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Potential Performance of Natural Polymer Grafted SiO_2/GNPs Hybrid Nanofluids for Enhanced Oil Recovery by Spontaneous Imbibition

Sinan S. Hamdi[1*], Hussain H. Al-Kayiem[2], Raed A. Jessam[3]

[1] Nanotechnology and Advanced Materials Research Center, University of Technology, Baghdad 10066, Iraq
[2] College of Engineering Technologies, University of Hilla, Al-Hilla 51001, Iraq
[3] Electromechanical Engineering Department, University of Technology, Baghdad 10066, Iraq

Corresponding Author Email: 130100@uotechnology.edu.iq

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ABSTRACT

Polymer-grafted nanoparticle-based nanofluids have garnered tremendous interest in EOR applications due to their efficacy in improving suspension stability with good flowability through the porous medium to enhance the static and dynamic EOR mechanisms under reservoir conditions. In this study, different structures of nanoparticles silica (SiO_2) and graphene nanoplatelets (GNPs) were successfully grafted with a natural polymer, Gum Arabic (GA), and combined to formulate novel hybrid nanofluids via a simple and eco-friendly process. The combined nanocomposite particles were characterized using Fourier transform-infrared spectroscopy, energy-dispersive X-ray spectroscopy, and transmission electron microscope. The dispersibility of developed hybrid nanofluids in high salinity brine (30,000 ppm) and high temperature (90°C) was assessed via zeta potential, particle size distribution, interfacial tension (IFT), contact angle, and spontaneous imbibition. The experimental findings showed that the IFT and contact angle of the system (oil/brine) were significantly reduced for long-term stability hybrid nanofluid at 0.1 mg/mL of GA-(80% SiO_2-20% GNP) by around 67% and 81%, respectively. Imbibition experiments revealed augmentation in the oil recovery by about 52% in mid-permeability sandstone rocks during injection of hybrid nanofluid, compared to GA-GNPs GA-SiO_2 nanofluids, respectively. These findings indicate that the syngenetic performance of formulated GA-(SiO_2-GNPs) hybrid nanofluids, even at ultra-low concentrations, can be an alternative and effective choice for improving sweep efficiency and oil recovery at HSHT reservoir conditions.

1. INTRODUCTION

The major source of non-renewable energy production has globally remained crude oil since the era of its discovery. Despite the abrupt evolution to pioneer an alternative source of energy in the last decades, due to inefficient preliminary recovery processes and a trickle production of oil from the current reservoirs, about 40% of the original oil is in place [1]. Moreover, increasing the worldwide energy demand for the oil and gas sector is depletion of hydrocarbon, meanwhile diminishing oil resources and the laboriousness for exploration of new oil reserves [2]. Consequently, chemical-enhanced oil recovery (C-EOR) has been introduced to recover the residual oil and meet the demands of oil energy that effectively contributes by around 50-60% as profitable energy compared to other existing energy resources [3]. However, the implementation of individual or binary combinations of C-EOR techniques (e.g., surfactant, polymer, foam and alkaline) is restricted due to the high cost of chemical materials that are harmful to the environment, thermal degradation of its molecules and damage to the reservoir at high salinity and high temperature (HSHT) conditions. Recently, nanoparticle additives have been introduced as a novel trend and alternative way owing to their unique physical, chemical, thermal, and mechanical properties and a high specific surface area to volume ratio that addressed the underlying mechanisms issues encountered with conventional C-EOR approaches. Their application has shown high performance in EOR by reducing interfacial tension, changing the wettability of core rock, and increasing the viscosity and mobility of the residual oil via increasing the capillary number [4]. Despite the potential EOR performance of nanoparticles for improving oil recovery, the low stability of the colloidal suspension and the agglomeration phenomena of nanoparticles at reservoir conditions of HSHT are the main challenges for nanofluid application in EOR [5].

One of the most effective development approaches is the direct grafting of the surfaces of the nanoparticles with a long chain of the polymer, which is shown to improve thermal stability and salt resistance with good flowability through the porous media at reservoir conditions [6]. However, a wide variety of organic and inorganic nanoparticles (SiO_2, Al_2O_3, TiO_2, Iron oxide, and Graphene) have been introduced to improve the polymer performance even with the presence of harsh salinity and temperature of reservoir conditions over the polymer or polymer nanoparticles alone. El-Hoshoudy et al. [7] evaluated the performance of synthesized polyacrylamide polymer-grafted SiO_2 nanoparticles during oil displacement. Results show that grafted nanoparticles exhibited high anti-salinity, temperature resistance, and shear resistance properties with thickening behaviour. In addition, the wettability of oil-wet rock surface may be altered to water-wet at a high salinity of 40,000 ppm and a high temperature of 90°C. The oil recovery of 2000 mg/L of polymer-grafted SiO_2 at HSHT was 60% of residual oil saturation. Behzadi and Mohammadi [8] studied the influence of modified SiO_2 with polyethene glycol and propyl chains on EOR by using glass micromodels. They attributed the improvement in oil recovery performance to the considerable wettability alteration of oil-wet to water-wet with modified nanoparticles. Rezvani et al. [9] reported that the contact angle, interfacial tension (IFT), and oil viscosity declined in the presence of chitosan polymer-coated Fe_3O_4 with seawater. They found that the oil recovery improved by 10.8% with 0.03 wt% of nanocomposite additives compared with the seawater injection. However, Bila et al. [10] evaluated the performance of diluted polymer functionalized silica nanoparticles in seawater up to 0.1% during the Amott test and oil displacement of water-wet core rock. They suggested that the wettability modification and IFT reduction can effectively increase oil recovery from 7 to 14 % of OOIP at 60°C, compared to water flooding.

A few research studies have recently targeted the application of polymers with nanocomposite particles to assist polymer flooding and increase cumulative oil recovery. Ali et al. [11] studied the influence of XG biopolymer-coated ZnO/SiO_2 NPs on reducing IFT at various conditions to demonstrate their efficiency in improving C-EOR performance. They noted that the IFT value between oil and low salinity polymeric nanofluid significantly decreases at 0.2 wt% of XG coated ZnO/SiO_2 under HTHP, with augmentation in oil recovery by almost 19.3% of OOIP. Furthermore, Lashari et al. [12] reported that polymeric hybrid nanofluids of SiO_2-GO with polyacrylamide (PAM) polymer showed a synergistic influence on contact angle reduction under high salinity and high temperature. Their findings indicated that the wettability of sandstone rock reasonably changed to water-wet at 0.05 wt% of the synthesized nanocomposite.

Polymeric nanofluids have been developed as a new class of hybrid C-EOR techniques that combine Nano-EOR and conventional to improve performance and overcome the challenges associated with individual components for EOR application, whether polymer or nanoparticles, at harsh reservoir conditions. According to the comprehensive study carried on in the literature, there is rareness in the experimental research on evaluation of the employment of hybrid nanofluids system-based (SiO_2/GNPs) nanocomposite and grafted with natural polymer GA as a C-EOR agent at HSHT. Although the promising results of hybrid nanofluids have improved C-EOR performance but are still suffering from the long-term dispersion and economic limitations for application under the harsh reservoir conditions HSHT. Nevertheless, there is a lack of existing research literature to quantify the mixture combination of the polymer-coated nanocomposite and determine the satisfied concentration for invasion within the porous media under extreme reservoir conditions.

The objective of this study is to develop a hybrid nanofluid system of SiO_2/GNPs grafted with natural polymer (GA) as an effective oil-sweeping agent using a simple and eco-friendly method of direct aqueous phase exfoliation in the presence of GA and evaluate its dispersibility for long duration at high saline media and elevated temperature. Additionally, the synergistic effect of polymer grafted composite nanoparticles at low concentration on static and dynamic petrophysical characteristics IFT reduction between oil and brine, fluid viscosity enhancement, and wettability alteration of the rock surfaces under oil reservoir conditions of HSHT. Moreover, spontaneous imbibition (SI) experiments were performed to validate the feasibility of implementing an efficient concentration of 0.01 wt% of hybrid nanofluid to improve the EOR process mechanisms.

