Assessment of xanthan gum and xanthan-g-silica derivatives as chemical flooding agents and rock wettability modifiers

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Abstract. Currently, biomolecules flooding in the underground reservoirs acquires sustainable interest owing to their availability and eco-friendly properties. The current study reported chemical displacement by xanthan gum as well as xanthan/SiO2 and xanthan grafted with vinylsilane derivatives. Chemical characterization evaluated by traditional spectroscopic methods. Investigation of fluids response to reservoir environment assessed through rheological performance relative to shearing rate, ionic strength, and thermal stability. A sequence of flooding runs generated on 10 sandstone outcrops with different porosity and permeabilities. Core wetness assessed through relative permeability curves at different water saturation. The flooding tests indicate that grafting of the silica derivative overcome the shortage of xanthan solution in flooding operations relative to the reservoir conditions. The ability of the flooding solutions to alter rock wettability explored through relative permeability curves at different water saturation. The results reveal that the synthesized composite was a promised agent for enhancing oil recovery and profile conformance.

Nomenclature

| Symbol | Definition                                      |
|--------|------------------------------------------------|
| \( \mu \) | The solution viscosity (CP)                    |
| \( \mu_0 \) | Pure solvent viscosity (CP)                    |
| \( \eta \) | Intrinsic viscosity (dLg \(c_0\)/C0)           |
| \( K_h \) | Huggins constant (dimensionless quantity)      |
| \( C \)  | Polymer concentration (dLg \(c_0\)/C0)         |
| \( M_w \) | Molecular weight (g/mol)                       |
| \( \gamma \) | Shear rate (s\(^{-1}\))                        |
| \( a \)  | Flow consistency (Pa s\(^{-n}\))               |
| \( n \)  | Flow behavior index (dimensionless parameter)  |
| \( \xi \) | Adsorbed layer thickness (\(\mu m\))           |
| \( r \)  | Average pore radius (\(\mu m\))               |
| \( R_{\Omega} \) | Residual resistance factor                     |
| \( R_i \) | Resistance factor                               |
| \( M \)  | Mobility ratio (dimensionless factor)          |
| Slug size | Slug concentration (g/L)/pore volume (cc)      |
| Slug efficiency | Slug concentration (lb)/recovered oil (bbl) |
| \( S_w \) | The average water saturation                   |
| \( S_{w_i} \) | The initial water saturation                   |

