Influence of non-covalently functionalized graphene nanoplatelets on viscosity and wettability for improved oil mobility at reservoir conditions

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Abstract. Noncovalent functionalized graphene nanoplatelets (GNPs) were successfully prepared with Gum Arabic as exfoliation solvent via an ultrasonicication-assisted process to produce a highly dispersed material under high salinity and high temperature conditions. The implementation of the functionalization groups was validated with Fourier transform infrared spectroscopy and Transmission Electron Microscopy. The functionalized graphene nanoplatelets with Gum Arabic were dispersed in 3 wt.% high salinity brine with various concentrations to prepare Gum Arabic-GNP/brine nanofluids. The dynamic viscosity of the produced nanofluid at different concentrations was higher than that of crude oil at a high temperature (90 °C) and a high shear rate (1000 L/s). The functionalized graphene with Gum Arabic altered the wettability of sandstone from oil to water and change the contact angle from 108° to 21° at 0.1 wt.%. Moreover, the value of contact angle reduced to 87% with presence 0.1 wt.% of GA-GNPs. These results are demonstrating that the GA-GNPs nanofluids could improve the mobility of the residual oil from the porous media to the production well with high efficiency of oil displacement.

1. Introduction
Since decades, nanofluids have been acquiring considerable concern with progressing of nanotechnology in various fields of industry. Nanofluids expression was proposed by Choi in 1995 [1], as an innovation of nanotechnology in heat transfer application, which consists of suspension exhibited high thermal conductivity by dispersion of a nanoscale materials, typical size less than (100 nm) in the base fluids [1]. Furthermore, the application of nanofluids in the oil and gas industry as a novel way more efficient than conventional fluids, economical and environment friendly [2]. Employment of nanofluids in chemical EOR have proven a significant potential to lower the interfacial energy of the colloidal system (between the oily and watery phase), a result of the high surface energy of nanoparticles. Also, it is used to modify the surface properties between the solid and liquid phases of the core with the presence of stable nanoparticles [3, 4]. In addition, the reduction in the viscosity ratio which are leading to increment the capillary number and eventually oil droplet is extracted and detached from the surface of rock pore by capillary force [5]. Most of literature have been reviewed the potentials of utilizing metal oxide nanoparticles like (SiO2, Al2O3, ZnO, TiO2, NiO, ZrO2 and Fe3O4) for enhance oil recovery [6, 7].
However, the main issue of these nanofluids are unstable colloidal suspension and agglomeration of the nanoparticles at reservoir conditions high salinity and high temperature (HSHT). High concentration of salts would have high effect of ionic strength that reduce the electrostatic double layer forces between nanoparticles. However, nanoparticles have tendency to agglomerate, because of the high specific surface area to volume and the existence of mutual van der Waals forces of attraction among them. They caused clogging the pore throat and declining the porosity and the permeability of the porous media [8, 9]. Moreover, disordering of the nanoparticles at the wedge film which was created at the triple contact line between the oil droplet with the surface of the core rock and the stable nanoparticles according to the new concept by Wasan and Nikolov [10]. Thus, decrement the extent of disjoining pressure, this force was formed in the wedge film depend on the size and stability of the nanoparticles. Consequently, diminishing the recovery of the trapped oil and subsequently reduction the sweep efficiency [9]. These challenges could be reduced by preparing self-stabilize nanoparticles to overcome the agglomeration and sedimentation of nanoparticles under the harsh environmental condition and displacing more quantity of the oil from the pore than either unmodified nanoparticles or dispersant alone [11].

Graphene as new generation of carbon nanostructures have been attracting the vast interest of the scientists and researchers, due to its unique and remarkable properties [12, 13]. A graphene monolayer is usually stacked by an intense van der Waals force between layers to form graphene nanoplatelets (GNPs), which have better thermophysical and rheological properties, higher surface area, more highly ordered graphitic carbon, and lower cost than monolayer graphene [14]. The innate problem of GNPs is low dispersion, high hydrophobicity and strong van der Waals interactions. Numerous techniques have been developed to exfoliate graphene by physical and chemical process [15, 16]. In the previous studies, Chemical functionalization with organic hydrophilic group such as (hydroxyl, carbonyl, and carbonyl, etc.) can be added the radical at the edge and/ or the basal of graphene for improving the dispersibility of graphene [17]. Moreover, stable dispersion of graphene oxidized by common chemical process (Modified Hummer’s method) [18], Also modified with metal oxide nanoparticles as hybrid nanofluid to stabilize the emulsion [19]. Some studies have utilized the polymer as surface modifier of graphene and graphene oxide (GO) to improve their dispersibility in high salinity of brine and high temperature. In this regard, Zuniga et al. [20], supposed to functionalize graphene oxide with a polyzwitterionic polymer to improve stability for a long period (140 days) at harsh conditions including high ionic strength of API and Arab-D brine and temperature. Luo et al. [21], prepared nanofluid of graphene amphiphilic Janus nanosheets by modified the surface of GO with alkylamine to investigate the colloidal stability of this nanofluid in unfriendly environments. Radnia et al. [22], synthesized amphiphilic graphene by direct functionalization of Nano porous graphene (NPG) prepared by chemical vapor deposition with sulfonic (-SO₂H) groups to enhance oil recovery. These functionalization techniques have used corrosive and harmful materials. Therefore, cost-effective and safe methods should be developed to functionalize graphene nanoplatelets.

