



Full Length Article

Hydroxyl-functionalized silicate-based nanofluids for enhanced oil recovery

Farad Sagala, Afif Hethnawi, Nashaat N. Nassar*

Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta T2N 1N4, Canada



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ABSTRACT

During the production life of the reservoir, wettability alteration from an oil-wet to a strongly water-wet condition and/or lowering the interfacial tension (IFT) between the water and oil phases is required at various stages to enhance oil recovery (EOR). Several chemical agents as potential wettability modifiers (e.g., surfactants and polymers) have been regarded and widely used in oil-wet systems. Recently, various nano-fluids, prepared by dispersing nanoparticles in brine solutions or solvents, have attracted attention as injecting fluid due to their unique properties. A large number of nanoparticles are being investigated for EOR applications either as stand-alone or in combination with surfactants and/or polymers. Because of its stability in brine even at low concentrations, totally or partially hydroxyl-functionalized nano-pyroxenes are capable of recovering additional oil after water flooding. However, the influence of their concentration on various parameters has not been previously investigated. Thus, in this study, we investigated the influence of nano-pyroxene on wettability, IFT and asphaltene aggregation. Wettability measurements were performed by contact angle measurements, imbibition experiments and wettability index to understand the underlying mechanisms. The interaction between nano-pyroxene and asphaltene size distribution was investigated as a function of nanopyroxene concentration by dynamic light scattering (DLS) measurements. Results from the IFT measurements, contact angle, imbibition experiments and core flooding tests confirm that nanopyroxene affects oil recovery. Contact angle and wettability index measurements confirmed that adsorption of the nanoparticles on the rock surfaces alters the wettability from intermediate wet to stronger water-wet in the absence and presence of initial water films. In the presence of irreducible water saturation during wettability index measurements, depending on the brine composition and pH, initial alteration with aging resulted in a mixed or intermediate wet that changed to stronger water-wet as the nanopyroxene concentration increased. Moreover, increasing the concentration of nanopyroxene resulted in a noticeable IFT reduction but not an ultra-low range that can remobilize trapped oil due to higher capillary forces. Core flooding tests indicated that nanopyroxene-based nanofluid injection offers ~12–14.5% additional oil in addition to waterflooding.

1. Introduction

The demand for oil as an energy source has been raising over the last few decades [1]. Even though the oil and gas industry faced some challenges in the last five years arising from unstable oil prices, it continues to play an important role in terms of energy supply. However, the unpredictable oil price translates itself into the need for more efficient, cost-effective and environmentally harmless ways of producing hydrocarbons [2]. Conventional oil production is declining, and exploration of new oil fields is also plummeting; thus, EOR techniques are required to extend the production of mature and already producing reservoirs [3–5]. Chemical flooding is a commonplace technology that has been extensively used for the past years in EOR [6]. Through injecting certain chemicals (e.g., alkaline, surfactants, and polymers),

better recovery is achieved due to the improvement of the mobility ratio, reduction of the IFT, and the wettability alteration of the rock [7]. For instance, the employment of water-soluble polymers to recover the tapped oil results in a mobility ratio of less than one. However, most of the oil is still trapped or adsorbed into the rock surface, because of the high capillary forces that arise due to oil-wet rock and high oil/water IFT [8]. Moreover, conventional EOR techniques such as alkaline flooding, surfactant flooding, polymer flooding, or a combination of one or more of these methods have other challenges [9,10]. High chemical consumption is among the commonly reported problems of chemical EOR. This is attributed to the reservoir heterogeneities, dilution with resident water, adsorption on rock surfaces especially at higher temperatures, chromatographic separation of the mixture, imbalanced salinity in the reservoir and breakdown of the chemicals by bacteria

* Corresponding author.

E-mail address: nassar@ucalgary.ca (N.N. Nassar).<https://doi.org/10.1016/j.fuel.2020.117462>

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and its adsorption on the rock surface [8]. Applying the conventional EOR flooding fluids individually or together not only has limited success in increasing the sweep and displacement efficiency but also adds extra operational and capital costs to the EOR process. Furthermore, crude oils compounds such as asphaltenes and resins, due to change in reservoir properties such as pressure and temperature, tend to interact with rock surface resulting in wettability alteration from initial water-wet to oil-wet which lowers the microscopic displacement efficiency [11,12]. In oil-wet reservoirs, spontaneous imbibition of water is not possible due to negative or smaller capillary forces [13]. In such situations, even during water injection, water bypasses the oil without displacing any significant amount of oil, resulting in poor sweep efficiency and early water breakthrough [14]. As such, efficient EOR techniques are required to mitigate these problems. Nanoparticles, in the form of nanofluids, are proposed as an alternative flooding fluid for EOR because of their potential ability to exhibit exceptional properties, owing to their small size and large surface area as well as dispersion ability [15]. The high dispersion of stable nanoparticles, depends on its functionality and interparticle interactions [16]. Nanofluids have been evidenced in the past decade, to offer tremendous advantages; they are thermally stable, highly reactive and offer favourable catalytic properties compared to the existing chemicals used in EOR [17,18]. Moreover, depending on the nanomaterial type, nanoparticles possess superficial ionic exchange properties that permit surface modification by grafting different organic groups on their surface which can improve their performance especially in harsh reservoir conditions [16,19]. EOR mechanism(s) for nanofluids have been reported in the literature [20]. Underlying mechanisms include viscosity reduction [21], wettability alteration [16,20], IFT reduction [22], structural disjoining pressure [23], asphaltene inhibition formation damage [24], etc., Giraldo et al. [25] postulated that alumina-based nanofluids can significantly alter an induced strong oil-wet wettability in sandstone cores to a water-wet state. The authors also found that the effectiveness of anionic surfactants as wettability modifiers can be improved by adding a relatively low concentration of alumina nanoparticles. Teng et al. [26] studied the performance of silicon dioxide (SiO_2) nanofluids in low permeability sandstone cores. The authors found that cyclic nanofluid injection can provide higher tertiary oil recovery than continuous nanofluid injection. Approximately 4.48–10.33% of additional oil could be recovered during the nanofluid injection. However, many nanomaterials are produced with rare metals and/or expensive ones that are not suitable for large scale implementation for the oil and gas industry applications. Therefore, more environmental-friendly and inexpensive practical materials must be produced. Tailor-made mineral-like nanomaterials, compatible with the environment with an economical-feasible synthesis method, should be considered as well.