ED: Displacement efficiency

1 Introduction

Nowadays, attention to chemical flooding grows up incrementally in the developing countries on the academic and technological scale due to increased energy consumption (Bera and Belhaj, 2016). Several efforts implemented to recover entrapped oil through improvement of sweeping efficiency (AfzaliTabar et al., 2017). Chemical processing by polymer flooding has a significant potentiality to recover about 35% of original oil in place after secondary water displacement (Hu et al., 2018). Polymer flooding either by conventional polymers, polymer/inorganic particles or by polymers-grafted vinyl monomers rely on three main strategies including; (1) improvement of the sweeping efficiency through mobility ratio controlling (Bai et al., 2018); (2) selective reduction of water phase relative permeability (Maghzi et al., 2014); (3) performing viscoelastic flow in the...
porous media (Kang and Zhang, 2013). On the reservoir scale, nanomaterials serve as wettability modifiers, interfacial tension reducing agents, and adsorbents on rock surface to minimize the adsorbate amount during flooding process (Bera and Belhaj, 2016; Zargartalebi et al., 2015). One of the widely implemented nanomaterials in oil field processing is the hydrophilic silica nanoparticles with different geometries and crystal structure (Zargartalebi et al., 2015). Ordered molecular sieved silica-based materials have uniform pores <50 nm, high surface area, abundant hydroxyl groups and narrow pore size distribution (Kovalchuk et al., 2005), so used in many applications involving catalysis, energy storage, and environmental remediation (Wang et al., 2016). Moreover, it displays adsorption criteria at the oil/brine/rock interfaces, which in turn producing shear and wetting action on the crude oil layer (Maghzi et al., 2014). Several reports stated the synthesis of different ordered mesoporous silicates and their application in improved oil recovery as rheology and wettability modifiers, or emulsion stabilizers as stated elsewhere (Bera and Belhaj, 2016; Hu et al., 2017). On the other hand, xanthan is a bacteriological water-soluble polysaccharide produced by Xanthomonas bacterium species through the biofermentation process, with a high molecular weight (>2 × 10^6 g/mol) (Kumar et al., 2017). Solutions of xanthan gum exhibit shear thinning (Pseudoplastic) behavior (Suh et al., 1990) and drag reducing criteria under subsurface environments (Zhong et al., 2013) in addition to their higher viscosity, and ease penetration into low permeability zones (Zhong et al., 2013) so preferred in the underground chemical flooding processes (Kumar et al., 2017). Theoretically, biopolymers are preferred rather than synthetic polymers owing to their availability, efficient biodegradability, and eco-friendly properties (Badwaik et al., 2016). On the industrial scale, xanthan solutions, as well as hydrolyzed polycryliclamides, suffer from chain degradation due to high ionic strength, bacterial attack, and thermal degradation under harsh reservoir environment (Li et al., 2018). Consequently, amendment to their rheological response conducted by mixing with inorganic silica nanoparticles (Maurya et al., 2017) or grafting with vinylsilane derivative to boost the shearing resistance, mechanical stress, robust thermal and salinity response, as well as toughness and anti-polyelectrolyte properties (Kumar and Sharma, 2018), through the formation of network assembly between nanoparticles and polymer architecture (Bera and Belhaj, 2016). Moreover, hybridization of the polymer backbone with thermo-sensitive pendant groups enhance polymeric chains stability (Liu et al., 2017; Pu et al., 2015). Inoculation of silane derivatives through biopolymer matrix reduce particles agglomeration and retard macromolecules propagation during polymerization process owing to nanoscale nucleation effect (El-Hoshoudy, 2018b). Many researchers stated the grafting of xanthan with vinyl monomers through typical free radical emulsion polymerization. Polymerized nanocomposites characterized by a dispersion of nanoparticles through polymer architecture so, exhibit preferred properties rather than conventionally filled polymers (El-Hoshoudy et al., 2016) and can be considered as a reasonable Enhanced Oil Recovery (EOR) agents due to their capability to reduce interfacial tension and alter wetting properties (Shamilov et al., 2017). Application of polymer-g-nanoparticles have been reported previously, and comprising the preparation of TiO2, SiO2, ZnO nanoparticles and their copolymerization/grafting with vinyl monomers for alteration of the sandstone rock wettability, and improvement of oil and water flow since they can flow through unswept zones, and enhance the sweeping effectiveness. This study reports about a facile synthesis of SiO2 nanoparticles through Stöber method then mixing with xanthan gum. Moreover, xanthan gum will be grafted with methylvb(is(trimethylsilyloxy)vinylsilane through free radical copolymerization. Interpenetrating xanthan network with vinylsilane monomers enhances its physicochemical and rheological properties (Pandey and Mishra, 2011). Rheological criteria screened at simulated reservoir environment related to mechanical shearing, salinity resistance, and thermal degradation. A sequence of flooding runs performed through sandstone cores using different flooding solutions including xanthan gum (XG), xanthan gum/SiO2 physical mixture and xanthan gum-grafted-silica composite (XG-g-silica). The incremental oil recovery and relative permeability curves investigated at different pore volumes and water saturation. The capability of the flooding solutions to alter rock wettability investigated through relative permeability curves. To the best of our knowledge, scarce reports deal with the application and modification of biopolymers composites in the field of EOR. Consequently, this work establishes a complementary foundation in the modification and implementation of xanthan biopolymer in oil field processing through enhancing recovery factor and altering wettability of sandstone rocks.

2 Experimental analysis

2.1 Materials

Sodium Dodecyl Sulfate (SDS ≥ 99%); ammonium hydroxide solution ≥99.99%; Hexadecyltrimethylammonium bromide (CTAB ≥ 99%); Hydrochloric acid (37%); Tetraethylorthosilicate (TEOS, 99.99%); Commercial xanthan gum used without further purification; Methylbis (trimethylsilyloxy) vinylsilane (IUPAC name; 1,1,1,3,5,5,5-heptamethyl-3-vinyltrisiloxane~98%); potassium persulfate “KPS” (K2S2O8; ≥99%; acetone ≥97%; methanol ≥97%. All reagents and materials supplied by Merck and used without additional treatment. All solutions were organized using double distilled (dd) water.

