrogels was carried out to investigate the effect of grafting and cross-linking of monomer chains on the thermal stability of the GG. The thermogram of the hydrogel after incorporating the biochar in the GH matrix forming the hydrogel GHB was also studied. TGA for guar gum samples showed three clear zones. The first zone at 30–120 °C of $\approx$10% weight loss is due to the presence of volatiles or moisture. The second decomposition step at 230–335 °C of about 56% weight loss is attributed to the degradation of the GG backbone (the secondary alcoholic group $-\text{CHOH}$). A third decomposition step at 335–680 °C of about 31% weight loss is attributed to further degradation of GG backbone through the loss of the primary alcohol group $-\text{CH}_2\text{OH}$. The thermogram of GH (Figure 3a) showed a three-stage decomposition mechanism. The first stage from 30 to 240 °C with a weight loss of $\approx$17% was attributed to the loss of volatiles or moisture. The second stage in the thermogram of GH at 240–450 °C with a weight loss of 30% is due to the elimination of side chains. The decomposition stage at 450–600 °C is the show weight of the guar gum backbone. For GH, it was clear that the initial decomposition temperature was shifted to a higher value (240 °C) compared to that of GG (230 °C), which indicates an enhancement in the thermal stability of the GG due to grafting and cross-linking. The thermogram for GHB (Figure 3b) showed four distinctive zones with an initial weight loss of 11% at 30–203 °C and is corresponding to the weight loss of water and volatiles. The second stage (203–330 °C) and third stage (330–458 °C) of weight losses 17 and 16%, respectively, can be due to the loss of the side chains and small molecules in biochar. The fourth decomposition stage of 40% weight loss may be due to the decomposition of the guar gum backbone. The decrease in the initial decomposition temperature in the GHB than the GH may indicate a more condensed and stable cross-linked polymeric network in GH than GHB. This may imply that the incorporation of biochar into the GH affects the polymeric network cohesion.

2.3. Rheological Properties. 2.3.1. Effect of Shear Rate on Viscosity and Mechanical Degradation. The shearing action of displacing fluids was assessed using various concentrations (1.0, 2.0, 5.0, and 7.0 g/L) at 25 °C and salinity of 35 000 ppm as indicated in Figure 4. It is obvious that all displacing fluids show shear-thinning behavior since the viscosity decreases with increasing shearing action because of the scission of the main chains of the displacing fluids. Hence, the polymer is classified as pseudoplastic (non-Newtonian fluid), which means that with increasing the shear rate, the viscosity decreases. Also, the reduction in viscosity through
different shear rates in the case of GHB is less than GH as shown in Figure 4.

2.3.2. Sand Pack Flooding Tests. Cumulative oil recovery related to injected pore volumes of the three fluids is summarized in Table 1. As shown in Figure 5, the cumulative oil recovery (% OOIP) and residual oil saturation resulting from waterflooding are 58.42 and 21.35%, respectively, after injecting 2.8 PV of 35,000 ppm saline water at 25°C.

Tertiary recovery was performed after waterflooding using different concentrations of GH and GHB solutions, as shown in Figures 6 and 7, respectively. The higher the polymer concentration, the higher the oil recovery up to the optimum concentration of polymer (5 g/L) after which the recovery of oil decreased. Decreasing the oil recovery after the optimum concentration can be attributed to polymer retention and pore blockage at higher polymer concentrations. In the case of GH, oil recovery increased by 1.84% with an increase in the concentration from 1.0 to 2.0 g/L and increased by 5.27% with an increase in the concentration from 2.0 to 5.0 g/L, while the oil recovery decreased by 8.16% when the concentration of polymer increased from 5.0 to 7.0 g/L. Thus, the maximum recovery in the case of GH as a tertiary recovery was achieved at the concentration of 5.0 g/L, after which the recovery factor decreased. At this concentration (5.0 g/L), an oil recovery of 72.11% was achieved compared to an oil recovery of 58.42% in the case of waterflooding alone. On the other hand, in the case of GHB, it is apparent that oil recovery increases by 5.26% with an increase in the concentration from 1.0 to 2.0 g/L. However, the oil recovery decreased by 2.11 and 4.21% with an increase in the concentration from 2.0 to 5.0 g/L and from 5.0 to 7.0 g/L, respectively. Thus, the maximum recovery in the case of GHB as a tertiary recovery was achieved at a concentration of 2.0 g/L after that the recovery factor decreased. In the case of GHB, the maximum recovery took place at a lower concentration compared to GH. This can be attributed to an earlier pore blockage caused by the less soluble GHB due to the presence of biochar in its composition. At this concentration, an oil recovery factor of 67.37% was achieved compared to an oil recovery of 58.42% in the case of waterflooding.