Gum Arabic (GA) is considered the oldest one among the natural materials, which it is widely used in the food, soft drink, drug delivery and emulsion (oil/water) [23, 24]. However, GA is utilized with nanoparticles due to its ability to stabilize the dispersion of aqueous fluid over a wide range of pH. Meanwhile, GA has contained the hydroxyl and carboxyl bonds with long chains and complex molecules structure, which are absorbed on the surface of nanoparticles to provide by the steric repulsive [25].

This work aimed to synthesize hydrophilic graphene via an economical and environmentally green process with GA through direct exfoliation with assistance of ultrasonic process. To the best of our knowledge, few researches have reported the synthesis and stability of GNPs through noncovalent functionalization of surfactant at high salinity and high temperature. Thus, functionalized GNPs with GA were well prepared in this study. The quantity and the grafting of the functionalization groups on the graphene layers were evaluated. Moreover, the effect of GA-GNPs with various concentration on the oil wettability on surface of the sandstone and the dynamic viscosity under reservoir conditions were investigated.
2. Methodology

2.1. Materials

Pristine Graphene nanoplatelets grade (C) have average particle size less than 2 µm and thickness of a few nanometers, with high specific area (750 m²/g) were used in this study as raw material. Gum Arabic was utilized as exfoliation solvent with high purity were purchased from Sigma Aldrich. Sodium Chloride (NaCl) salt with purity ≥ 99.5% and purified deionized water (18.2 MΩ) at 25 ºC were used to prepare high salinity brine. All the materials were used as received without any further purification.

2.2. Experimental set up

2.2.1. Preparation of GA-GNP nanofluids. In the first step of exfoliation process 0.5 gram of GA was mixed with 100 ml of deionized water (DW) at ambient temperature for 0.5 hour. Afterward, 1 gram of GNPs was added to the solution and stirred for 1 hour, to obtain the homogeneous suspension of nanoplatelets. Next, the mixture of suspension was dispersed by using probe sonicator (Ultrasonic processor, 750 Watt, and frequency 25 KHz) to reduce the van der Waals forces between the graphene layers. An ice bath was used to prevent the evaporation of the exfoliated solvent and to maintain its temperature near ambient temperature. The parameters for exfoliation the nanoplatelets were selected to successfully expel the layers of graphene with fewer defects at 60% amplitude for the apparatus and 2 hours of time for sonication. After exfoliation, the sample was centrifuged by speed (3000 rpm) for 15 minutes to remove the large layers of graphene and discarded. The supernatant was re-centrifuged to high speed 7500 rpm for 30 minutes. The final supernatant rinsed with ethanol and deionized water three times and filtrated to get rid of the extra amount of the dispersant (GA). The final solution of the exfoliated GNPs with GA denoted as GA-GNPs, dried in the oven at 60 ºC for 48 hours.

2.2.2. Characterization of GA-GNPs. The functionalized GNPs with GA were characterized by using Fourier Transform infrared spectroscopy (Perkin Elmer- FTIR) and morphological characteristics was investigated by Field-Emission Transmission Electron Microscope (FETEM, Model; JEM-2100F).

2.2.3. Characterization of nanofluids. The final product of GA-GNPs was re-dispersed with various weight concentrations 0.01, 0.05 and 0.1 wt. % in high salinity brine (3 wt. % NaCl) as a base fluid by mild sonication for 1 hour. The contact angle measurement was used to evaluate the wettability alteration of glass slices as sandstone rock core. These slices of the substrate were aged in various fluids which are included a different concentration of the prepared nanofluids for 24 hours at 80 ºC. The contact angle of oil droplet with the slices of glass was carried out by using Goniometer (Ramé-hart 260), the glass slice is immersed inside the visual cuvette filled with brine and droplet of crude oil is injected and released by an inverted needle to captured at the bottom of the glass slice. Afterward, magnified side view images of oil droplet were taken and analyzed to measure the contact angle by advance software to process the image of the droplet.

The dynamic viscosity of the nanofluids was investigated in rotational module by using HR-1, Discovery Hybrid Rheometer. The GA-GNPs NFs with different concentrations were examined at high temperatures. The prepared nanofluids (16 mL) were loaded between the concentric cylinders and allowed to attain temperature stabilization for 5 minutes. The test was carried out at various temperatures (25-90 ºC) and a constant shear rate (1000 L/s).