2. MATERIALS AND METHODS

2.1 Materials

The natural polymer GA, with 99% purity, was purchased from TIC GUMS, Malaysia. GA polymer was classified as a nonionic surfactant, and it was used as a green surface functionalization agent for nanoparticles to inhibit their agglomeration in the aqueous solution by a steric repulsive force [13]. Further, 2D carbon nanomaterials of pristine graphene nanoplatelets (GNPs) - grade C purchased from Sigma-Aldrich and Silica (SiO_2) nanoparticles were obtained from US Research Nanomaterials Inc. The chemical and physical properties of the purchased nanoparticles are summarized in Table 1.

Table 1. The essential properties of nanomaterials provided by the chemical supplier

Nanomaterials	**Purity (%)**	**Specific Surface Area (m^2/g)**	**Average Particle Size (nm)**	**Bulk Density (g/cm^3)**
Graphene Nanoplatelets (GNPs)	99.5	750	< 2 μm and thickness with a few nm	0.2-0.4
Silicon Dioxide (SiO_2)	99.5	180-600	20-30	<0.10

Sodium chloride (NaCl purity ≥ 99.5%), absolute ethanol, and toluene with high purity were procured from Merck Sdn Bhd, Malaysia. All the chemical materials were used without any further purification. Malaysian light crude oil was experimentally utilized for petrophysical investigations. The density and viscosity of used crude oil were measured to be 0.827 g/cm^3 and 8.13 mPa·s at ambient conditions, respectively.

2.2 Synthesis of GA polymer grafted (SiO_2/GNPs)

In this study, the combination of (SiO_2/GNPs) nanocomposite particles with GA polymer was prepared similar to the procedure of GA polymer grafted GNPs. The grafting process of GNPs with GA natural polymer through a direct aqueous phase exfoliation process was developed successfully to obtain highly dispersibility graphene nanosheets under reservoir conditions. The designated process details of functionalized GNP layers with moiety groups along the main chain of a natural polymer process have been reported in earlier research studies [14, 15]. In a typical process, the combination of nanocomposite particles was performed by adding a suitable weight of SiO_2 nanoparticles to GA-grafted GNPs at a weight ratio of 20:80 in 50 mL of absolute ethanol and purified deionized water. It was agitated for 1 h. The weight ratio was appointed to sustain the formulating homogeneous dispersion. Thereafter, the solution of nanocomposite particles was relocated to mix with 1 gm of GA in 50 mL of deionized water (DW) for 1 h at ambient temperature to obtain a suspension of polymeric solution. The homogenous suspension of 0-D nanoparticles with polymeric fluid was transferred to the ultrasonication process for 1 hour at mild sonication (40% of power sonication) in an ice bath to acquire a homogenous distribution of SiO_2 nanoparticles on the surface of GNPs layers. The resultant dispersion of nanocomposite particles was centrifuged at 10000 rpm for 0.5 hours. The collected nanocomposite particles were purified by washing three times with 50 mL of DW and then dried in an oven at 70℃ for 24 h to produce polymer-grafted (SiO_2/GNPs) nanocomposite for further characterizations, as illustrated in Figure 1.

The mono and hybrid nanofluids were prepared via a two-step method. The grafted nanoparticles with natural polymer were immediately added in high salinity brine (30000 ppm) as a base fluid at a certain concentration. After that, homogenous dispersion was produced through mild sonication for 1 hour at room temperature to produce as a second step, without further chemical addition like stabilizing agent or pH alteration. The final samples of single nanoparticles and nanocomposite products were marked by GA- SiO_2, GA-GNPs, and GA-(SiO_2-GNPs), respectively.

2.3 Nanocomposite characterizations

The quality and quantity of synthesized nanocomposite in this research were characterized by utilizing Fourier transform infrared spectroscopy (FTIR) and energy-dispersive X-ray spectroscopy (EDX) to identify the chemical analysis and the interaction between SiO_2 nanoparticles with the surface of 2D nanosheets in the presence of functional groups of GA polymer. The morphology of SiO_2/GNPs nanostructure was assessed using high-resolution transmission electron microscopy (HR-TEM) to investigate an interface's interaction of 2-D GNPs surface layer decorated with SiO_2 nanoparticles.

2.4 Dispersion stability of hybrid nanofluids

The dispersibility of prepared hybrid nanofluids was evaluated by zeta potential and hydrodynamic light scattering measurements to investigate the effect of free ions in the brine solution and elevated temperature on the colloidal stability of hybrid polymeric nanofluids over the long term. The zeta potential measurements were performed to validate the electrostatic repulsive potential for the colloidal system of polymer-grafted NPs in high-salinity brine. In addition, the hydrodynamic particle size distribution was conducted to emphasize the nanosuspension stability for a long time under subterranean conditions of high salinity and high temperature. Zetasizer, Nano ZS, model Malvern Instruments Ltd., UK, was designated to analyze the zeta potential and average particle size distribution of hybrid nanodispersion.

2.5 Interfacial tension and contact angle measurements

In this study, the measurements of IFT between the crude oil and polymeric hybrid nanofluids were employed by a simple pendant drop technique through a Goniometer/Tensiometer (Model: Ramé-Hart 260, USA), as presented in Figure 2. The shape of the oil droplet was fitted and detected according to the Young-Laplace Eq. (1); the IFT value of the equilibrium oil droplet was determined by analyzing the image of the suspended drop shape through image processing software (DROP image software):

$$\gamma = \frac{\Delta\rho \, g \, {R_o}^2}{\beta} \tag{1}$$

where, $\Delta\rho$ is the difference between the density of the oil droplet and the surrounding fluid of aqueous phase (g/cm^3), g is the gravitational acceleration (cm/sec^2), R_o is the radius of curvature at the drop apex (cm), and β is the shape factor.

The IFT experiments prepared nanofluids performed at different temperatures to investigate the impact of temperature on the value of IFT in the presence of functionalized nanoparticles. Eventually, each IFT experiment was repeated multiple times, and the mean value was calculated with a standard deviation of ± 0.01 mN/m.

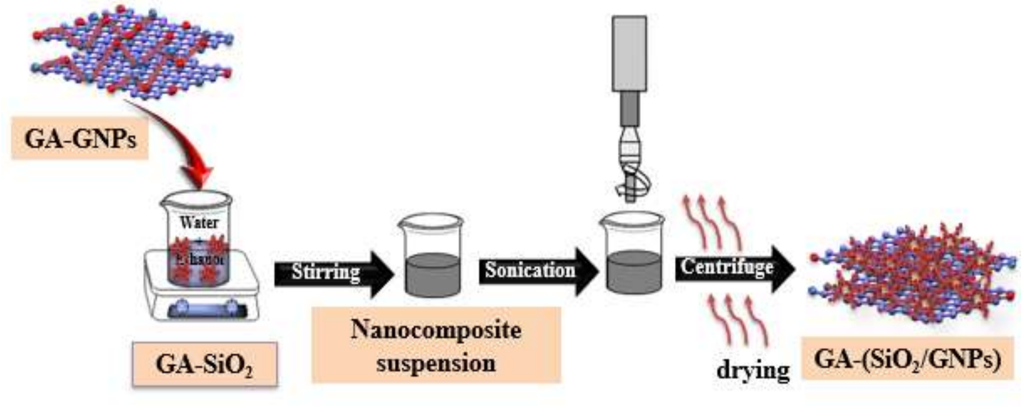
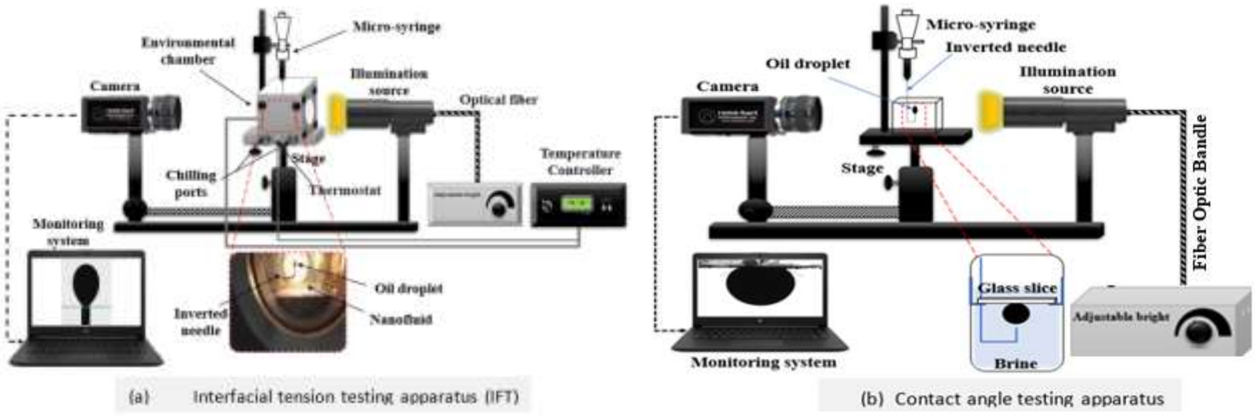