Moreover, secondary recovery was performed using the optimum concentration of GH and GHB, which resulted from the tertiary recovery stage, as shown in Figure 8. It was clear

Figure 4. Effect of the shearing rate on the apparent viscosity of guar gum hydrogel (GH) and guar gum/biochar composite hydrogel (GHB) at a temperature of 25°C.

| Table 1. Flooding Conditions and Oil Recovery by Brine, Guar Gum Hydrogel (GH), and Guar Gum/Biochar Composite Hydrogel (GHB). |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | |
| injected fluid | slugs size | Vp (mL) | Voi (mL) | Vwc (mL) | Vor (mL) | Sai (slugs efficiency) | cum. oil recovery | cum. recovered oil (×10⁻⁴ bbl) | cum. recovered oil (% OOIP) | slug size | cum. oil recovery | cum. recovered oil (×10⁻⁴ bbl) | cum. recovered oil (% OOIP) |
| | | | | | | | | | | | | | |
| saline water | 0.0011 | 53.13 | 48.65 | 21.35 | 0.55 | 51.35 | 48.65 | 15.14 | 0.67 | 3.87 | 58.42 | 0.00 | 55.5 |
| guar gum hydrogel (GH) | 0.0022 | 17.97 | 14.32 | 60.75 | 0.59 | 19.46 | 16.76 | 25.52 | 17.34 | 3.65 | 65.26 | 10.92 | 61.05 |
| guar gum/biochar (GHB) | 0.0044 | 33.25 | 31.5 | 63.5 | 0.36 | 31.3 | 33 | 17.84 | 0.37 | 3.6 | 64.74 | 6.737 | 67.37 |
| | | | | | | | | | | | | | |
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that during the injection of GH and GHB as secondary recovery, the yield of oil recovery was higher than the recovery from waterflooding. Using the tertiary recovery optimum concentration (5 g/L) of GH in a secondary recovery stage, the oil recovery increases by 12.11% compared to water-flooding. The enhancement in oil recovery using GH and GHB as secondary and tertiary recoveries confirmed that economical and technical success can be achieved by polymer flooding in both secondary and tertiary recoveries.19 In general, guar gum-based derivatives (GH and GHB) increased water injection viscosity, enhanced the mobility ratio, and achieved good sweep efficiency as shown in Table 2. The sweep efficiencies were calculated according to the earlier reported method.16

The derivative GH was more effective as a secondary and tertiary recovery than GHB. This can be attributed to the observed higher water solubility of GH compared to GHB during the preparation of flooding solutions. The increased water solubility of GH compared to GHB can be attributed to the higher polysaccharide content in the GH than the GHB by about 10%.

2.3.3. Rock Wettability Alteration and Displacement Efficiency. Relative permeability curve, waterflooding behavior, and capillary pressure that govern the oil recovery efficiency are closely related to the wettability.49 In this study, we evaluate the rock wettability by monitoring the contact angle via time and relative permeabilities50 to oil and water (Kr and Ko) during the displacement as displayed in Figure 9a,b. In the case of the contact angle method, as shown in Figure 9a, it is apparent that the GH at the concentration (5 g/L) has the ability to slightly increase the wettability of the rock toward water-wet. On the other hand, distilled water changes the wettability from stronger water-wet to weaker water-wet. It is worth mentioning that no contact angle measurements were conducted for GHB as we got maximum recovery from GH. Figure 9b shows the relationship between the relative permeability of rock to oil and water versus water saturation in case of waterflooding at 2 and 5 g/L of GHB and GH, respectively. It is clear from the figure that the cross-points of relative permeability Kr = Ko for these solutions occurred at water saturations of 0.74, 0.78, and 0.81 in the above-mentioned cases, respectively. This indicated that using either of these two types of biopolymer improves the rock wettability to water. In addition, at the optimum concentration of 5 g/L of GH, the rock wettability to water improved more than the optimum concentration of GHB (2 g/L). This is proved by the decrease in the amount of residual oil and the increase in water saturation in the case of GH than GHB. These results are consistent with the results obtained by Soliman et al.17