In this study, iron-silicate pyroxene materials, known as aegirine ($\text{NaFeSi}_2\text{O}_6$), comply with the aforementioned requirements and offer cheap options for large scale commercialization are considered [27]. In comparison to silica nanoparticles, that are commonly used for EOR applications [28], pyroxene nanoparticles do not require well-monitored synthesis conditions (e.g., calcination at higher temperatures and freeze-drying like in the case of silica) [29]. In fact, silica nanoparticles, without surface coating or functionalization, are characterized by having high tendency to agglomerate due to lack of stability, especially in high salinity and at high-temperature conditions [30]. In term of synthesis, nanopyroxene materials can be prepared at mild hydrothermal conditions and require no calcination which offers options for scalability for pilot and field applications [27]. As characterized previously, nanopyroxene surface has a superficial ion exchange characteristics, permitting its surface modification [27]. Thus, nanopyroxene can be considered as a better alternative for silica nanoparticles for EOR applications. In our previous study, totally hydroxyl tri-ethoxy-octyl-silane functionalized-nanopyroxene, compared with partially and non-functionalized nano-pyroxene, has proven to enhance the recovery of additional oil from a sandstone core by spontaneous imbibition and

core flooding tests [16]. It has been reported that adding the functionalized nanopyroxene to brine was capable of reducing the IFT and alter the oil-wet induced wettability to water-wet [16]. The results obtained from the core flood revealed that, in the presence of brine, nanoparticle type as well as their functionality, played an important role in the oil recovery. Similar to our previous study, core flooding experiments have been reported to describe the influence of different parameters of nanoparticle injection on oil recovery [31,32]. However, these studies lack the understanding of how oil recovery is affected by nanoparticles at different initial wetting conditions using both static and dynamic experiments especially in sandstone reservoirs. Moreover, the effect of initial brine composition and pH on the initial rock wettability and how the rock wettability may alter when contacted with oil containing polar components in the presence and absence of nanoparticles is not clearly understood. Herein, in continuation of our previous work, the role of pyroxene-based nanofluid for EOR applications in Berea sandstone cores under the influence of various hydrodynamic and wetting conditions is being investigated. Thus, the effects of different initial wetting conditions using various concentrations of fully hydroxylated/partially hydrophobic nanopyroxene were investigated by performing contact angle measurements, spontaneous imbibition tests, determining the Amott-Harvey index of an induced oil/intermediate-wet sandstone rocks and core flooding tests.

2. Materials and methods

2.1. Materials

Synthetic brine (SB), representing formation brine, was prepared from sodium chloride (NaCl) at 2.0 wt% (20,000 ppm), and deionized water, was used as the base fluid for dispersing the nanoparticles in all experiments. The triethoxy (octyl) silane (TOS) with 99% purity was purchased from Sigma Aldrich and used as received. Decane (99% purity), NaOH (99% purity) potassium bromide (KBr, 99%), sodium chloride (NaCl 99%), n-heptane, methanol, and toluene (99%) were all purchased from VWR (Canada) and used as received without any purification. The oil phase was provided by a local oil company in Calgary, Canada. The viscosity of the crude oil is 31.30 ± 0.02 cP, density 0.872 g/cm^3 , asphaltene content of 5.09 wt%, and acid number < 0.1 all measured at 25°C . The hydrophobic nanopyroxene particles used in this study were prepared in house as detailed in our previous study [16]. The density, pH and viscosity were measured using a pycnometer and Brookfield viscometer as $1 \pm 0.05 \text{ g/cm}^3$, 6.75 ± 0.05 and 1.05 ± 0.05 cp at 25°C respectively. For testing the oil recovery, sandstone cores, with a porosity of 19–22% and permeability of 60–100 mD, were prepared at Kocurek Industries Inc. (Caldwell, TX) and used as received.

2.2. Nanoparticle and nanofluid synthesis and characterization

The fully hydroxylated nanopyroxene nanoparticles (HPNP) were synthesized from the virgin sample of nanopyroxene (NPNP) by completely anchoring the agent of triethoxy (octyl) silane (TOS) on NPNP surface as reported in our initial study. [16] The summary of the synthesis is also shown in Fig. 1. For nanofluid synthesis, nanofluids of three different concentrations 25, 50, and 100 ppm were dispersed in synthetic brine (2 wt% NaCl) using an orbital shaker and ultrasonicated until the nanoparticles were uniformly dispersed in brine. Pre-adjustment for the pH of the nanofluids to 10 was achieved by a standard solution 0.1 M NaOH to improve their dispersion and stability as reported previously [16]. Table 1 shows the physical properties of the brine and prepared nanofluids. The hydrodynamic size distribution of nanoparticles in brine was analyzed before and after pH adjustment using dynamic light scattering (DLS), Malvern Nano Sight NS300 supplied by Malvern Instruments Ltd, USA. For comparison purposes, brine alone with pH similar to the nanofluids was used for all experiments to

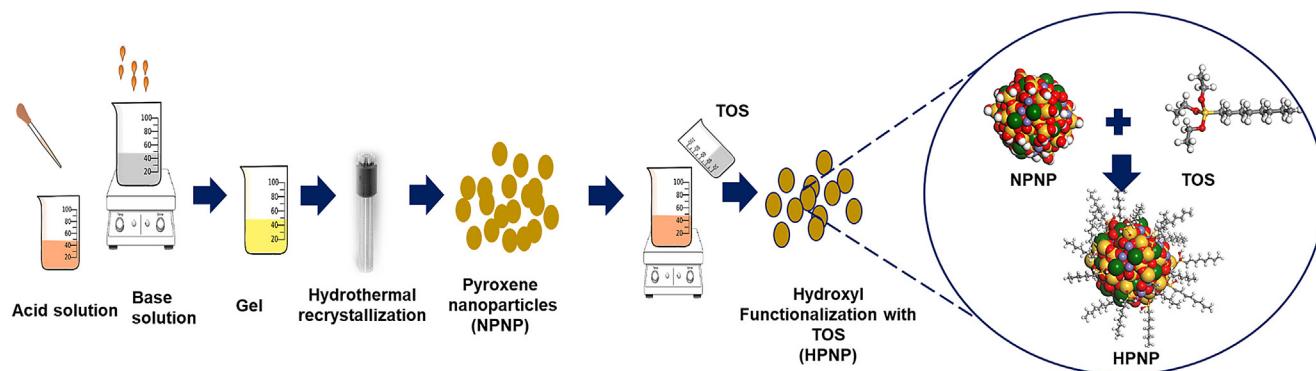


Fig. 1. Step-by-step schematic illustration of nanoparticle synthesis and its application for oil recovery.

Table 1

Physical properties of the brine and prepared nanofluids at 25 °C.

Fluid	Density (g/cm ³)	pH	Viscosity (cp)
Brine	1.009 ± 0.010	6.52 ± 0.05	1.01 ± 0.01
HPNP-25 ppm	1.008 ± 0.010	10 ± 0.05	1.01 ± 0.01
HPNP-50 ppm	1.009 ± 0.010	10 ± 0.05	1.02 ± 0.01
HPNP-100 ppm	1.010 ± 0.010	10 ± 0.05	1.03 ± 0.01
Brine -pH-10	1.015 ± 0.010	10 ± 0.05	1.01 ± 0.01

determine its effect on recovering residual oil, since the NaOH used in the pH adjustment is an alkaline that has an effect on EOR.

2.3. n-C₇ asphaltenes extraction and effect of nanopyroxene concentration on the asphaltene aggregate size

2.3.1. Asphaltene extraction

Asphaltene content in the oil sample was determined by a standard procedure reported elsewhere [33]. Experimentally, 10 mL of oil was added to 400 mL of n-heptane in a closed bottom flask. The mixture was boiled for 35 min to expedite the precipitation process and allowed to cool down. After that, the mixture was filtered using 0.45- μ m filter paper under a vacuum dryer and then weighed. The amount of asphaltene precipitated was obtained from the mass collected and its elemental analysis is provided in Table 2.