Figure 1. Schematic illustrated the procedure of synthesis of nanocomposite of (0-D/2-D) nanoparticles by two-step method



(a) Interfacial tension testing apparatus (IFT)

(b) Contact angle testing apparatus

Figure 2. The schematic of the Goniometer utilized for (a) IFT and (b) contact angle measurements at ambient and elevated temperatures

The contact angle of an oil droplet beneath the sandstone slides' surface was determined using a conventional sessile drop analysis through a Goniometer device (Model: Ramé-Hart 260, USA), as shown in Figure 2. The prepared samples of core rock were saturated and aged with crude oil under a vacuum pressure of 30 MPa for 15 days at room temperature to completely restore the wettability of the porous media into the oil-wet state. The oil-wet slides were aged inside plugged glass vials of various fluids, which involved different concentrations of the prepared nanofluids for 24 h at 90°C and then dried in an electric oven at 80°C for 1 h. The measurement range of 0-180° at ambient conditions, with accuracy and resolution ± 0.1° and 0.01°, to evaluate the impact of functionalized nanoparticles with polymer on altering the wetness of oil-wet sandstone core rocks. The treated sandstone slides were immersed inside a transparent glass cuvette filled with brine, and the micro-oil droplet was gently injected and released via an inverted needle to be captured at the bottom of the slide. Afterwards, the magnified side view images of the oil droplet were taken via camera, and the droplet shape analysis system, DROP image software, computed the three phases' contact angle.

2.6 Spontaneous imbibition test

SI is one of the most efficient invasion processes to quantitatively evaluate the wettability alteration of the core rock according to the efficiency of oil displacement through an imbibition mechanism [16, 17]. In this research, the experiments of SI were performed with three different types of grafted nanoparticles as compared with brine solution, to investigate the effect on the wettability alteration and oil recovery at reservoir conditions. The tests of SI were conducted using a fabricated Amott cell, as shown in Figure 3. The volume of expelled oil was monitored through a graduated glass tube at the upper part of the Amott cell, with an uncertainty of 0.05 mL.

At first, the core samples of Berea sandstone used in this test were cut into an appropriate length with the pot of imbibition cells. The core plugs were cleaned and dried based on the procedure as mentioned above in section 2.5. The porosity and permeability of the short core plugs were measured using the Poroperm apparatus. Then, the prepared samples of core rock were dry saturated and aged with crude oil under vacuum pressure 30 MPa for 2 weeks at room temperature to attain the change in the wettability of the porous media completely into the oil wet.

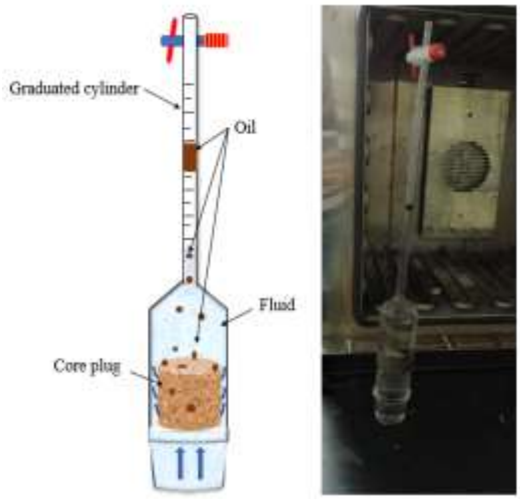


Figure 3. Schematic of Amott cell used in the SI experiment

After oil saturation, the samples were cleaned to remove extra oil on the surfaces of the core, and the weight of the samples was measured to determine the volume of oil seeped inside the pore channels. The core samples were preheated in the oven at 90°C for 1 hour prior to the imbibition process. Hence, the aged core plugs were placed in the annular cavity of different imbibition cells, which are filled with various imbibition fluids of brine and prepared nanofluids to an adequate level. Subsequently, the cells loaded with cores and desired fluids were put into the electric furnace with an accurate controller temperature under 90°C. The process of SI for all the experiments was carried out under 90°C to mimic the harsh reservoir circumstances of HSHT. The volume of released oil from the core was collected into the measured tube at the upper part of the Amott cell, and the cells were kept inside the oven until the volume of expelled oil was held constant. The imbibition oil recovery was recorded as a function of time by dividing the volume of displaced oil at specified time intervals by the volume of OOIP based on the following equation:

$$S_{or} = 1 - \frac{V_{wi}}{V_{oi}} \tag{2}$$

where, V_{oi} and V_{wi} are the volumes of initial oil saturation and water after the imbibition process, respectively.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of hybrid nanocomposite

The chemical functional groups on the surface of grafted nanocomposite particles of GA-SiO_2 and GA-GNPs were identified through FTIR spectroscopy in the range of wavelength absorbance between 400-4000 cm^{-1}. Figure 4 illustrates the comparison in the chemical composition for a sample of GA-(SiO_2-GNPs) hybrid nanocomposite to GA polymer grafted SiO_2 and GNPs, respectively. The FTIR spectrum of nanocomposite particles showed four distinctive peaks observed around 800, 1100, 1634, and 3435 cm^{-1}, which are attributed to indicative bands of functionalized silica with overlapping the amino groups (N-H) in the hydroxyl bands of (O-H) stretching vibration [18, 19]. However, the minor absorbance peaks that appeared at wavelengths 2930 and 2360 cm^{-1} are related to symmetric stretching of the alkanes band (C-H) and carboxylic band (COOH) [20, 21]; these bands are consistent with obtained FTIR spectroscopy peaks of GA-GNPs. These identification peaks of the FTIR spectrum affirmed that the SiO_2 nanoparticles were successfully incorporated on the surface of GNPs nanosheets via the physicochemical interaction, resulting in the formation of a GA grafted (SiO_2-GNPs) hybrid nanocomposite.