The proposed mechanism for displacement of the oil from the rock surface and the slight enhancement in the water wettability during GH and GHB flooding is shown in Figure 10

Figure 10a,b shows the proposed mechanism for the oil−water wettability enhancement and the oil displacement from the rock surface. In Figure 10a, the GH and GHB polymer matrix contains acidic groups, which are the sulfonic acid

![Figure 5](https://example.com/f5.png)

**Figure 5.** Cumulative oil recovery for waterflooding.

![Figure 6](https://example.com/f6.png)

**Figure 6.** Cumulative oil recovery of GH relative to injected pore volume as a tertiary recovery.

![Figure 7](https://example.com/f7.png)

**Figure 7.** Cumulative oil recovery of the GHB relative to injected pore volume as a tertiary recovery.

![Figure 8](https://example.com/f8.png)

**Figure 8.** Cumulative oil recovery of polymer GH and polymer GHB relative to injected pore volume as secondary recovery.
Table 2. Wettability Alteration and Displacement Efficiency

| Injected Fluid                  | $S_{in}$ | $S_{w} (k_w = k_o)$ | $S_{fr} (BT)$ | Displacement Efficiency (ED) (%) | $S_{wf} (%)$ | Recovery Factor (% OOIP) |
|--------------------------------|----------|---------------------|---------------|---------------------------------|-------------|------------------------|
| Waterflooding                  | 0.4865   | 0.737               | 0.735         | 0.77                            | 55.21       | 21.35                  | 58.42 |
| 2 g/L of guar gum/biochar composite hydrogel | 0.4865   | 0.782               | 0.775         | 0.805                           | 62.03       | 18.11                  | 64.74 |
| 5 g/L of guar gum hydrogel (GH) | 0.4865   | 0.812               | 0.83          | 0.84                            | 68.84       | 15.14                  | 70.53 |

Figure 9. Curves of injected fluids. (a) Contact angle versus time for guar gum hydrogel and (b) oil and water relative permeability curves.

breakthrough higher than waterflooding; hence, GH and GHB have an effect on delaying water breakthrough. Results of displacement efficiency ($E_o$), average water saturation at breakthrough, and flood front water saturation at breakthrough are summarized in Table 4.

3. CONCLUSIONS

In this work, two guar gum-based hydrogels were investigated as effective biopolymers for enhanced oil recovery in high-salinity reservoirs. The main findings are summarized in the following points:

- Guar gum-based hydrogel (GH) was prepared successfully by graft copolymerization using acrylamide and AMPS and cross-linked using MBA. The proposed mechanism for the grafting was free-radical mechanism using potassium persulfate as initiator.
- A composite (GHB) based on the newly synthesized hydrogel was also prepared by incorporating biochar in the polymer matrix.
- The newly synthesized hydrogels, GH and GHB, were characterized by FTIR. The IR charts confirm the successful grafting and incorporation of the biochar within the polymeric matrix.
- The thermal stability of GH and GHB was investigated by TGA. Hydrogel GH showed higher thermal stability than the native guar gum, while the incorporation of the biochar affected the polymeric network cohesion and hence decreased the thermal stability of GHB.
- Flooding tests were conducted on sand pack model under harsh reservoir conditions (high salinity), and the ultimate oil recoveries were reported relative to the injected pore volume.
- Flooding tests results showed that the waterflooding process achieved an ultimate oil recovery of 58.42% at a temperature of 25 °C.
- The addition of the guar gum/biochar composite hydrogel (GHB) enhanced the oil recovery to 64.74 and 67.37% in secondary and tertiary recoveries, respectively, at an optimum concentration of 2 g/L.
- The addition of (GHB) enhanced the oil recovery by 70.53 and 72.11% in secondary and tertiary oil recoveries, respectively, at the optimum concentration of 5 g/L.