2.3.2. Aggregation size study

One of the proposed mechanisms for nanoparticle enhanced oil recovery is oil viscosity reduction, which is usually attributed to destabilization or adsorption of the asphaltene present in the crude oil [34]. To investigate the role of nanoparticle concentration on n-C₇ asphaltene aggregation, 0.1 wt% of n-C₇ were added to different toluene-heptane (Heptol) solutions such as, Heptol 50, Heptol 60 and Heptol 70 mixtures to obtain the initial conditions for testing the nanoparticles. Then

the solution was sonicated for 1 h and aliquots of the solution were taken to determine the n-C₇ aggregate size (d_{asp}) using a dynamic light scattering (DLS) Zetasizer Nano ZS9, Malvern Panalytical, Canada Inc. After that, to investigate the role of nanoparticles on n-C₇ disaggregation and stabilization, Heptol 60 was selected for testing the nanoparticles and three different nanoparticle concentrations, i.e., 25, 50, and 100 ppm of HPNP were added to Heptol 60 and again sonicated for 1 h each. All measurements were repeated in triplicates per sample as a function of time, and the mean size was used to build the aggregation curves as a function of time. All experiments were performed at 25 °C.

2.4. Interfacial tension (IFT) measurements

The IFT between the oil and the brine/nanofluids was measured by using a tensiometer (Biolin Scientific, Sweden) at different temperatures (25, 30, 40, 50 and 60 °C), following the procedure reported in our previous study [16]. For each IFT measurement, the chamber was filled with the aqueous phase. Then, an oil droplet was created through a needle and the IFT measured by using the pendant drop technique. IFT was determined for a given time interval. All measurements were repeated in triplicates, and the mean \pm standard error (5%) of the mean was reported.

2.5. Preparation of the Oil-wet cores plugs, substrates and pre-saturation

Berea sandstone core plugs with 2.54 cm diameter and an average length of 4.0 cm were used to perform imbibition experiments. Prior to imbibition experiments, all cores were first dried up to 90 °C to obtain a constant weight. The initial weights of the dried cores were measured. Two saturation procedures were followed prior to imbibition experiments: (1) cores with 100% initial oil saturation and (2) cores with irreducible water saturation. To obtain full core oil saturation, each core was placed inside a round bottom flask containing crude oil. Then, the flask was connected to the vacuum pump for 24 h, resulting in a fully saturated core. The porosity of the fully oil-saturated cores was recalculated with respect to oil to confirm full core saturation using the weight difference between the dry and fully saturated cores, bulk volume and oil density. For cores with initial water saturation or at irreducible water saturation (S_{wi}), dry cylindrical cores were saturated with brine under vacuum for 24 h. After that, pore volume (PV) and porosity were determined from the weight difference, which was obtained from brine density and bulk volume. To establish ionic equilibrium between brine and the rock constituents, brine saturated cores were left soaked in the same brine solution for about 5 days. After that, cores were mounted in the Hasler core holder and flooded with oil in all directions to alleviate end effects. To drive the core plugs to irreducible brine saturation, oil flooding at lower injection rates of 0.05 cm³/min and, confining pressure not > 500 psi were used. Using this method, cores could remain consistently saturated with initial water close to 25–30%. The oil injection pressure was in the range of 50–66 psi. This

Table 2
Asphaltene elemental analysis.

Element	%
C	82.24
H	7.34
N	1.13
O	4.7
S	4.4
H/C	1.05
Mo	0.0033
Ni	0.0233
W	0.0032
Fe	0.0038
V	0.1086
K	0.0017

last procedure was also used in measuring the wettability index as proposed by Anderson et al. [14]. After establishing initial oil saturations with the designated crude oil, the cores were completely submerged in a solution of oil and n-heptane to cause surface precipitation of asphaltene on the mineral surface to alter the initial wettability. The fully saturated cores (100% oil saturation) were aged at 80 °C for 20 days in a closed container. Using initial core weights prior to oil saturation, the oil initially in place (OOIP) was obtained after the aging period. To avoid the escape of light ends during the aging process, the aging container was covered with aluminum foil and sealed with high-temperature glue. Table S1 of the Supporting Information shows the summary of the cores used in the imbibition experiments.

2.5.1. Contact angle and spontaneous imbibition of oil wet sandstone rocks

To assess the effect of nanoparticle concentration on the contact angle, the wettability of the core plugs before and after the treatment with different concentrations of nanofluids was evaluated by contact angle measurements. Sandstone substrates were cut, then aged in a mixture of 1:40 solution of crude oil/n-heptane at 80 °C and atmospheric pressure for 24 h. Later, the substrates were dried in an oven for 6 h at 60 °C. Oil aged substrates were then submerged into the prepared brine, brine at pH 10 or nanofluids of different concentrations (25, 50 and 100 ppm) for 48 h at 60 °C. Each substrate was dried in an oven at 60 °C for 24 h. Contact angle measurements between sandstone substrate and brine or nanofluids of different concentrations and oil drop system of the substrates treated with either brine or different nanofluids were performed with an accuracy of $\pm 3^\circ$. The angles were then analyzed to quantify the effect of the nanofluid concentration on contact angle and wettability alteration.

Wettability alteration was also quantified using spontaneous imbibition tests to support the contact angle measurement results with cores 100% saturated with oil. Imbibition experiments were performed using Amott cell to assess the performance of variously prepared nanofluids in altering the wettability of the oil-wet core plugs in comparison to brine or brine at pH 10. The cores were immersed in imbibition cells, which were filled with either brine or various concentrations of nanofluids. The imbibition experiments were conducted at 60 °C. The produced oil volume from the cores as the fluids spontaneously imbibe in the cores was expressed as a percentage of original oil in place (% of OOIP) and was plotted against time.

2.5.2. Effect of nanopyroxene concentration on wettability index

To evaluate the effect of nanopyroxene concentration on the wettability index, the Amott-Harvey relative displacement index method was used [14]. Cores were first driven with oil to irreducible water saturations close to 25% by core flooding as discussed in Section 2.5. To investigate the role of nanoparticle concentration on the wettability index, brine was injected into the core and later displaced with oil to reduce the core plugs to irreducible water saturation (IWS). Then, the oil-saturated cores, were immersed in standard Amott cells containing either brine, brine at pH 10 or nanofluids of different concentrations. The volume of oil displaced by spontaneous imbibition of the imbibing fluids was measured as the volume of produced oil reached a constant value (v_{osp}). Then, the core was mounted in a Hassler core holder and brine or nanofluid was injected to forcefully displace any remaining oil. The volume of oil displaced by brine or nanofluids was recorded as v_{of} . After that, the same brine saturated core plug from the previous test was immersed in oil. The volume of brine produced by spontaneous imbibition of oil was measured as the volume of produced brine reached a constant value v_{wsp} . Finally, the core was again oil-flooded forcefully to displace any movable brine/nanofluids and the amount of brine displaced by forced imbibition of oil was measured v_{wif} . The difference between displacement by water ratio I_w and displacement by oil ratio I_o gives the Amott-Harvey relative displacement index WI (Eq. (1)). Properties of the used core plugs for the imbibition test are listed in Table S2 of the Supporting Information. The produced oil was

measured with an accuracy of ± 0.05 mL due to errors that may have occurred during core saturation and when reading the volumes of the produced oil during spontaneous and forced imbibition. The Amott-Harvey relative displacement index WI was then used to quantify the wettability of the rock with and without nanoparticles.

$$WI = I_w - I_o = \frac{v_{osp}}{v_{oT}} - \frac{v_{wsp}}{v_{wT}} \quad (1)$$

2.5.3. Effect of initial water saturation and pH on wettability alteration

To determine the wettability index, cores were first driven to irreducible water saturation as proposed by Anderson [14]. However, the presence of initial water saturation, composition and pH affects wettability during the aging process. Therefore, we investigated their effects prior to imbibition with various fluids; despite the fact that many researchers [35,36] conducted imbibition studies and created initial oil-wet conditions in the laboratory using 100% fully saturated oil core plugs. In reality, reservoirs contain initial water saturation with various ions. Therefore, it is important to investigate the effect of this initial water saturation, composition and pH on wettability alteration and later determine the role of nanopyroxene-based nanofluids on wettability reversal.