2.2 Synthesis of nano-SiO2 and XG-g-silica composite

SiO2 synthesis performed according to the Stöber method with some modification (Stöber et al., 1968; Wang et al., 2016). Typically, 2.0 g of CTAB was dissolved in 120 g of dd water until complete solubility. Then, add 8.0 mL of concentrated ammonical solution (33.0 wt %). After that, add 10 mL of TEOS drop wisely under continuous stirring at 200 rpm for 40 min, where a uniformly colloidal solution formed progressively during TEOS addition and continue...
stirring overnight. The product was filtrated and washed with deionized water and ethanol, and then vacuum dried at 80 °C for 17 h. Ordered mesoporous silica obtained by calcination at 550 °C for 4 h. Synthesis of XG-g-silica composite carried out according to the following procedure. In a 500 mL Erlenmeyer three-neck flask supplied with a condenser, thermometer, and nitrogen source dissolve 1.3 g of SDS in 350 mL of dd water, then add 3.0 g of xanthan gum and stir vigorously until complete dissolution. Under nitrogen flooding add 0.06 g of 1,1,1,3,5,5,5-heptamethyl-3-vinyltrisiloxane and 0.4012 g of KPS under continuous stirring and adjust the temperature at 65 °C. The reaction continues for 4 h, then cooled down to room temperature. XG-g-silica composite precipitated by dissolving in distilled water, ethanol, acetone, and then Soxhlet extraction with acetone for 5 h at 50 °C. The chemical reaction as illustrated in Scheme 1 (Supporting Information) is initiated by the formation of the propagating sites on xanthan gum with the aid of initiator followed by their copolymerization with activated vinyl monomers through a typical free radical polymerization reaction. The ionic composition of the saline solutions used in rheological measurements and flooding experiments is provided in Supporting Information.

2.3 Measurement and characterization

FTIR spectroscopy collected on American FTS-3000 spectrophotometer using KBr pellets in the range of 500–4000 cm⁻¹. NMR analysis carried out with a Bruker spectrometer. The peaks logged after 32 shots, using deuterium oxide (D₂O) solvent. The spectrum processed with Mnova software for peaks identification (El-hoshoudy et al., 2019). Transmission Electron Microscopy (TEM) images monitored on JEM-2100F high-resolution transmission electron microscope operating at 200 kV. The samples were distributed in ethanol and then dried on the copper (Cu) grid (Wang et al., 2016). Thermal Gravimetric Analysis (TGA) carried out on TA-instrument SDT thermogravimeter under nitrogen flooding at 50 mL/min. About 5–7 mg of the sample was vacuum dried at 60 °C then subjected to thermal analysis. Molecular weight determined through estimation of intrinsic viscosity in 0.1 mol NaCl at 25.0 °C with a Ubbelohde capillary viscometer through the dilution extrapolation method (El-Hoshoudy et al., 2016; Hu et al., 2018). Brookfield programmable DV-II⁺ rheometer used for measurement of the apparent viscosity related to mechanical shearing, saline concentration, and the temperature effect. All spectroscopic characterization and analysis are provided in Supporting Information.