4. EXPERIMENTAL SECTION

Materials, methods, and equipment used in this study are demonstrated as follows:

4.1. Materials. Analytical grade (98%) acrylate monomers (acrylamide, Am, and 2-acrylamido-2-methylpropane sulfonic acid, AMPS) were obtained from Fluka, Germany. Guar gum (Mn 220 000) was purchased from Alashar, Egypt. Biochar was obtained by the pyrolysis of orange peel at 350 °C, from Shabin El Kom, Egypt. Potassium persulfate (KPS, analytical grade) and N,N'-methylene bisacrylamide (MBA) were purchased.
from Aldrich. The oil viscosity was determined utilizing a rolling ball viscometer, while the oil density and API gravity were determined using a pycnometer of 10 mL capacity. Results from viscosity and density measurements are shown in Table 3.

4.2. Synthesis and Characterization of Hydrogels.

4.2.1. Synthesis of Guar Gum Hydrogel (GH).

The synthesis of guar gum-based hydrogel took place via a free-radical polymerization technique. Guar gum (5 g) was dissolved in 50 mL of distilled water. The mixture of monomers (Am, 2 g; AMPS, 2 g) was added to the guar solution at 40 °C and stirred for 1/2 h for uniform mixing. When the temperature reached 70 °C, potassium persulfate (0.7 g) was dissolved in 5 mL of distilled water and added to the mixture. After mixing for 15 min, the mixture was allowed to cool. When the reaction mixture reached 40 °C, MBA (0.05 g) in distilled water (5 mL) was added to mixture with a purge of N₂. The water bath was kept at 70 °C for 3 h to complete the polymerization reaction to obtain GG-g-(Am-AMPS) hydrogel, GH. The hydrogel formed was cut into little pieces, washed by distilled water and ethanol to remove the unreacted monomers and other chemicals, and then dried overnight in an oven at 60 °C.

4.2.2. Synthesis of Guar Gum/Biochar Composite Hydrogel (GHB).

For the preparation of GG-g-(Am-AMPS)/biochar hydrogel (GHB), biochar (0.6 g) was added to the GG solution (5 g in 50 mL distilled water) to form a viscous solution. Then, the same procedure used for the preparation of GG-g-(Am-AMPS) (GH) hydrogel was followed and the GHB was obtained as a black residue.

4.2.3. Fourier Transform Infrared (FTIR) Spectroscopy of the Newly Synthesized Hydrogels.

FTIR measurements for the guar gum and the products GH and GHB have been carried out to confirm the successful formation of the products GH and GHB. For the measurement, 2 mg of the sample (GG, GH, or GHB) was mixed with KBr (300 mg) and then compressed in the form of a disk or pellet. The disk was then placed in a specific holder in the IR spectrometer to allow the IR beam to fall on the disk of sample. The FTIR spectra were obtained on a Bruker Optik GmbH Ettlingen spectrometer, using KBr disk, operating in the range of 4000−400 cm⁻¹.

4.2.4. Thermogravimetric Analysis (TGA).

The thermal stability of the hydrogels was assessed using a TG-50 instrument from Shimadzu. The heating was carried out at the temperature range of room temperature to 600 °C with a heating rate of 10 °C/min under nitrogen gas atmosphere.

4.3. Rheological Tests.

4.3.1. Viscosity Measurements of the Synthesized Hydrogels.

The rheological properties of polymer solutions were measured using OFI testing equipment (OFITE) model 800 8-speed electronic viscometer. Solutions were prepared by dissolving GG, GH, or GHB in distilled water to obtain concentrations of 2 g/L and 5 g/L. The viscosity measurements were performed using a rotating cylinder viscometer. The results are shown in Figure 11.

Table 3. Crude Oil Physical Properties

| properties, unit | values at room temperature |
|------------------|---------------------------|
| density, g/mL    | 0.85                      |
| API Gravity, °   | 31                        |
| viscosity @ 25 °C, cp | 7.31                  |

Figure 10. Proposed mechanism for oil displacement from the sandstone surface by the anionic group (sulfonate group) in the GH and GHB polymer matrix.

Figure 11. Fractional flow curves of injected fluids for guar gum hydrogel GH and guar gum/biochar composite hydrogel (GHB).
of guar gum hydrogel (GH) and guar gum/biochar composite hydrogel (GHB) were prepared with different concentrations (1.0, 2.0, 5.0, and 7.0 g/L) with a salinity (NaCl) of 35 000 ppm. The viscosity of these solutions was measured at room temperature (25 °C), atmospheric pressure, and different shear rates (5.11, 10.22, 51.09, 170.30, 340.60, 510.90, and 1021.80 s⁻¹).