To investigate the effect of pH on wettability alteration in the presence of monovalent ions, a test known as the bottle test was used as reported elsewhere [37]. Crushed sandstone rock was used as a sample. Pre-treatment procedure was followed to prevent leaching of ions from the glass to the actual test solution. Eight glass vials (one for each pH to be tested) were equilibrated with 4 cc of the test brine and left for 48 h. The brine was then discarded. After that, 4 g of sand were added to each empty vial and equilibrated for 48 h with a new brine of appropriate pH. Brine was then withdrawn and saved in the second series of vials. Then, oil was added in each vial containing the sand and vigorously shaken to mix oil with the wet sand. Shaking was performed twice a day and then brine was added back to the vials. With this technique, a water-wet system could be identified when oil floats on top and sand is left at the bottom. For a non-water wet case, oil sticks on the sand and sand appears to be discolored or saturated with oil as shown in Fig. S3 in the Supporting Information. The experiment was performed at 25 °C.

2.6. Core flooding experiments

Fig. 2 shows a schematic representation of the core flooding experimental setup. The aim of the core flooding tests was to evaluate the capability of nanopyroxene-based nanofluids as potential agents of enhancing oil recovery in sandstone reservoir rocks after water flooding with various concentrations. At the beginning of each test, a core was inserted in the sleeve and then mounted in the core-holder. Low pressure (~250 psi) CO₂ gas was passed through the sample for 1 h. Because of its high diffusivity, CO₂ can displace and replace any air trapped in the pores. The remaining CO₂ after evacuation would readily be dissolved in the saturating dead brine and evacuated from the core sample during the later in-situ saturation process. After flushing the sample with CO₂, all the flowlines and the sample inside the core-holder were evacuated using a vacuum pump for 6 h. Then, the core sample was saturated using brine, confining pressure was kept at 600 psi and the injection rate was set to 0.2 cm³/min. The injection rate approximates typical reservoir velocities (corresponding to a Darcy velocity of 1ft/day) [38]. The average steady pressure drop was obtained and used in the estimation of the absolute permeability using Darcy's law. Then, the core was saturated with oil (drainage process) until there was no more brine being produced to establish the initial core saturations. Primary brine flooding (imbibition process) was initiated and continued until single-phase brine was being produced. Then, HPNP nanofluids of different concentrations as 25, 50 and 100 ppm in separate experiments were injected into the core at the same injection rate with approximately 0.5–1 PV of nanofluids being injected to evaluate their effects on

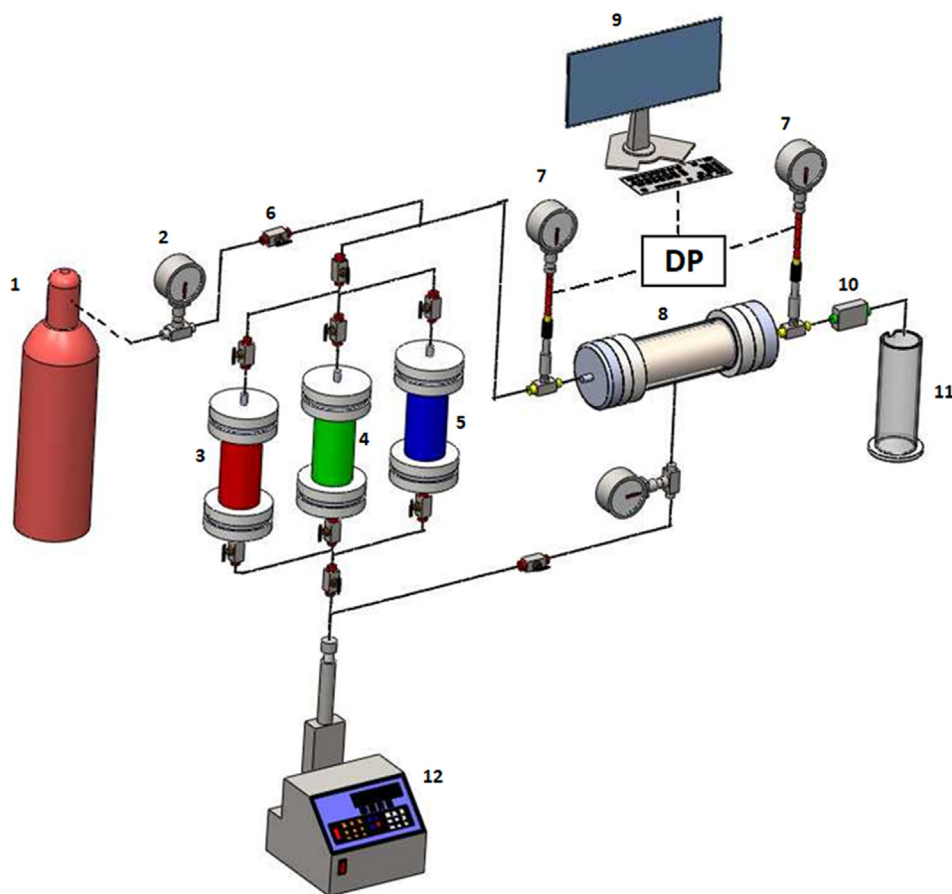


Fig. 2. Displacement test diagram: (1) carbon dioxide cylinder, (2), manometer gauge, (3), (4), and (5) transfer cells for oil, brine, and nano-fluids respectively, (6) valves, (7) pressure transducer, (8) core holder, (9) data acquisition computer, (10) back pressure regulator, (11) collector, (12) ISCO pump, (13) overburden pressure gauge.

the remaining residual oil after brine injection. The produced oil from the core was collected and measured in a two-phase fluid collector. The experiment was performed at 60 °C using heating tapes to generate the heat source. Table S3 of the Supporting Information shows the summary of core plug properties used in the core flooding experiment.