2.4 Core physical properties and flooding experiments

Flooding runs performed through core flooding system on sandstone cores that considered as a clastic sedimentary rock of high porosity and permeability due to the presence of quartz and/or feldspar minerals in its constituents (Boggs and Boggs, 2009; McGeary et al., 2001; Porter, 1987). Core samples subjected to Soxhlet extraction with toluene, followed by vacuum drying at 80 °C for 24 h. After that, the cores immersed into desiccator filled with a brine solution of 20 g/L salinity for one day to assure complete brine saturation (Bai et al., 2018). The physical properties and geometries of the 10 cores and flooding conditions are reported in Supporting Information. The cores porosity was calculated using imbibition method in which the dry weight was reported. After that, the cores were soaked in formation water until they were fully saturated, and weight after saturation was reported. The bulk volume calculated through Vernier caliper, which used to measure the length and diameter of cylindrical cores. The cores were located inside the core holder and soaked with a single liquid phase (water/oil), then single cylinder displacement-pump operated to allow fluid flow through the core, where the readings of flow rate and pressure difference recorded as a function of time (Salehi et al., 2014). Saturated cores were placed inside the core holder where the flooding experiment performed at room temperature and a constant injection rate of 3.0 cc/min. A single cylinder pump injected the crude oil until ejection of brine ceased off (El-Hoshoudy, 2018b; El-Hoshoudy and Desouky, 2018; El-Hoshoudy et al., 2018). The displaced brine represents the initial oil in place (Voi) and the remaining brine inside the core represents the connate water saturation (Scw). After that, the core flooded with brine solution until oil ceased off (oil cut <1%). The volume of oil, water, as well as displacing time, and pressure drop recorded at each injected pore volume (Fig. 1).

3 Results and discussion

3.1 Rheological properties

3.1.1 Intrinsic viscosity and molecular weight

Intrinsic viscosity determined from Huggins formula (Goldberg et al., 1947) as indicated in equation (1). Plotting specific viscosity [=(μ – μ₀)/μ₀] versus concentration (c) on the Cartesian scale then extrapolating the curve to infinite dilution (zero concentration) give intrinsic viscosity value which equates to the slope of the line (Hu et al., 2018). The polymer molecular weight determined by Mark-Houwink relation in 0.1 M NaCl at 25 °C (Chiantore, 2005) as shown
Table 1. Computed intrinsic viscosity and molecular weight of XG-g-silica composite.

| C (gdL$^{-1}$) | [(μ-μ₀)/μ₀] | [μ-μ₀]/C | η (dLg$^{-1}$) | $M_w$ (g/mol) |
|---------------|-------------|----------|--------------|-------------|
| 0.5           | 90.0        | 180.98   | 133.24       | 8.40 x 10^6|
| 0.4           | 70.0        | 173.72   |              |             |
| 0.3           | 50.0        | 164.70   |              |             |
| 0.2           | 30.0        | 153.92   |              |             |
| 0.1           | 14.3        | 141.38   |              |             |

in equation (2). The calculated intrinsic viscosity, as well as molecular weight, are summarized in Table 1 and Figure 2:

\[
\frac{[\mu - \mu_0]}{\mu_0} = [\eta] + k_h[\eta]^2C, \quad (1)
\]

\[
[\eta] = 0.0000017(M_w)^{1.14}. \quad (2)
\]

3.1.2 Mechanical degradation and shear rate effect

Mechanical deformation occurs when the polymer molecules subjected to a high shear rate at low permeability of reservoir rock, and result in a reduction of mobility ratio by 80% (Maerker, 1975). By shear applying, the fluids perform 1 of the 4 distinct rheology profiles: thixotropic, Newtonian, non-Newtonian, and dilatant. In this section, the shearing action of the displacing fluids evaluated through different concentrations (1.0, 1.5, and 2.0 g/L) at 25 °C as depicted in Figure 2. It is apparent that all fluids exhibit shear thinning behavior as the viscosity decrease by shear action increase (Pu et al., 2015) due to the chain scission then tend to be stable, so they belong to pseudoplastic profile (non-Newtonian fluid; Ye et al., 2013). Viscosity related to shear rate by power-law relation (Xu et al., 2011) as shown in equation (3):

\[
\mu = \omega^{-n}, \quad (3)
\]

shear thinning nature controlled by $n$-value, as increasing of $n$-values above zero ($n > 0$), indicate that the fluids exhibit shear thinning effect (El-Hosshoudy, 2018a). The calculated $n$-values of the three displacing fluids at a concentration of 2.0 g/L (Fig. 3d) are summarized in Table 2. It’s clear that viscosity reduction in XG-g-silica composite and XG/SiO$_2$ is lesser than xanthan gum, also XG-g-silica composite exhibit the highest ($K$ and $n$) values, which indicate that insertion of the silica increase elasticity of composite owing to the hydrogen bonding formation between silanol groups and hydroxyls of xanthan, which give rise to elastic structure with high shear degradation resistance. Moreover, silica particles act as a physical cross-linker embedded through polymer chains, which provide enough roughness against chains scission and mechanical degradation, so improve rheological properties of composite solutions (AfzalTabar et al., 2017). These results accomplished with Maghzi et al. (2013) who showed the same trend when SiO$_2$ nanoparticles used as a rheology modifier in polymers solutions.