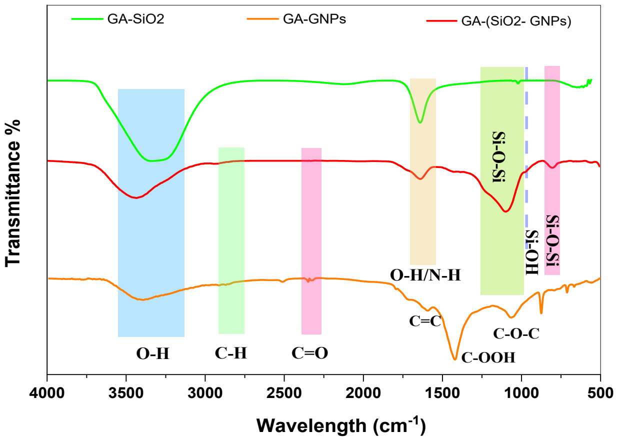
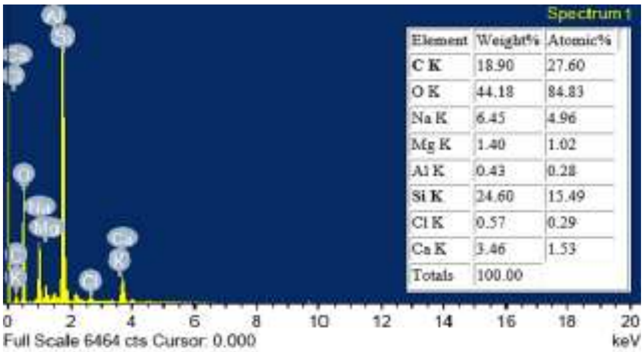


Figure 4. FTIR spectrum of the prepared hybrid nanocomposite compared with individual GA-SiO_2 and GA-GNPs

For an additional quantitative investigation to verify the success of the developed hybrid nanocomposite, the elemental combination analysis of GA-(SiO_2-GNPs) was determined by the EDX spectrum, as shown in Figure 5. The characteristic peaks confirmed silicon, oxygen, and carbon in the composition of the nanocomposite sample with minor elements such as Al, Cl, Mg, and Na correlated to the standards of (Al_2O_3, MgO, Albite, KCl, and Wollastonite ($CaCO_3$)) and used for the system calibration. The EDX results showed the regular distribution of GA-SiO_2 on the 2D layer of GA-GNPs, which provides clear evidence of the attachment and formation of hybrid nanocomposite via a simple, economical, and green method.

The morphological characteristics of nanocomposite particles have been achieved via Transmission electron microscope (TEM) techniques to determine the surface morphology of a combination of different shapes (0-D/2-D) nanoparticles and distribution of SiO_2 nanoparticles on the bi-layers of GNP nanosheets. The high-resolution TEM images were uniform and densely anchored on both surfaces of GNP 2-D nanosheets with GA-SiO_2 nanoparticles, as depicted in Figure 6.



Element	Weight%	Atomic%
C K	18.90	27.60
O K	44.18	84.83
Na K	6.45	4.96
Mg K	1.40	1.02
Al K	0.43	0.28
Si K	24.60	15.49
Cl K	0.57	0.29
Ca K	3.46	1.53
Totals	100.00	

Figure 5. EDX analysis of hybrid nanocomposite samples at different weight content of GA-GNP and 20% GA-SiO_2

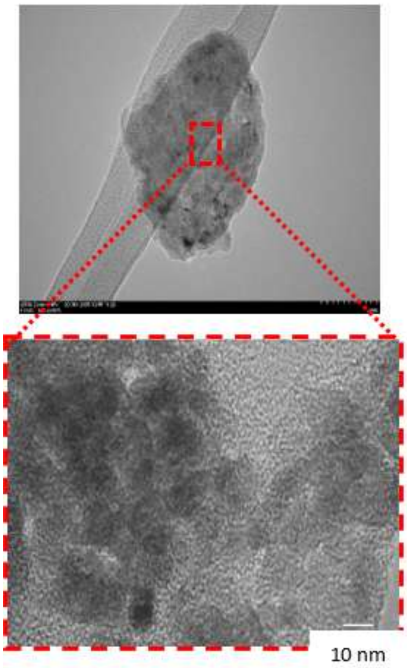


Figure 6. TEM images of hybrid nanocomposite at different magnifications, showing the homogeneity of anchoring of GA-SiO_2 on the GA-GNPs surface layer

The homogeneity of decoration was due to an effective functional group on SiO_2 and GNPs nanoparticles, under the impact of ultrasonication energy, which led to homogenous dispersion of hybrid nanoparticles. Moreover, the abundance of OH^- increased the chemical attachment of SiO_2 at the edges and plane of the 2D graphene nanostructure, resulting in the dense anchored of SiO_2 nanoparticles on the nanosheets. The high-resolution TEM images provide another evidence: The visible few layers of decorated GNPs with grafted SiO_2 nanoparticles in the range of particle size of 10-20 nm diameter, indicating well dispersibility and uniform distribution of hanged GA-SiO_2 along the surface of functionalized GNPs.

3.2 Dispersion stability of hybrid nanofluids

The dispersion stability of colloidal nanoparticles is a critical key for successful oil production in the scenario of nanofluid injection under the drastic reservoir conditions of HSHT. The absolute values of zeta potential, hydrodynamic particle size distribution of suspension 0.1 mg/mL of GA-(SiO_2/GNPs) nanocomposite particles in high salinity brine, and the pH value after one day of preparation in comparison with individual grafted nanoparticles, are as presented in Table 2. It can be observed that the high negative zeta potential value and small average diameter size value at the sample of hybrid nanosuspension with high content of GA-GNPs confirmed that the negative functional groups of GA polymer on the surface of SiO_2 nanoparticles promoted their dispersibility in high salinity brine. As expected, the combination of grafted nanoparticles (80% SiO_2-20% GNPs) with negatively charged functional groups exhibited a high value of zeta potential -42 mV and a mean particle size distribution of less than 200 nm. Therefore, the hybrid nanofluid with 20 wt.% of GNPs at a low concentration is considered a high colloidal stability sample with low electrostatic interaction in the high salinity aqueous media. Comparatively, the recorded value of zeta potential for SiO_2-GNPs hybrid nanofluids at a low concentration is more negative than that reported by Tajik et al. [22].

Table 2. Results of zeta potential values, average hydrodynamic diameter size, and the pH value of dispersed mono and hybrid nanofluids in high salinity brine after one day

Nanofluids	ζ (mV)	Std Dev., (mV)	d (nm)	Std Dev., (nm)	pH	Std Dev., (%)
GA-(SiO_2-20%GNPs)	-42	2.03	146	1.84	8.03	0.01
GA-GNPs	-47	0.87	122	0.98	7.83	0.01
GA-SiO_2	-38	1.97	20	0.4	7.86	0.01

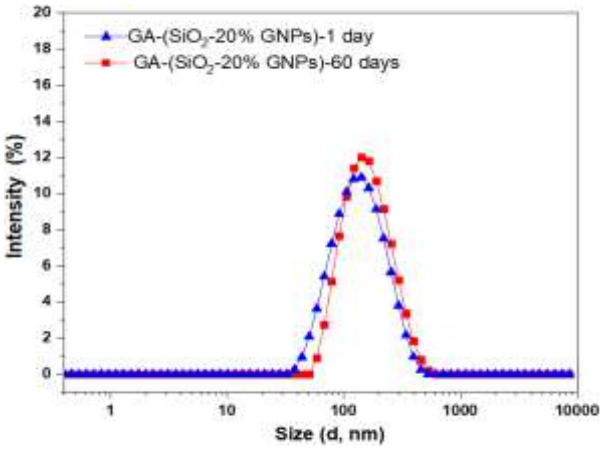


Figure 7. The particle size distribution for a sample of GA-(SiO_2-20 % GNPs) hybrid nanofluid after one day and 60 days

The long-term dispersion stability for a superior sample of hybrid nanofluids was further ascertained with particle size distribution after one day and 60 days in high-salinity brine, as shown in Figure 7. After one day and 60 days, the average particle size distribution observed was only a broad single peak at 146 and 149 nm, respectively.

The particle size distribution outcomes revealed similar descriptions to those of GA-GNPs, which confirmed the dispersion of integrated hybrid nanocomposite particles in high-salinity brine. Moreover, the slight change in the particle size distribution provided further evidence that GA-(SiO_2-20% GNPs) with functional groups has a convenient dispersion in high salinity brine during a long period over 60 days.