3. Results and discussion

3.1. Core Plugs, Nanoparticle, and nanofluid characterizations

The core and nanoparticle characterizations were conducted by using SEM, EDX and XRD. The analysis showed that the sandstone cores

consisted of mainly quartz as shown in Fig. S1(a–d) in the Supporting Information. Fig. 3a shows the SEM image of the hydroxylated nanopyroxene, Fig. 3b shows the particle size distribution based on the DLS experiment at two pH levels. Results of a semiquantitative EDX elemental analysis and the mappings of the nanopyroxene elements that confirms the presence of oxygen, silicon, iron, and sodium in a ratio roughly consistent with nanopyroxene are provided in the supporting information Table S4 and Fig. S2. Due to the presence of other elements besides silica in the nanopyroxene structure, this makes nanopyroxene a superior nanomaterial over the commonly used silica for EOR applications. The presence of other elements allows nanopyroxene to possess superficial ionic exchange properties that permits nanoparticle

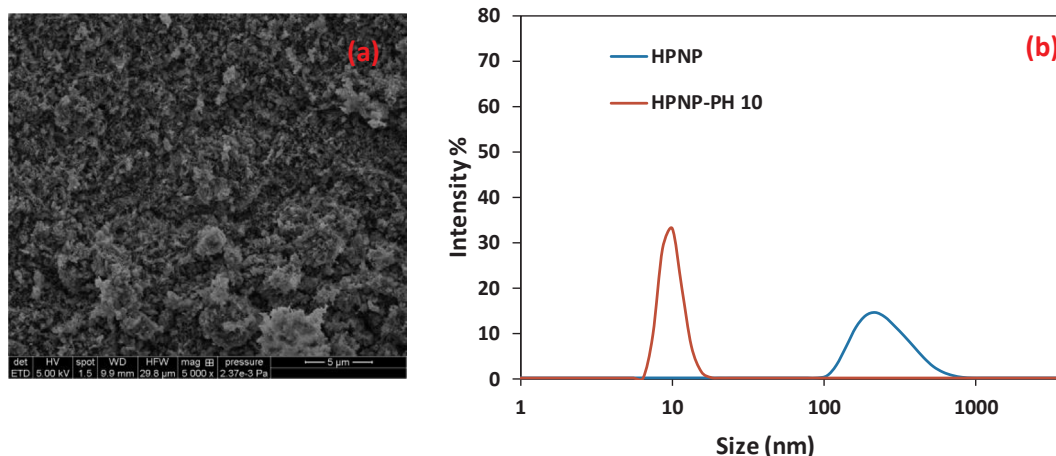


Fig. 3. Scanning electron microscope (SEM) of hydroxylated-nanopyroxene and (b) particle size distribution based on the DLS experiment (before and after pH adjustment) blue and red respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

surface modifications.

Fig. 3(b) shows the DLS results obtained for the nanofluids at two levels of pH. As noticed, different distribution of hydrodynamic size was achieved for the nanofluid of HPNP, by varying the pH of the medium. At high pH (adding negatively charged hydroxyl groups) the major distribution of hydrodynamic size was around 10 nm, indicating the stability of HPNP. While the absence of stability for HPNP was noticed at normal pH with the major distribution of hydrodynamic size around 300 nm. The hydrodynamic size distribution obtained by the DLS results for the nanofluid solution can help elucidate the structural properties of the nanoparticles. The HPNP, according to our previous study, is composed of TOS-grafted nanopyroxene. The surface of nanopyroxene contains sodium, silicon, iron, and oxygen, with silicon iron atomic ratio (Si/Fe) of (2/1). Pyroxene nanoparticles are composed of nano-aegirine materials that have superior surface properties [27]. As reported previously, the synthesis of nano-aegirine by hydrothermal recrystallization method forms granulated nanocrystals with surfaces that offer superficial ion-exchange properties [27]. The surface of the nano-pyroxene has a Si-O-Fe bond type that resembles that of zeolites, where a proton can be anchored (ion exchange of the sodium that is compensating the negative charge on iron). The Si-O-Fe bond, under aqueous medium, can form hydroxylated silicon as well as negatively charged iron ions. Thus, the surface offers great tendency for anchoring various polymers and legends. Reducing the pH (adding protons) causes electrostatic charge neutralization, which subsequently lowers its steric stabilization. However, at higher pH, on the other hand, the nanoparticles tend to remain more stable without neutralizing the surface, resulting in the formation of more stable nanofluids. For this purpose, at low pH, there is more tendency for surface neutralization (close to the point of zero charge), which results in nanoparticle agglomeration due to lower nanofluid stability.

3.2. Characterization of the crude oil sample and sandstone rock and the implication to the rock wettability

The type of reservoir rock formation and mineralogical composition, sandstone or carbonates influences the interaction between the polar components in crude oil and the rock [12,39]. For the oil sample used in this study, the method proposed by Lante et al. [40] was used to determine the oil components; saturates, aromatics, resin, and asphaltene (SARA). The quantification of SARA (maltenes) was performed assuming a response factor for flame ionization detector (FID) of resins as 0.73, as shown in Table 3. Crude oil has higher fractions of saturates (42.7%) and aromatics (20.6%). It can be noticed that the oil also had a significant fraction of asphaltenes 5.09% and resins 31.60%, respectively. The presence of asphaltenes and resins, based on their solubility in the crude oil and the reservoir conditions, plays a major role in altering the wettability of a sandstone rock from water-wet to oil-wet. When they interact with the rock surface, they tend to precipitate and then adsorb on the rock surface especially as temperature and pressure varies hence changing the initial core wettability. Wettability alteration of the rock affects the oil microscopic displacement efficiency at various stages of oil recovery. In the absence of a water film, the major mechanism for interaction is polar interaction [12]. With higher saturate and aromatic composition, the interaction between the rock and oil would be minimal, and the wettability alteration towards oil-wet may

be negligible [41]. Sandstones surfaces are anionic, hydrophilic and negatively charged in nature in contrast to carbonates which are normally cationic and positively charged [39]. This makes sandstone strongly water-wet by nature, due to their strong affinity for water. However, Buckley et al. [12] noted that the presence of clay in sandstones improves its interaction with the polar components in the crude oil. Asphaltenes and resins have higher molecular weights and multifunctional characteristics hence their adsorption on specific mineral sites is the major cause of wettability changes [42,43]. Moreover, the adsorption of these components on specific mineral sites depends on the stability and thickness of the water film. Some of the researchers suggested that the presence of a thin water film on the rock surface reduces the adsorption of asphaltenes on the mineral surface and can affect their adsorption kinetics [11]. Other parameters that affect the adsorption of asphaltenes include chemical and structural nature of the mineral substrate, asphaltenes and resins content in crude oil, and the presence of asphaltenes and resins in crude oil in form of aggregates and the ability of the hydrocarbons fraction in crude oil to stabilize or dissolve these aggregates [12,43]. XRD characterization of the sandstone in Fig. S1 in Supporting Information shows diffractograms of powdered sandstone rock samples. A single major peak at 26.8 corresponds to quartz. There are a couple of trace minerals that the JADE Identification software was able to match such as kaolinite and glauconite that indicate the presence of clay minerals. Hence the polar components could easily interact with this clay and change the original wettability of the sand surface.

The presence of interaction between sandstone and crude oil was confirmed by using the FTIR analysis, as shown in Fig. 4.

For that purpose, the FTIR analysis was used to detect the structure of chemical species and provide qualitative measurement, based on the adsorption and molecular vibration peaks. The results of the FTIR test for neat sand before and after its interaction with crude oil are presented in Fig. 4. Presence of infrared spectra of neat sand shows two well-known characteristic band of clay obtained at wavenumber of 776.33 cm^{-1} and 1080.17 cm^{-1} , the region of stretching vibration for Si-O-Si symmetric and asymmetric bond, respectively. Thus, the sandstone contains silica as main component, confirming the results obtained by the XRD analysis. For the crude oil sample, it can be noticed from the spectrum that the aforementioned peaks are not present. However, two adsorption peaks obtained for the crude oil sample at 2958 and 2850 cm^{-1} correspond to the stretching vibrations of C-H and CH_2 and these bands tend to be slightly shifted to 2851.85 cm^{-1} and 2924.64 cm^{-1} after interacting with the sandstone rock. This slight shift in the C-H and CH_2 bands confirms the interaction of oil with sandstone making it more oil wet. The Si-O-Si bands that are obtained around 1000 cm^{-1} for oil wet sandstone appeared to be wider than that for the raw sandstone sample, which can also be attributed to the oil-sandstone interaction.