3.1.3 Ionic strength response

Petroleum reservoirs have different degrees of salinity ranged from high to moderate salt content (Ahmadi and Shadizadeh, 2018). During polymer flooding, xanthates solutions greatly affected by the high ionic strength of the formation water (Zhong et al., 2013). Effect of salinity on displacing fluids investigated at different slug concentrations (1.0, 1.5, and 2.0 g/L) and different salinities (3.5, 10.0, 15.0, and 20.0 g/L) at room temperature as shown in Figures 4a–4c. Viscosity rises up with polymer concentration increase due to intensified intermolecular association (Zhong et al., 2013). Viscosity reduction and degradation of xanthan gum by incremental salt addition, resort to the dipole ionic interaction among the formation water cations (Ca$^{2+}$, Na$^+$) and oxygen (COO$^-$) of ester in xanthan polymer chains (Maghzi et al., 2014), consequently the elongated molecules converted into helical structural conformation with reduced hydrodynamic volume resulting in viscosity falling down (Hu et al., 2018). Figure 4d compares salinity resistance of the three fluids at a slug...
concentration of 2 g/L and salinity of 20.0 g/L. In the case of XG/SiO2 physical mixture, a charge neutralization occurs between negatively charged silica nanoparticles and positively charged cations in the saline solution, which reduce the electrostatic repulsion within polymer chains. Moreover higher surface area of silica nanoparticles allows adsorption of polymer chains on its surface forming a tough hybrid network with reduced electrostatic repulsion (Hu et al., 2018). On the other hand, XG-g-silica composite yields a boosted viscosity rather than XG and XG/SiO2 due to the formation of an intramolecular association between silanol groups (Si–O\(^-\)) and formation water cations, so reduce cations competition to attack polymer chain (Maghzi et al., 2014). Moreover, insertion of silica through polymer chains form crosslinked network structure with large hydrodynamic volume (i.e., silica act as a crosslinking agent) which prohibit curling and coiling of polymer chains by salt addition (Yang-Chuan et al., 2008).

Fig. 3. Effect of the shearing rate on the apparent viscosity of (a) XG-g-silica composite; (b) physical XG/SiO2 mixture; (c) xanthan gum (XG) polymer; and (d) comparison of three cases at a concentration of 2.0 g/L.

Table 2. Flow consistency and flow behavior coefficients.

| Fluid                  | \(a (\text{Pa s}^{-1})\) | \(n\) | \(R^2\) | Adj. \(R^2\) |
|------------------------|-------------------------|------|--------|-------------|
| XG                     | 890.00                  | 0.761| 0.9977 | 0.9973      |
| XG/SiO2                | 1259.82                 | 0.789| 0.9958 | 0.9950      |
| XG-g-silica composite  | 1865.81                 | 0.797| 0.9983 | 0.9979      |

Concentration of 2 g/L and salinity of 20.0 g/L. In the case of XG/SiO2 physical mixture, a charge neutralization occurs between negatively charged silica nanoparticles and positively charged cations in the saline solution, which
Fig. 4. Effect of salinity on displacing fluids. (a) XG-g-silica composite; (b) XG/SiO$_2$ physical mixture; (c) XG-polymer; and (d) comparison of three injected fluids at concentration = 2 g/L and salinity = 20 g/L.
Fig. 5. Effect of temperature on displacing fluids. (a) XG-g-silica composite; (b) XG/SiO$_2$ physical mixture; (c) XG-polymer; and (d) comparison of three injected fluids at concentration = 2 g/L and temperature = 70 °C.
3.1.4 Thermal degradation