Figure 8 illustrates the average value of hydrodynamic particle size of dispersed GA-(SiO_2-20 % GNPs) samples in high salinity and aged into the heating control system under different temperatures of 30, 50, 70, and 90°C, respectively. After ageing one day at different temperatures, the mean hydrodynamic particle size was varied, with the particle size value for all hybrid nanofluid samples being less than 200 nm.

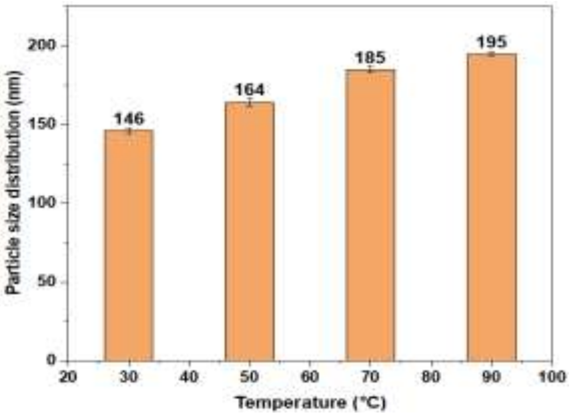


Figure 8. The average value of hydrodynamic particle size of dispersed GA-(SiO_2-20% GNPs) in high salinity brine under various temperatures

Furthermore, the hybrid nanofluids remained homogeneously dispersed without any agglomeration or precipitation after ageing at high temperatures. Hence, the results deduced that the configuration of GA-(SiO_2-20% GNPs) hybrid nanofluid with functional groups on the surface led to an upsurge in the steric repulsive force and subsequently improved the colloidal stability under severe environmental conditions of HSHT.

3.3 Interfacial tension evaluation

The IFT measurement between the immiscible fluids of crude oil and GA (SiO_2-GNPs) hybrid nanofluids was further investigated under HSHT to evaluate the comprehensive performance of GA polymer grafted nanocomposite at the cruel reservoir conditions. The IFT measurements of a superior stable sample of a low concentration of 0.1 mg/mL of GA-(SiO_2-20% GNPs) hybrid nanofluid in high salinity brine were investigated under reservoir temperature of 90°C by comparing with mono nanofluids of GA-SiO_2 and GA-GNPs, as demonstrated in Figure 9. The presence of GA-(SiO_2-20% GNPs) nanocomposite particles that besieged the crude oil droplet under the influence of temperature is significantly reduced the equilibrium IFT value of the system to approximately 4.73 mN/m. However, the equilibrium IFT value of the system between the crude oil and the brine was remarkably reduced to 14.51 mN/m at an elevated temperature of 90°C. When the grafted nanocomposite particles at a low concentration of 0.1 mg/mL of GA-(SiO_2-

20% GNPs) surrounded the crude oil droplet under HSHT, the IFT value significantly declined from 14.51 to 4.73 mN/m at high-temperature 90°C. This result signifies a high reduction in the IFT value of the system by around 67% compared with that of brine and single constituent nanofluid injections under HSHT conditions.

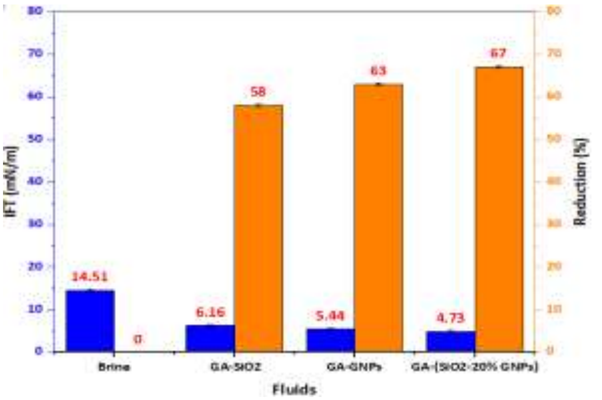


Figure 9. Impact of GA polymer grafted single and hybrid nanoparticles on the value of IFT between oil/ brine at 90°C

The results of IFT reduction are ascribed to simultaneously synergistic effects of developing the individual nanoparticles of hydrophilic GA-SiO_2 with amphiphilic GA-GNPs. Also, the effective amphiphilic functional groups of GA polymer decorated the surface of the nanocomposite, which probably acts as a surfactant at the interface between the oily and watery phases. It is worth noting that the oil-brine IFT declines in the structure of hybrid nanocomposite particles due to extreme adsorption at the oil-brine interface. Indeed, the high surface area of GNPs nanosheets as a carrier for GA-SiO_2 nanoparticles and amphiphilic moieties have assembled at the interface border, which may create an additional layer and thus expand the interface between the crude oil and brine. Further, it is likely attributed to stabilizing grafted hybrid nanocomposite in the high ionic electrolyte and high temperature at the interface with repulsive forces, which contributed to extending the liquid-liquid interface and thus reducing the IFT of the system. This consideration agrees with the findings of Tajik et al. [23], who reported the effect of high salinity ionic compounds with the existence of functional groups on the IFT reduction.

3.4 Wettability alteration

The wettability alteration of the core rock surface during nanofluid seepage inside the heterogenous porous media is an important second component in lowering capillary force and improving oil recovery. However, altering wettability from oil-wet to water-wet is a more convenient and efficient approach to liberate trapped oil inside the pore throat. The wettability of an oil droplet on a rock surface was determined by measuring the static and dynamic contact angles at three phases. Figure 10 shows the comparison in the value of measured contact angle for oil-wet sandstone slides treated with GA-(SiO_2-20% GNPs) hybrid nanocomposite with the absence of nanoparticles. The contact angle of the oil droplet underneath the oleophilic glass slice treated in the brine was changed from 147° to 108°, resulting in an alteration of the wettability from the oil-wet to intermediate. When the lipophilic sandstone slice was treated in a vial of hybrid nanofluid at 90°C for 24 hours, the contact angle dropped by about 84%, and the measured value was about 20.23° at 0.1 mg/mL of GA-(SiO_2-20% GNPs). This remarkable change in the shape of the oil droplet with a mean contact angle value of 20.23° indicates the system wettability has altered from oil-wet to relatively water-wet.

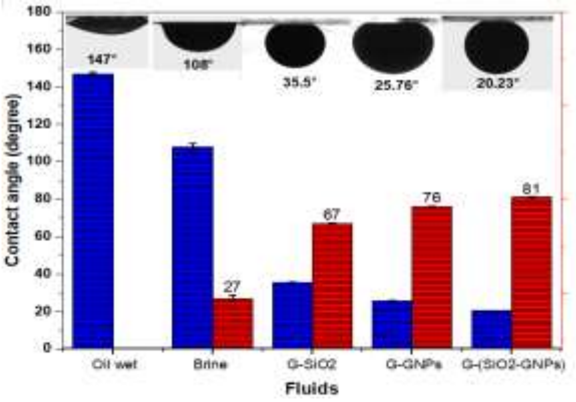


Figure 10. The contact angle of the oil droplet below the untreated and treated sandstone slices with various mono and hybrid nanofluids

Further, it is worth noting that the estimated contact angle of the hybrid nanocomposite has a greater tendency to the water wet than the values of individual nanofluids and expands the region of non-wetting along the rock's surface. This observation can be attributed to the intense adsorption of the grafted hybrid nanocomposite with functional groups at the contact region between three phases of the solid surface and immiscible liquids. In this context, the oil-wetting rock surface has been effectively modified into a water-wet state via the decoration of the solid surface with a low concentration of GA-(SiO_2-20% GNPs) nanocomposite particles.