3.2.1. Effect of nanoparticle concentration on asphaltene disaggregation

To evaluate the interaction between nanopyroxene and the n-C₇ asphaltene aggregates, kinetic tests were performed at ambient conditions and the effect of nanopyroxene concentration on n-C₇ asphaltene disaggregation was investigated. Asphaltenes, as a complex fraction of crude oil, is highly soluble in toluene and insoluble in n-heptane [44]. The complexity refers to presence of large percentages of complex organic materials (aliphatic or aromatic). The elemental analysis presented in Table 2 showed that 90 wt% of the asphaltene composed of organic compounds (large hydrocarbons contains various functional groups derived from N, O, and S) and very low mass fractions of heavy metals (< 0.5 wt%). For that purpose, asphaltene's adsorption behavior, depending on the precipitation method, has limitations and cannot be easily observed. The investigation is not possible without obtaining the optimal solubilizing conditions for the asphaltenes. Since asphaltenes are insoluble in n-heptane increasing the heptane in the solution increases the rate at which n-C₇ asphaltene self-associate to form larger

Table 3
SARA Analysis of the Crude Oil Sample.

Parameters	%
saturates	42.7
aromatics	20.6
resins	31.6
asphaltenes	5.09

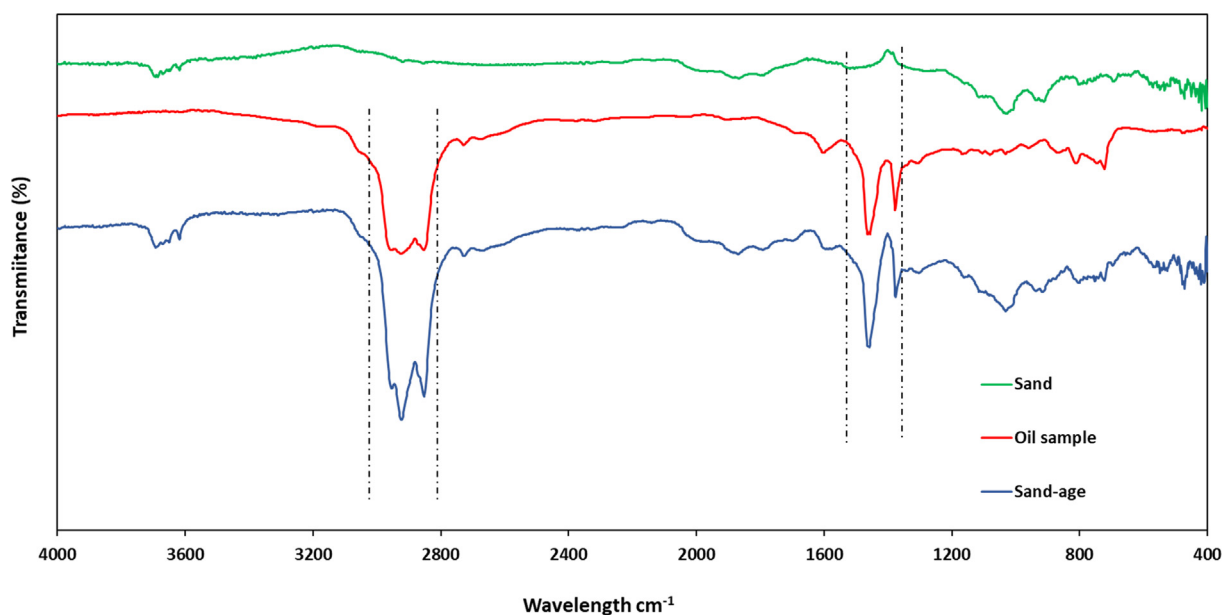


Fig. 4. FTIR spectra of sand (green), oil sample (red) and sand after aging with oil (blue) at the framework of 400–4000 cm^{-1} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

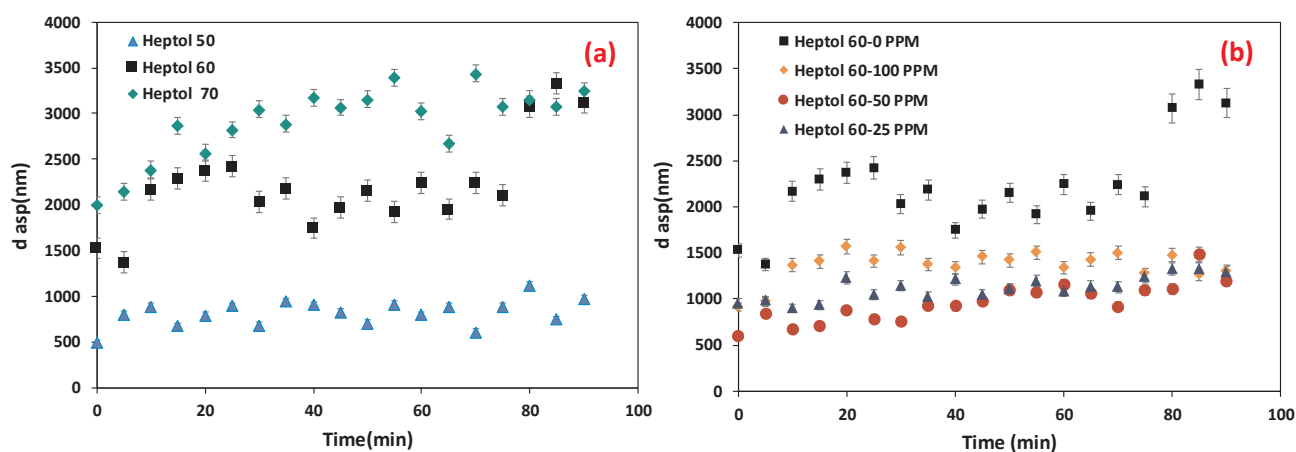


Fig. 5. Kinetics of n-C₇ asphaltene aggregation in Heptol 50,60, and 70 solutions (a) and (b) kinetics of n-C₇ asphaltene aggregation in Heptol 60 in the presence of 0, 25,50 and 100 ppm.