Thermal degradation of the three displacing fluids estimated by measuring solution viscosity at different shear rates and two temperatures (25 °C and 70 °C) as displayed in Figure 5. The results indicate that viscosity reduction in case of XG/SiO2 and XG-g-silica composite due to high temperature was not significant as compared with the XG polymer at the same temperature. For more illustration, XG-g-silica and XG/SiO2 at 70 °C and 60 s⁻¹ yield viscosity values of 23.5 and 19.75 mPa s respectively, while xanthan gum viscosity equals 12.5 mPa s. This higher thermal resistance of XG-g-silica composite resort to the generation of an intramolecular association between silanol group (Si–OH) and formation water cations, in addition to insertion of silica through polymer backbone which gives rise to reinforced three-dimensional hybrid network (Hu et al., 2018). While XG/SiO2 exhibit reasonable heat resistance due to the enrichment of endothermic intramolecular interaction with temperature increasing (El-Hoshoudy et al., 2016; Ye et al., 2013). Moreover, the formation of hydrogen-bonding between silanol groups (Si–OH) and carbonyl groups (C=O) (Hu et al., 2018; Maurya and Mandal, 2016) of ester in xanthan gum form compacted, rough structure which can resist high salinity and temperature. These observations are in great compliance with Giraldo et al. (2013) who proved that SiO2 nanoparticles can enhance the thermal resistance and mitigate the polymer decomposition by high temperature.

3.2 Core flooding tests

Core flooding conducted through three phases at a salinity of 20 g/L and 25 °C. The 10 cores were flooded with different concentration of xanthan gum, XG-g-silica composites, and (XG/SiO2) physical mixture to obtain the optimum concentration which yields the maximum oil recovery. Cumulative oil recovery related to injected pore volumes of the three fluids are summarized in Table 3 and Figure 6. It’s apparent that maximum recovery in case of XG and XG-g-silica composite achieved at concentration = 2.0 g/L, while in case of XG/SiO2, the maximum recovery achieved at 1.5 g/L after that recovery factor decreased. This may be justified according to the following interpretation. In the case of XG-polymer, increasing of slug concentration increases the flooded solution viscosity, which in turn enhances sweeping efficiency and oil recovery factor (El-Hoshoudy, 2019; El-hoshoudy et al., 2019). Moreover, it is apparent that oil recovery increase by 6.14% with increasing the xanthan gum concentration from 1.0 to 1.5 g/L while the oil recovery only increased by 2.77% when the concentration of polymer increases from 1.5 g/L to 2.0 g/L. This indicates that the higher the polymer concentration, the higher the oil recovery, but the increase in the oil recovery reduces with further increase in the polymer concentration owing to polymer retention and blockage. These results match with Wang et al. (2012) who showed that additional oil recovery can be obtained with a high concentration of polymer solutions. In the case of (XG/SiO2) decreasing of recovery factor at slug concentration > (0.75 g/L of XG + 0.75 g/L of SiO2) resort to an accumulation of SiO2 nanoparticles at higher concentrations, which in turn cause clogging of the pore throats and permeability reduction. These results are highly compatible with Hendraningrat et al. (2013) who stated that increasing hydrophilic nanoparticles concentration adversely affects the oil recovery owing to impairment of the reservoir rock permeability. In the case of XG-g-silica composite, achieving of maximum recovery at 2.0 g/L reveals that silica uniformly distributed in the polymer matrix, and would not be precipitated during core flooding. The mobility control of three displacing fluids over formation water was quantified by $R_l$ and $R_d$ is provided in Supporting Information.