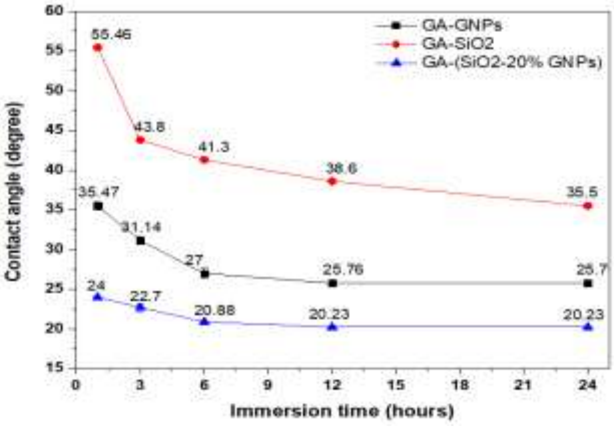


Figure 11. The dynamic contact angle of the triple phases system (oil/brine/ lipophilic sandstone slice) treated with different nanofluids

Figure 11 displays the variation in the contact angle of oil-wetting sandstone slides immersed in the best samples of GA-(SiO_2-20% GNPs) hybrid nanofluid, GA-SiO_2, and GA-GNPs as a function of soaking time. When the oleophilic slice was immersed in the hybrid nanofluid for over 1 hour at a temperature of 90°C, the contact angle of an oil droplet on the slice surface was dramatically changed from 147° to 24° into relatively water wet.

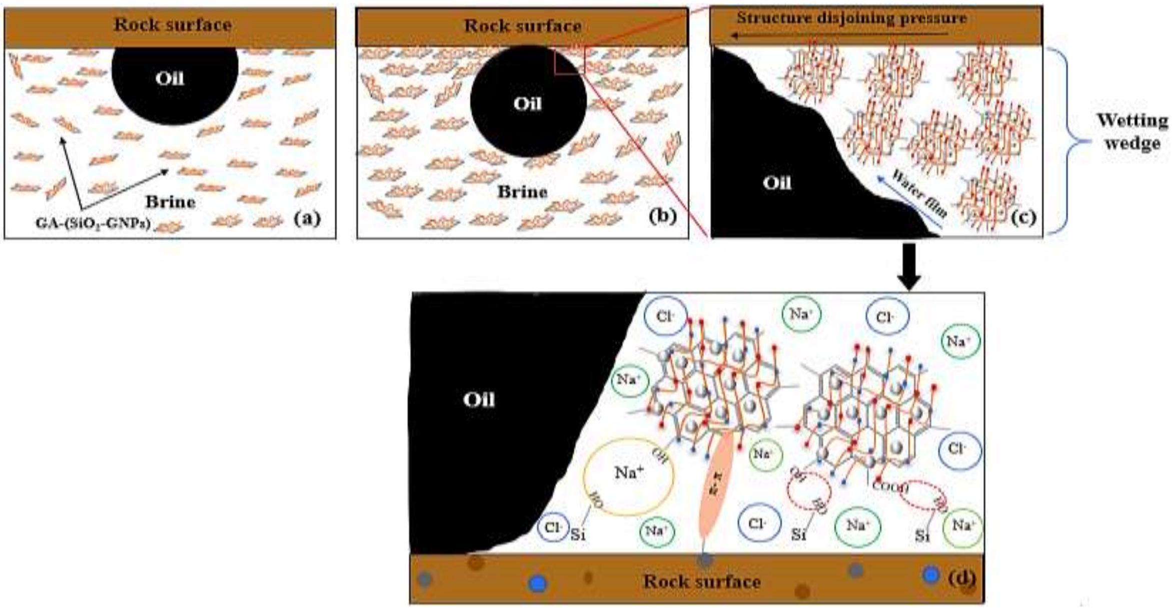


Figure 12. Schematic view for changing the wettability of the surface rock in the presence of GA-(SiO_2-GNPs) hybrid nanocomposite at the triple interfaces (solid/oil/brine)

However, as the treating time increased in the hybrid nanofluid, the hanging oil droplet began to displace from the slice surface within a narrow contact angle to reach an equilibrium value of 20.23° after 12 hours. In the meantime, the trend of 0.1 mg/mL of GA-(SiO_2-20% GNPs) has a considerable degree of reduction in the contact angle, indicating a desirable performance for separating the oil from the surface of the core rock.

The rapid adsorption of nanocomposite at the three phases contact region would lead to lower IFT between oil and brine, and the triple contact line shrinkage would inhibit the oil droplet from adhering to the rock during the detachment mechanism. The functional groups of hydroxyl, carboxyl, and amino bonds that decorated the surface structure of (SiO_2-GNPs) hybrid nanocomposite may play an important role in changing the wettability via interaction with silanol groups (Si-OH) along the surface of the rock in the presence of the salt cations of (Na^+). Consequently, the hydrogen bridging has formed between the chemical moieties in the nanocomposite structure and the hydroxyl groups on the surface of the solid surface. Further, electrostatic interactions (π-π) between the edges or planes of GA-GNPs nanosheets and negative ions on the rock surface enhanced the adsorption of the nanocomposite on the solid surface, expanding the water film and changing the wettability into water-wet states, as represented schematically in Figure 12. As a result, the structural disjoining pressure in the three-phase (oil-solid-nanofluid) contact region is formed by the arrangement of functionalized nanocomposite with high electrostatic repulsion and the effect of Brownian motion. This pressure drives to expand the wedge film at the triple contact spot and thus detach the oil from the slice surface. Hence, it can be concluded that GA-(SiO_2-20% GNPs) at a low concentration of 0.1 mg/mL has great potential to alter the wettability of oily surface to water wet over a short period as a result of the combination of effective individual constituents in the structure of nanocomposite. The contact angle findings are completely consistent with the results of functionalized nanocomposites on altering the wettability in the current and previous research studies Bahraminejad et al. [24], AfzaliTabar et al. [25], and Omidi et al. [26].

3.5 Spontaneous imbibition

For further insights, the imbibition test was conducted to investigate the performance of GA-(SiO_2-GNPs) hybrid nanofluid for altering the wetness in the underlying mechanism for EOR at the reservoir environment of HSHT. Figure 13 shows the imbibition recovery of the oil-wet core sample immersed in the optimum hybrid nanofluid compared with mono nanofluids at 90°C versus seepage duration over 168 hours. The properties of Berea sandstone core samples were used in the intended test of SI, as reported in Table 3. Apparently, the oil imbibition behaviour for all samples revealed the same trend with the imbibition equivalent time, which means that no more could be extracted from the core with increasing time. As expected, the highest oil recovery was recorded at around 77% for the immersed core plug, even with a low concentration of 0.1 mg/mL of GA-(SiO_2-20% GNPs) over 168 hours.

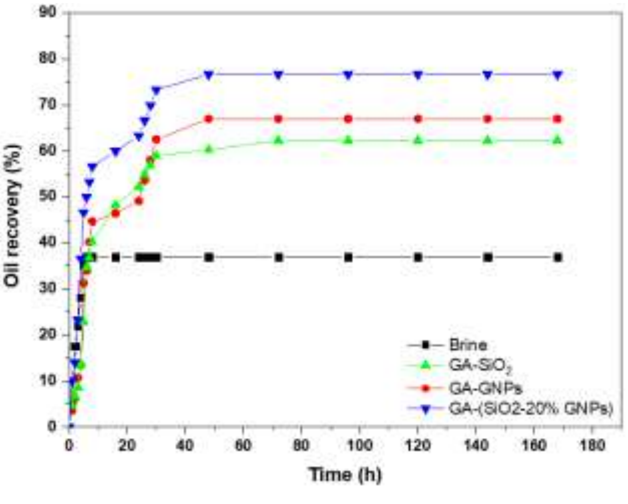


Figure 13. Comparative the performance of hybrid nanofluid-based high saline brine for oil recovery via imbibition mechanism with individual constituent nanofluids at 90°C for 168 hours

However, the oil extraction with developed hybrid nanofluid GA-(SiO_2-20% GNPs) was remarkably enhanced to 52, 20, and 13% increment the quantities of expelled oil in the cells loaded with brine, and the best samples of GA-SiO_2 and GA-GNPs nanofluids via capillary imbibition, respectively. These findings are consistent with claims of IFT, and wettability alteration results that GA-(SiO_2-20% GNPs) hybrid nanofluids at low concentration possess preferable performance to release the oil inside the pore channels under HSHT. At different stages of the imbibition test, the amount of expelled crude oil from the core sample immersed in the Amott cell loaded inside the best sample of GA-(SiO_2-GNPs) hybrid nanofluid, as depicted in Figure 14.