agglomerates [45,46]. Without complete solubilization, precipitation of asphaltenes will interfere with the determination of its interaction on the rock surface. Thus, solvent mixture at various volume ratio should be used to achieve the best test conditions. Fig. 5(a) shows the orientation of the n-C₇ with Heptol ratios 50, 60 and 70 V/V. The aggregated size was increasing as the amount of n-heptane in Heptol solutions increased Heptol 60 was selected to test the aggregation kinetics of n-C₇ asphaltenes with and without nanoparticle dispersion. As shown in Fig. 5(b), it can be observed that the presence of nanoparticles reduced the aggregate size of the n-C₇ asphaltenes. It is worth mentioning that nanoparticle concentration affected the aggregation size. There is a reduction trend of n-C₇ asphaltenes as the concentration of the nanoproxene increased from 25 to 50 ppm. When the concentration increased to 100 ppm the size increased again probably due to the formation of big flocs of n-C₇ asphaltenes and nanoparticles in the solution. This implies that there is an optimum concentration required to reduce the self-association of n-C₇. Increasing the concentration beyond an optimum value may not reduce the size of n-C₇ asphaltenes aggregates. Nassar et al. [45] found that the ability of the nanoparticles to reduce the aggregate size of n-C₇ asphaltenes depends on their ability to diffuse into the solution. The presence of nanoparticles changes the

nature of the asphaltene aggregation, most likely by introducing multiple nucleation centers. The proposed possible mechanism of asphaltene inhibition includes modulation of the aggregate morphology, reduction of gelation point and rheological yield stress. However, as the nanoparticle concentration increases, the aggregation phenomena dominates the growth, and the aggregate size increase rapidly. When the aggregates grow larger enough, the hydrodynamic pressure prevails so that disintegration becomes significant until equilibrium is reached [44,45]. Subsequently, the reduction in aggregate size is significant with an optimum nanoparticle concentration used. It is also appropriate to note that a different behavior of nanoparticle-asphaltene interaction may be obtained when different crude oil or asphaltene are used. Therefore, this optimum concentration may not necessarily be applicable to all other types of asphaltene and crudes.

3.3. Effect of nanoparticle concentration on interfacial tension

Fig. 6 shows the IFT values for brine, brine at pH 10 and at 25, 50 and 100 ppm of HPNP nanofluids, at various temperatures. Experimental results from the measured IFT indicated that increasing the concentration of the nanoparticles could noticeably reduce the IFT but

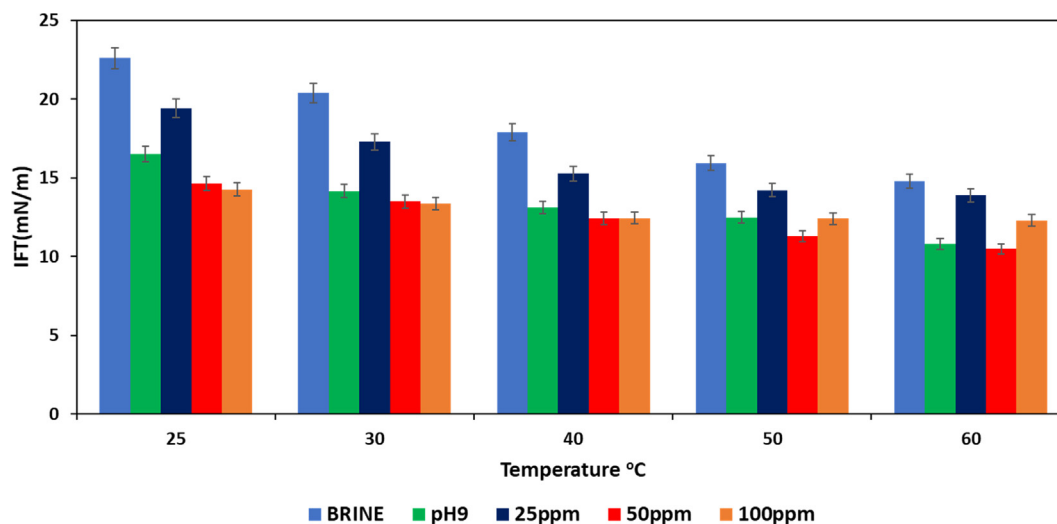


Fig. 6. IFT of oil-fluid phases at different temperatures and atmospheric pressure.

not significantly enough to remobilize residual oil after the initial water flooding. It was evident that IFT was reduced as the temperature increased for all the fluids used. In order to remobilize residual oil, ultra-low IFT reduction is required to achieve a very high capillary number that can remobilize the trapped oil. During water flooding, the capillary number ranges from 10^{-7} to 10^{-5} . To increase the capillary number to at least 10^{-3} , which is the critical capillary number required for residual oil to start being remobilized, requires ultra-low IFT values [47]. Therefore, IFT reduction is most likely not among the mechanism for recovering trapped oil by using this nanomaterial even when the concentration is increased. However, it is noticeable but not significant for the trapped oil recovery. Probably, increasing the concentration of nanoparticles beyond an optimum result in the formation of agglomerates, which reduces their dispersity at the oil-water interface. Moreover, increasing the nanoparticles may not guarantee additional oil recovery. Rather it may be uneconomical which may limit its application for pilot and field studies during the scale-up process.

3.4. Quantification of rock wettability before and after treatment with and without water films

During oil production, the wettability of sandstone reservoirs at various stages of oil production may be altered from strongly water-wet to oil-wet, which can affect the oil recovery rates [12,48]. The proposed mechanism of interactions that result in the wettability of sandstone rocks being altered from strong water-wet to oil-wet include the following: Polar interaction that predominates normally in the absence of water films between the solid and oil and acid-base interaction that controls the surface charges at the solid-water and oil-water interface. Other mechanisms include surface precipitation which depends mainly on crude oil solvent properties with respect to asphaltenes and resins and finally ion binding or specific interaction between charged sites and higher valency ions [12,49]. In this study, wettability alteration with and without the presence of initial water films was considered. In the absence of initial water films i.e 100% cores saturated with oil, the cores were treated with a mixture of crude oil and n-heptane using a solution of 1:40 causing surface precipitation of asphaltenes on the surface of sandstone rock. The rocks were again aged for 20 days at 80 °C and the wettability of the rock before and after alteration was determined by contact angle measurements, spontaneous imbibition and relative index method or the Amott-Harvey wettability index (IW). As shown in Fig. 7(a) the substrate after aging was close to oil-wet which confirms the procedure used in changing the initial water-wet state of the core. Therefore, the predominate mechanism(s) that caused

the wettability of the surface to change in the absence of water film were precipitation onto the surface and polar interaction. For the imbibition test, the treated core (oil-wet) expelled no oil for the first 5 days, and maximum oil recovery of approximately 5% was reached after 20 days. On the other hand, the water-wet sandstone recovered oil immediately after the first day, as seen in Fig. 9a confirming the initial wettability of the core and the treatment which is consistent with the contact angle measurements. Moreover, for the oil wet rock sample under brine alone, oil was produced only from two sides of the core rather than all sides of the core indicating a co-current flow controlled by mainly gravity. This explains the lower recoveries during brine imbibition. For the water-wet core, oil was produced from all faces indicating counter-current flow governed by mainly capillary forces. In the presence of irreducible water saturation, before and after aging the cores, the measured index IW was +0.87 before treatment, which indicated that the cores were initially strongly water wet. After treatment, IW of core samples changed to -0.31, which is considered intermediate wet/mixed wet [14].