4.3.2. Rock Wettability Measurement. The core sample with the shape of a circular coin was fully saturated with brine (100 000 ppm NaCl) overnight at room temperature (25 °C) and tilted in the solution with the optimum concentration of GH (5 g/L). Then, a droplet of oil was injected into the lower surface of the core sample and the contact angle of the droplet was measured using the sessile drop method reported elsewhere.56

4.4. Flooding Tests. 4.4.1. Sand Pack Apparatus. Flooding runs were carried out through the displacement model, which is mainly composed of a sand pack filled with unconsolidated sand with specific size as shown in Table 2, which resulted in reasonable values of porosity (30.35%) and permeability (721.85 mD). The displacement model is shown in Figure 12. Nitrogen gas from a nitrogen cylinder with a pressure regulator (pressure adjusted to 20 Psi) was used to displace the fluids into the sand pack. Accumulators are used to store the brine solution, crude oil, and polymer solutions (GH and GHB). The sand pack can be used as an alternative to the reservoir rock to perform enhanced oil recovery studies, and it is made of steel of length 27.657 cm (10.889 in.) and inner diameter 5.296 cm (2.085 in.), which includes steel caps at both ends of the sand pack. Pressure gauges are used to measure the inlet pressure and outlet pressure, hence facilitating the measurement of the pressure drop along the sand pack. The fluids that are produced during the flooding runs were collected in a graduated cylinder (collector).

4.4.2. Preparation of Sand Pack. Unconsolidated sand with size 0.149–0.297 mm is used to prepare the sand pack for injection. Screens and filters are installed at the inlet and outlet of the sand pack to get a good distribution of fluid during flow through the porous medium and prevent migration and sand removal during the displacement runs. The porosity of the sand pack is measured based on the saturation fluid method. Besides, the sand pack absolute permeability was measured based on Darcy’s law. The sand pack was saturated with brine at a salinity of 100 000 ppm NaCl. Then, the oil was injected into the sand pack to displace the brine solution (100 000 ppm NaCl) until completely saturating the model with oil and completely producing all of the movable water to calculate the initial oil saturation and connate water saturation. Details of the sand pack are listed in Table 4.

4.4.3. Displacement Experiments. 4.4.3.1. Waterflooding. Flooding was performed through a sand pack saturated with brine of 100 000 ppm NaCl and a temperature of 25 °C. The waterflooding run was performed using 35 000 ppm saline water, where water was continually injected (4.8 PV in tertiary recovery and 2.8 PV in secondary recovery) until no further oil was produced from the sand pack. Then, the produced oil and water that were collected through various graduated tubes have been recorded to calculate the cumulative oil recovery and residual oil saturation, to develop the relative permeability saturation curve and fractional flow curve, and to compare with the other polymer flooding in the following experiments.

4.4.3.2. Guar Gum Hydrogel (GH) and Guar Gum/Biochar Composite Hydrogel (GHB) Flooding. After the waterflooding process, the sand pack was flooded with GH and GHB solutions as a tertiary recovery at different concentrations (1.0, 2.0, 5.0, and 7.0 g/L) in brine solution with 35 000 ppm using slug size (0.2 PV) to get the optimum concentration, which gives the maximum oil recovery. Moreover, the sand pack was flooded with the optimum concentration detected from the tertiary recovery of GH and the secondary recovery of GHB solutions using slug size (0.2 PV).

Table 4. Sand Pack Properties

| properties, unit | values   |
|-----------------|----------|
| sand size, mm   | 0.297    |
| length, cm      | 27.657   |
| diameter, cm    | 5.296    |
| area, cm²       | 22.03    |
| bulk volume, ml | 609.488  |
| pore volume, ml | 185      |
| porosity, %     | 30.35    |
| permeability, mD| 721.85   |
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Notes
The authors declare no competing financial interest.

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ABBREVIATIONS USED

AMPS 2-acrylamido-2-methylpropane sulfonic acid
Am acrylamide
GG guar gum
MBA N,N′-methylene bisacrylamide
GH guar gum hydrogel
GBH guar gum hydrogel/biocar
EOR enhanced oil recovery
FTIR Fourier transform infrared
t TGA thermogravimetric analysis

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