Table 3. The properties of Berea sandstone core plugs

Property	**Core Parameter**		
	GA-SiO₂	**GA-GNPs**	**SiO₂-GNPs**
L. (cm)		3.135	
Dia. (cm)		3.83	
k (milli Darcy)	375.2	374.8	373.5
φ (%)	14.2	14.4	14.9
PV (cm^3)	7.47	6.94	7.161
OOIP (cm^3)	6.87	6.5	7.1
S_{oi} (%)	92	94	99

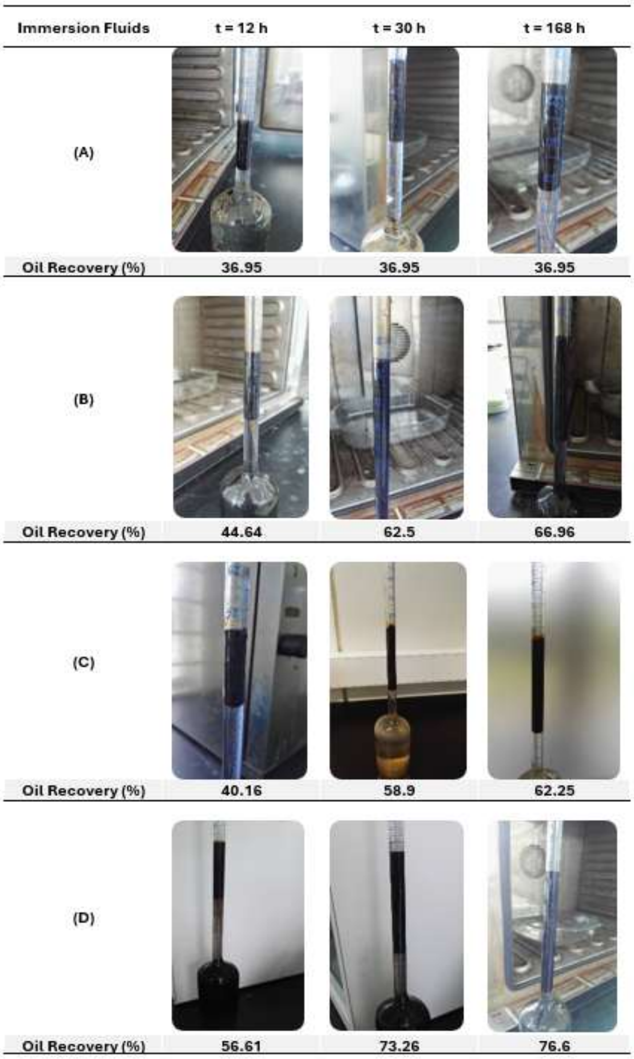


Figure 14. SI experiments at different stages of (A) Brine (30,000 ppm of NaCl), (B) GA-GNPs, (C) GA-SiO_2, (D) GA-(SiO_2-20% GNPs) nanofluids under HSHT

According to the characterizations mentioned before, the contact angle reduction of wettability alteration was more effective than IFT reduction between oil and brine even with a low concentration of GA-(SiO_2-20% GNPs) hybrid nanofluid. As a result, IFT reduction was not the predominant mechanism for capillary imbibition, but it was sufficient to seep the nanofluids into the deep core rock pores. In this way, the nanocomposite structure under the driving of capillary force imbibed into the pores of the core plug to adsorb and spread promptly inside the pores for alteration of the pores' surface oil-wetness to water wet. As time progressed, the hybrid nanofluids kept imbibing into the core from all directions, which spread to form the structural disjoining pressure and reduce the effect of the capillary pressure in the narrow channels. Ultimately, the crude oil mobilized from the pore throats and a large quantity of oil was recovered under the imbibition mechanism [27, 28]. A comparison of the imbibition experimental results of GA-(SiO_2-20% GNPs) hybrid nanofluid under HSHT with the literature is not possible due to a lack of similar findings.

4. CONCLUSIONS

In this study, the polymeric hybrid nanofluid system of GA polymer grafted (SiO_2/GNPs) was successfully prepared using direct aqueous phase exfoliation in the presence of GA. The potential performance of the developed hybrid nanocomposite GA-(SiO_2-GNPs) was evaluated through an SI approach. Combining 20 wt.% of GA-GNPs nanosheets with GA-SiO_2 nanoparticles enhanced their colloidal stability over a long period at HSHT with no agglomeration or precipitation. The long-term dispersibility measurements of hybrid nanofluids at a low concentration of 0.1 mg/mL in high-salinity brine and under high temperatures indicated the thermal stability of the hybrid nanodispersion, with an average hydrodynamic particle size of less than 200 nm and the zeta potential greater than -30 mV. The findings of the imbibition experiments showed that hybrid nanofluids could recover an additional oil quantity than single constituent nanofluids by about 77% of OOIP at reservoir environments. The overall results pointed out the promising potential of the developed GA-GNPs and hybrid nanofluids with ultra-low concentration for EOR application, which could enhance oil recovery with satisfying performance under reservoir conditions of HSHT.

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REFERENCES

[1] Thomas, S. (2008). Enhanced oil recovery-an overview. Oil & Gas Science and Technology-Revue de l'IFP, 63(1): 9-19. https://doi.org/10.2516/ogst:2007060

[2] Gbadamosi, A.O., Junin, R., Manan, M.A., Agi, A., Yusuff, A.S. (2019). An overview of chemical enhanced oil recovery: Recent advances and prospects. International Nano Letters, 9: 171-202. https://doi.org/10.1007/s40089-019-0272-8

[3] Abam, F.I., Nwankwojike, B.N., Ohunakin, O.S., Ojomu, S.A. (2014). Energy resource structure and on-going sustainable development policy in Nigeria: A review. International Journal of Energy and Environmental Engineering, 5: 102. https://doi.org/10.1007/s40095-014-0102-8

[4] Peng, B., Zhang, L., Luo, J., Wang, P., Ding, B., Zeng, M., Cheng, Z. (2017). A review of nanomaterials for nanofluid enhanced oil recovery. RSC Advances, 7(51): 32246-32254. https://doi.org/10.1039/C7RA05592G

[5] Hendraningrat, L., Li, S., Torsaeter, O. (2013). Enhancing oil recovery of low-permeability Berea sandstone through optimized nanofluids concentration. In SPE Asia Pacific Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia, SPE-165283. https://doi.org/10.2118/165283-MS

[6] Ureña-Benavides, E.E., Lin, E.L., Foster, E.L., Xue, Z., Ortiz, M.R., Fei, Y., Larsen, E.S., Kmetz, A.A., Lyon, B.A., Moaseri, E., Bielawski, C.W. (2016). Low adsorption of magnetite nanoparticles with uniform polyelectrolyte coatings in concentrated brine on model silica and sandstone. Industrial & Engineering Chemistry Research, 55(6): 1522-1532. https://doi.org/10.1021/acs.iecr.5b03279

[7] El-Hoshoudy, A.N., Desouky, S.E.M., Betiha, M.A., Alsabagh, A.M. (2016). Use of 1-vinyl imidazole based surfmers for preparation of polyacrylamide–SiO_2 nanocomposite through Aza-Michael addition copolymerization reaction for rock wettability alteration. Fuel, 170: 161-175. https://doi.org/10.1016/j.fuel.2015.12.036