3. Results and discussion

3.1. Characterization of GA-GNPs

The pristine and noncovalent functionalized graphene nanoplatelets were analysed through FTIR spectroscopy to evaluate the grafted GNPs with chemical bonds of the GA molecules as shown in
figure 1. The FTIR results of Functionalized GNPs with GA exhibited different characteristic peaks with pristine, these involved a carboxylic band (C=O) at 2350 cm\(^{-1}\) [26]. Moreover, hydroxyl (COOH) deformation at the peak 1422 cm\(^{-1}\) which are agreement with the symmetric vibration of carboxylic acid group. Furthermore, 2923 cm\(^{-1}\), 1067 cm\(^{-1}\), 870 cm\(^{-1}\), and 712 cm\(^{-1}\) which are correspond to the stretching of (C-H) alkanes band, epoxy absorbance band (C-O-C), (C-O) and (C-OH) bending in and out of plane deformation respectively [25], due to attachment of the GA molecules on the basal and edges of graphene. The hydroxyl group (-OH) appear with a strong and broad peak at 3400 cm\(^{-1}\), which are related to absorption the (-OH) from ethanol alcohol and the chemical groups from GA [27]. Based on the results of FTIR with existing peaks compared to the pristine sample, which starkly confirms the successful grafting of Arabic gum functional groups to the GNP\(\_\)s plane.

**Figure 1.** FTIR of (a) GA modified GNPs and (b) pristine GNPs.

Figure 2 shows the morphology analysis of pristine and functionalized GNPs with GA by high resolution TEM imaging which observed the disorder of the structure after the ultrasonication process. Meanwhile, the transparency and wrinkles of functionalized graphene nanosheets indicate to the successful process of noncovalent functionalization of graphene with Gum Arabic.

**Figure 2.** TEM image of (a) Pristine GNPs and (b) GA modified GNPs at high magnification.

3.2. **Characterization of GA-GNPs nanofluids for improving oil mobility**

Table 1 summarizes the dynamic viscosity of the different concentrations of prepared nanofluids and crude oil at ambient and high temperatures with a constant shear rate. It should be mentioned the dynamic viscosity of all nanofluids at high temperature with a high shear rate is lower than ambient temperature. However, the viscosity of crude oil declined from 8.13 mPa\(\cdot\)s at 25 ºC to 1.81 mPa\(\cdot\)s at
90 °C and high shear rate of 1000 L/s. The viscosity ratio between the crude oil and various concentrations of GA-GNPs nanofluid at high temperature and high shear rate is higher than unity.

| Fluids          | Viscosity (mPa.s) |
|-----------------|-------------------|
|                 | 25 °C | 90 °C |
| Crude Oil       | 8.13  | 1.81  |
| 0.01 wt.% GA-GNPs | 4.13  | 2.69  |
| 0.05 wt.% GA-GNPs | 4.14  | 2.71  |
| 0.1 wt.% GA-GNPs | 4.16  | 2.72  |

The contact angle of an oil droplet on the surface of treated slices with functionalized GNPs at 80 °C for 24 hours was illustrated in figure 3. The wettability of treated slices with three concentration of GA-GNPs nanofluids was altered to water wet. Eventually, the shape of the droplet changed, and the contact angle was recorded 21° at 0.1 wt. % of GA-GNPs nanofluid. In comparison, the contact angle with was 108° in the brine. In this regard, the contact angle declined to 87% with high concentration of GA-GNPs. These results were due to the functionalized graphene nanofluids that achieved the water wet with the presence of nanoplatelets at a region of contact between the surface of the solid and liquid of (oil-brine). The functionalized graphene nanosheets adsorbed and spread along the glass slides to change the wettability from oil wet to water wet. Therefore, the oil droplet detached the surface of the porous and subsequently the oil simply to moved and displaced into the production well.

![Figure 3](image)

**Figure 3.** The contact angle of oil droplet below the untreated and treated glass slices with GA-GNPs at different concentrations.

4. Conclusion
Noncovalent functionalization of GNPs with GA has been successfully synthesized by economical and green environmentally process. The noncovalent functionalization of graphene layers was validated by using FTIR and FETEM. The adsorbing and spreading of GA-GNPs along the glass slides have led to altering the wettability from oil to water wet with reducing in the value of contact angle to 87%. However, the viscosity of the prepared nanofluid still higher than the viscosity of the crude oil at high temperature and high shear rate (90 °C and 1000 L/s) and the viscosity ratio higher than unity. Hence, the high stability of the GA functionalized GNPs at harsh conditions which is leading to high viscosity, altered the wettability to water wet could improve the oil mobility with increasing the sweep efficiency and resulting in favorable oil displacement.

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