### Supporting Information

#### Table 3. Flooding conditions and oil recovery by XG, XG/SiO2, and XG-g-silica.

| # Core | Injected fluid | Slug conc. (g/L) | Slug conc. (lb) | Slug size (% PV) | $V_p$ (cc) | $V_a$ (cc) | $V_{mc}$ (cc) | $V_{mr}$ (cc) | Saturation (% PV) | Recovered Oil (cc) | Recovered Oil (% OOIP) | Oil recovery efficiency ($\times 10^{-4}$ lb/bbl oil) |
|--------|---------------|-----------------|----------------|-----------------|---------|---------|-----------|-----------|-----------------|-----------------|-------------------|--------------------------|
| 2F     | Brine         | 0.0022          | 0.00           | 0.00            | 15.34   | 10.49   | 4.85      | 4.40      | 68.40           | 31.60           | 28.70              | 6.01                      |
| 4p     | XG-polymer    | 0.0022          | 0.00           | 55.01           | 18.18   | 11.60   | 5.05      | 3.07      | 66.00           | 34.00           | 22.00              | 7.01                      |
| 1R     | Physical (XG/SiO2) | 0.0022          | 0.00           | 101.03          | 14.85   | 9.80    | 5.05      | 3.27      | 66.00           | 34.00           | 22.00              | 6.52                      |
| 2p     | Physical (XG/SiO2) | 0.0044          | 0.00           | 135.65          | 14.74   | 10.10   | 4.64      | 3.10      | 68.50           | 31.50           | 21.00              | 7.00                      |
| 1F     | Physical (XG/SiO2) | 0.0022          | 0.00           | 62.39           | 16.03   | 10.71   | 5.32      | 2.69      | 66.80           | 33.20           | 16.80              | 8.00                      |
| 3P     | Physical (XG/SiO2) | 0.0033          | 0.00           | 82.77           | 18.12   | 11.60   | 6.52      | 1.70      | 64.00           | 36.00           | 9.40               | 9.90                      |
| 1P     | Physical (XG/SiO2) | 0.0044          | 0.00           | 115.77          | 17.28   | 11.00   | 6.27      | 3.09      | 63.70           | 36.30           | 17.90              | 7.90                      |
| 5P     | XG-g-silica composite | 0.0022          | 0.00           | 64.44           | 15.53   | 10.29   | 5.23      | 1.34      | 66.30           | 33.70           | 8.60               | 8.97                      |
| 2R     | XG-g-silica composite | 0.0033          | 0.00           | 104.38          | 14.37   | 9.60    | 4.77      | 1.19      | 66.80           | 33.20           | 8.30               | 8.40                      |
| 1KL    | XG-g-silica composite | 0.0044          | 0.00           | 122.61          | 16.31   | 11.50   | 4.81      | 1.26      | 70.50           | 29.50           | 7.70               | 10.25                     |

Since rock wettability influence relative permeability curves and capillary pressure which in turn control the recovery factor (Bera and Belhaj, 2016). In this study, we evaluate...
the rock wettability by monitoring the oil and water relative permeabilities ($K_{ro}$ and $K_{rw}$) during the core displacement (Ahmadi and Shadizadeh, 2018) as displayed in Figure 7a. It’s apparent that the cross-points of the water and oil relative permeability curves in case of XG, XG/SiO$_2$, and XG-g-silica composite are observed at $S_w$ @ $K_{ro} = K_{rw} = 0.60401$, 0.685, and 0.715 respectively. This behavior proves that silica insertion increase water wettability from weak water wet to strong water wet, and this is in great compliance with Al Matroushi et al. (2015) and Moradi et al. (2015), who stated that “silica nanoparticles act as water wetting agents for sandstone rock, so increase recovered oil amount”. Increasing of water-wet characteristics by silica addition resort to hydrophilic characters of silica with spreading hydroxyl (–OH) groups on its surface so can form hydrogen bridging with formation water, which in turn construct hydrophilic coating layer on the rock surface (Zargartalebi et al., 2015). Moreover, nanomaterials form three-dimensional structure at the interface of rock/oil/brine, which gives rise to structural disjoining pressure, so nano-fluids act as a wedge-like knife detaching the oil from the rock surface (Bera and Belhaj, 2016; El-Hoshoudy et al., 2016; Wasan and Nikolov, 2003) and increase recovery factor. Since changing wettability from oil wet to water wet improves the recovery factor during water flooding (Ahmadi and Shadizadeh, 2018) so the XG-g-silica and XG/SiO$_2$ can be considered as a good EOR alternative. Moreover, the fractional flow curves of the three displacing fluids at a concentration of 2.0 g/L as shown in Figure 7b, indicate that XG-g-silica solution is more shifted to the right side which means high average water saturation, more efficient displacement, and a lesser amount of residual oil ($S_w$) (Attia, 2005; Sayyouh et al., 1993). Results of displacement efficiency ($E_D$) and average water saturation are calculated according to equation (4) and summarized in Table 4:

$$E_D = \frac{S_w - S_{wi}}{1 - S_{aw}}. \tag{4}$$

Figure 7c shows the relation between relative permeability ratio ($K_{ro}/K_{rw}$) and water saturation ($S_w$) for different injected fluids at concentration of 2.0 g/L. It is observed that the main portion of the relative permeability ratio saturation curve is quite linear. The fitting line of the middle part after neglecting the inlet and outlet of curve yields empirical correlation (Eq. (5)):

$$\frac{K_{ro}}{K_{rw}} = ae^{-bs_w}. \tag{5}$$

It is noticed that the values of “b” are relatively constant in the three different injected fluids, but values of “a” are different as shown in Table 4. By increasing the value of “a” at any water saturation, the fractional flow of water decreases, hence the displacement efficiency increases. Therefore, XG-g-silica composite yields displacement efficiency more than XG/SiO$_2$ physical mixture and XG-polymer as exhibited in Figures 7b and 7c. Figure 7d and Table 5 show the relation between water saturation at cross points and residual oil saturation. The results

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**Fig. 6.** Cumulative oil recovery of displacing fluids. (a) Cumulative oil recovery of the three injected fluids relative to injected pore volume; (b) comparison of cumulative oil recovery of the three injected fluids at a concentration of 2 g/L.
Fig. 7. Curves of three injected fluids. (a) Oil and water relative permeability curves; (b) fractional flow curves; (c) relative permeability ratio saturation curve; (d) water saturation at cross points versus residual oil saturation.
showed that residual oil saturation decreased with increasing the water saturation at cross points which means the rock wettability had been changed from oil-wet to water-wet and from weak water-wet to strong water-wet due to the presence of silica nano-particles.

4 Conclusion

Modification of biopolymer precursors is an efficient method to boost their ability in EOR processing at high ionic strength and temperature. In this study, SiO$_2$ successfully synthesized and characterized, then xanthan gum grafted with vinylsilane derivative via free radical initiation. The response of the displacing fluids to mechanical, ionic and thermal degradation investigated at the high shearing action and harsh reservoir conditions. A comparative evaluation of xanthan gum, XG/SiO$_2$ physical mixture, and XG-g-silica composite as flooding agents performed on outcrop sandstone cores. Moreover, wettability alteration is measured by relative permeability saturation curve. Based on these observations, the following conclusions can be drawn:

- The mixing or grafting of silica derivatives greatly improves the rheological properties of xanthan gum to withstand higher salinity and temperature.
- Relative permeability curves and fractional flow curves indicate that the presence of silica precursors modify the wetting action of cores to more water-wet and improve displacement efficiency which in turn enhance the oil recovery.
- The cumulative oil recovery increased by increasing xanthan gum fluid concentration and the maximum oil recovery is achieved at 2 g/L.
- Oil recovery increases by increasing the concentration of XG/SiO$_2$ physical mixture up to 1.5 g/L, but with further increasing the concentration of XG/SiO$_2$ physical mixture, the amount of oil will decrease.
- XG-g-silica composite can be considered as a reasonable agent to enhance the oil recovery where has a great effect on interfacial tension reduction and wettability alteration.

Supplementary material

Supplementary material is available at https://www.ogst-journal.org/10.2516/ogst/2020004/olm

Table S1. Ionic composition of saline solutions used in rheological and flooding tests.

Table S2. Physical properties and dimensions of core samples.

Table S3. Pressure differential profiles of the three displacing fluids (XG, XG/SiO$_2$, and XG-g-silica composite).

Fig. S1. Fourier Transformation spectroscopy of SiO$_2$, and XG-g-silica composite.

Fig. S2. $^1$H NMR spectra (a) Xanthan gum and (b) XG-g-silica composite respectively.

Fig. S3. Thermal gravimetric analysis of SiO$_2$, Xanthan gum, and XG-g-silica composite.

Fig. S4. TEM photographing of (a) SiO$_2$, and (b) XG-g-silica composite.

Scheme S1. Formation reaction of XG-g-silica composite.

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