[8] Behzadi, A., Mohammadi, A. (2016). Environmentally responsive surface-modified silica nanoparticles for enhanced oil recovery. Journal of Nanoparticle Research, 18: 266. https://doi.org/10.1007/s11051-016-3580-1

[9] Rezvani, H., Riazi, M., Tabaei, M., Kazemzadeh, Y., Sharifi, M. (2018). Experimental investigation of interfacial properties in the EOR mechanisms by the novel synthesized Fe_3O_4 Chitosan nanocomposites. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 544: 15-27. https://doi.org/10.1016/j.colsurfa.2018.02.012

[10] Bila, A., Stensen, J.Å., Torsæter, O. (2020). Polymer-functionalized silica nanoparticles for improving water flood sweep efficiency in Berea sandstones. E3S Web of Conferences, 146: 02001. https://doi.org/10.1051/e3sconf/202014602001

[11] Ali, J.A., Kolo, K., Khaksar Manshad, A., Stephen, K.D. (2019). Low-salinity polymeric nanofluid-enhanced oil recovery using green polymer-coated ZnO/SiO_2 nanocomposites in the Upper Qamchuqa Formation in Kurdistan Region, Iraq. Energy & Fuels, 33(2): 927-937. https://doi.org/10.1021/acs.energyfuels.8b03847

[12] Lashari, N., Ganat, T., Ayoub, M.A., Kalam, S., Ali, I. (2023). Coreflood investigation of HPAM/GO-SiO_2 composite through wettability alteration. Journal of Molecular Liquids, 371: 121130. https://doi.org/10.1016/j.molliq.2022.121130

[13] Zhang, H., Shan, G., Liu, H., Xing, J. (2007). Surface modification of γ-Al_2O_3 nanoparticles with Gum Arabic and its applications in adsorption and biodesulfurization. Surface and Coatings Technology, 201(16-17): 6917-6921. https://doi.org/10.1016/j.surfcoat.2006.11.043

[14] Hamdi, S.S., Al-Kayiem, H.H., Muhsan, A.S. (2020). Natural polymer non-covalently grafted graphene nanoplatelets for improved oil recovery process: A micromodel evaluation. Journal of Molecular Liquids, 310: 113076. https://doi.org/10.1016/j.molliq.2020.113076

[15] Hamdi, S.S., Al-Kayiem, H.H., Alsabah, M.S., Muhsan, A.S. (2022). A comparative study of dispersed and grafted nanofluids of graphene nanoplatelets with natural polymer in high salinity brine for enhanced oil recovery. Journal of Petroleum Science and Engineering, 210: 110004. https://doi.org/10.1016/j.petrol.2021.110004

[16] Mason, G., Morrow, N.R. (2013). Developments in spontaneous imbibition and possibilities for future work. Journal of Petroleum Science and Engineering, 110: 268-293. https://doi.org/10.1016/j.petrol.2013.08.018

[17] Meng, Q., Liu, H., Wang, J. (2017). A critical review on fundamental mechanisms of spontaneous imbibition and the impact of boundary condition, fluid viscosity and wettability. Advances in Geo-Energy Research, 1(1): 1-17. https://doi.org/10.26804/ager.2017.01.01

[18] Tran, T.N., Pham, T.V.A., Le, M.L.P., Nguyen, T.P.T., Tran, V.M. (2013). Synthesis of amorphous silica and sulfonic acid functionalized silica used as reinforced phase for polymer electrolyte membrane. Advances in Natural Sciences: Nanoscience and Nanotechnology, 4(4): 045007. https://doi.org/10.1088/2043-6262/4/4/045007

[19] Ekka, B., Sahu, M.K., Patel, R.K., Dash, P. (2019). Titania coated silica nanocomposite prepared via encapsulation method for the degradation of Safranin-O dye from aqueous solution: Optimization using statistical design. Water Resources and Industry, 22: 100071. https://doi.org/10.1016/j.wri.2016.08.001

[20] Sumayya, A., Panicker, C.Y., Varghese, H.T., Harikumar, B. (2008). Vibrational spectroscopic studies and ab initio calculations of L-glutamic acid 5-amide. RASAYAN Journal of Chemistry, 1(3): 548-555.

[21] Supriyanto, G., Rukman, N.K., Nisa, A.K., Jannatin, M., Piere, B., Abdullah, A., Fahmi, M.Z., Kusuma, H.S. (2018). Graphene oxide from Indonesian biomass: Synthesis and characterization. BioResources, 13(3): 4832-4840. https://doi.org/10.15376/biores.13.3.4832-4840

[22] Tajik, S., Nasernejad, B., Rashidi, A. (2017). Surface modification of silica-graphene nanohybrid as a novel stabilizer for oil-water emulsion. Korean Journal of Chemical Engineering, 34: 2488-2497. https://doi.org/10.1007/s11814-017-0125-y

[23] Tajik, S., Shahrabadi, A., Rashidi, A., Jalilian, M., Yadegari, A. (2018). Application of functionalized silica-graphene nanohybrid for the enhanced oil recovery performance. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 556: 253-265. https://doi.org/10.1016/j.colsurfa.2018.08.029

[24] Bahraminejad, H., Khaksar Manshad, A., Riazi, M., Ali, J.A., Sajadi, S.M., Keshavarz, A. (2019). CuO/TiO_2/PAM as a novel introduced hybrid agent for water—oil interfacial tension and wettability optimization in chemical enhanced oil recovery. Energy & Fuels, 33(11): 10547-10560. https://doi.org/10.1021/acs.energyfuels.9b02109

[25] Tabar, M.A., Rashidi, A., Alaei, M., Koolivand, H., Pourhashem, S., Askari, S. (2020). Hybrid of quantum dots for interfacial tension reduction and reservoir

alteration wettability for enhanced oil recovery (EOR). Journal of Molecular Liquids, 307: 112984. https://doi.org/10.1016/j.molliq.2020.112984

[26] Omidi, A., Manshad, A.K., Moradi, S., Ali, J.A., Sajadi, S.M., Keshavarz, A. (2020). Smart-and nano-hybrid chemical EOR flooding using Fe_3O_4/eggshell nanocomposites. Journal of Molecular Liquids, 316: 113880. https://doi.org/10.1016/j.molliq.2020.113880

[27] Liu, J., Sheng, J.J., Wang, X., Ge, H., Yao, E. (2019). Experimental study of wettability alteration and spontaneous imbibition in Chinese shale oil reservoirs using anionic and nonionic surfactants. Journal of Petroleum Science and Engineering, 175: 624-633. https://doi.org/10.1016/j.petrol.2019.01.003

[28] Zhou, H., Zhang, Q., Dai, C., Li, Y., Lv, W., Wu, Y., Cheng, R., Zhao, M. (2019). Experimental investigation of spontaneous imbibition process of nanofluid in ultralow permeable reservoir with nuclear magnetic resonance. Chemical Engineering Science, 201: 212-221. https://doi.org/10.1016/j.ces.2019.02.036

NOMENCLATURE

d	particle size distribution (nm)
g	gravitational acceleration ($m.s^{-2}$)
S_{oi}	initial oil saturation (%)
S_{or}	residual oil saturation (%)
L	length (cm)
Dia	diameter (cm)
k	permeability (milli Darcy)
PV	pore volume (cm^3)

Greek symbols

ρ	density ($g.cm^{-3}$)
γ	Interfacial tension (mN/m)
φ	porosity of the porous media (%)
ζ	zeta potential (mV)

Abbreviations

C-EOR	chemical-enhanced oil recovery
DW	deionized water
EOR	enhanced oil recovery
EDX	energy dispersive X-ray
FTIR	Fourier transform-infrared spectroscopy
GA	gum Arabic
GNPs	graphene nanoplatelets
HSHT	high salinity and high temperature
IFT	interfacial tension
NPs	nanoparticles
OOIP	original oil in place
SI	spontaneous imbibition