3.5. Effect of nanoparticle concentration on contact angle

Contact angle is a quantitative technique of measuring the wetting preference of a surface in the presence of more than one phase. According to Anderson et al. [50] a surface is either water wet, intermediate wet or oil-wet if the contact angle is between 0–75°, 75–105° and 105–180°, respectively when the contact angle is measured through the denser phase. Fig. 7 shows the oil drop contact angle measurements that were obtained in the presence of (a) brine-0 ppm nanofluids (b) brine at pH 10, (c) 25 ppm nanofluid, (d) 50 ppm nanofluid, and (e) 100 ppm nanofluid. The estimated contact angles were around 76, 103, 106, 132, and 139°, respectively measured through a less dense phase. Evidently, as we increase the nanofluids concentration the contact angle increases, indicating that the core wettability is altered from intermediate wetting to strongly water-wetting condition. Worth mentioning that although the highest concentration (100 ppm) resulted in a more water-wet state, oil recovery of using higher concentrations beyond the optimum may not necessarily result in higher oil recovery. At higher concentrations, nanoparticles tend to form clusters or aggregates and if injected in the porous medium, they can block the reservoir pores and reduce the fluid mobility. Therefore, an optimum concentration is always desirable for appropriate EOR applications [26,51]. The increase of contact angle as the concentration increases is related to the disjoining mechanism that causes the structural disjoining force to increase towards the vertex and detach more oil as the concentration

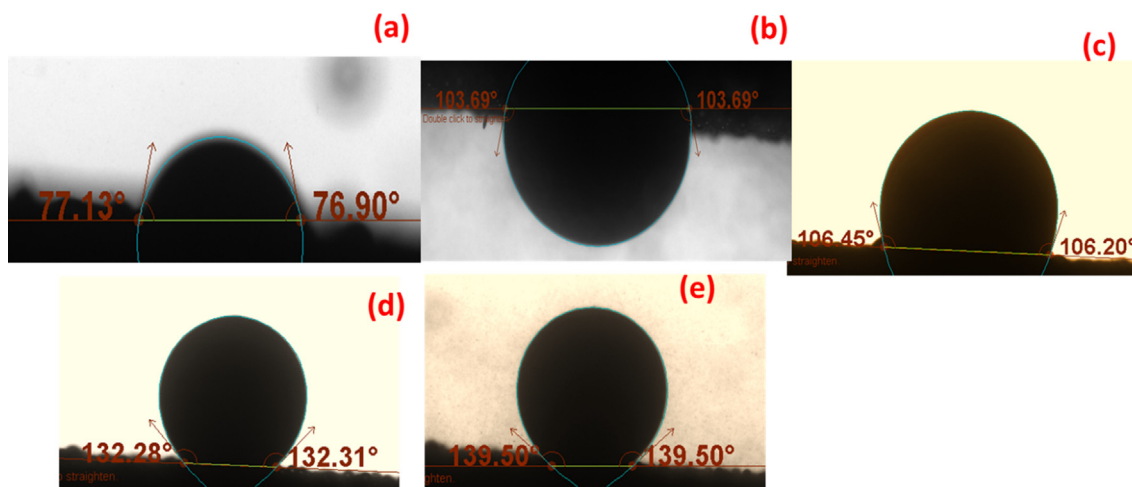


Fig. 7. Contact angle measurements before and after treatment with nanofluids: (a) oil drop/brine/substrate (0 ppm), (b) brine with pH 10, (c) oil drop/25 ppm nanofluid/substrate, (d) oil drop/50 ppm fluid/substrate, (e) oil drop/100 ppm fluid/substrate.

increases. Structural disjoining pressure is correlated with the ability of the nanofluid to spread on the surface as a result of the interfacial tension imbalance between the solid, oil phase and an aqueous phase. These interfacial forces decrease the contact angle of the aqueous phase (nanofluids) to almost 1° resulting in a wedge film. This wedge film acts to separate formation fluids such as oil from the formation surface due to hydrophilic and hydrophobic moieties of the nanoparticle adsorption on the surface altering the induced oil-wet to strongly water-wet which affects the oil, water and rock contact [16].

3.6. Effect of nanoparticle concentration on wettability index and imbibition rate

Unfortunately, there is no standard universal technique for quantifying the wettability of the reservoir rock. However, the most common methods and industrially recognized techniques used to obtain quantitative information on the rock wettability are the imbibition rate measurements and the Amott Harvey index(I) [50]. Similarly, the wettability of core materials can qualitatively be obtained by comparing the imbibition rates of a given imbibing fluid [52,53]. Generally, as the rock oil wetness increases, the rate of water imbibition decreases. To compare the rate of imbibition for different core plugs, the initial rock conditions must be duplicated [54]. This has been fulfilled by using cores that are initially 100% saturated with oil. This has been used frequently but does not represent what happens in the reservoir [55]. This procedure allows the core to have uniform homogenous wettability conditions that provide better comparisons for imbibition recovery for different rocks [54]. However, there are other factors that affect the alteration of the core wettability from water-wet to strong oil-wet such as the rock type, presence of irreducible water saturation and its composition, crude oil type, aging time and temperature [12,50]. In determining wettability index(WI), using the Amott-Harvey relative displacement method, cores were first driven to irreducible water saturation [14], and then aged in crude oil. Therefore, in this study, we investigated the role of initial water saturation towards wettability alteration and later, investigated the role of nanoparticles on the relative index with and without nanofluids. Originally water-wet sandstones where driven to irreducible water saturation. When treated with oil/heptane mixture at high temperature (90°C) for a long period (4 weeks) resulted in an intermediate wet state or partially water-wet system as shown in Fig. 8. The wettability index ranged from intermediate to more water-wet in the presence of nanoparticles and it was dependent on the nanoparticle concentration. This is in line with both the contact angle measurements and imbibition tests. A detailed summary of the Amott relative displacement measurements is provided in Table S5 of

the Supporting Information.

The effect of nanoparticle concentration on the imbibition rate was also studied using fully hydroxylated nanoparticles (HPNP). The imbibition experiments were conducted at 60°C with cores 100% saturated with oil and others at irreducible water saturation, using brine, brine at pH 10 or nanofluids of different concentrations in the range of 25–100 ppm. The results are summarized below. As seen in Fig. 9a and b, the imbibition rate increases as the concentration increases. For the cores without initial water saturation, there was a delay in the spontaneous imbibition of all the fluids due to the strong interaction of the asphaltenes and the rock at the surface which made the outer surface of the core strongly oil-wet. The induction time decreased following the order HPNP 100 ppm < 50 ppm < 25 < pH 10 < brine. This indicates that as the concentration increased, more nanoparticles could diffuse to the rock detaching more oil from the surface and changing the surface towards more water-wet, and more oil could start to be mobilized due to the shift from negative to positive capillary force. This indicates a significant impact of nanoparticle concentration on wettability alteration.

3.7. Effect of zero water saturation on the core wettability

In several studies, researchers have conducted imbibition studies without irreducible water saturations [16,35,36] and have created initial oil-wet conditions using silica surfaces in the laboratory by saturating cores with 100% oil and then aged them in oil. Under these conditions, wettability alteration occurs when polar functional groups present in the oil and polar sites of the mineral surface interact [12]. This results in non-uniform distribution of surface-active components around the core, phenomena known as chromatographic separation that causes non-homogeneous wetting conditions [56]. Normally, the measured contact angles are intermediate or weak water-wet and the interaction between the rock and oil is minor even after aging under temperature or with time [12]. This was also evident based on the obtained contact angle measurements in Fig. 7a, with brine alone after aging, wettability of the rock was still weakly oil-wet. However, it is important to note that these interactions are based on the used crude oil/asphaltene properties in the current study, as different asphaltene in other crude oils may show different behavior depending on their composition/behavior of the polar groups present. From the imbibition experiment in Fig. 9a, after 5 days, no oil was recovered from the cores under brine. The induction time for the fluid to start spontaneously imbibe increased in the order brine > pH10 > 25 ppm > 50 ppm > 100 ppm. Austad et al. [56] reported that very little or no imbibition may be observed in the induction time, especially for cores that are

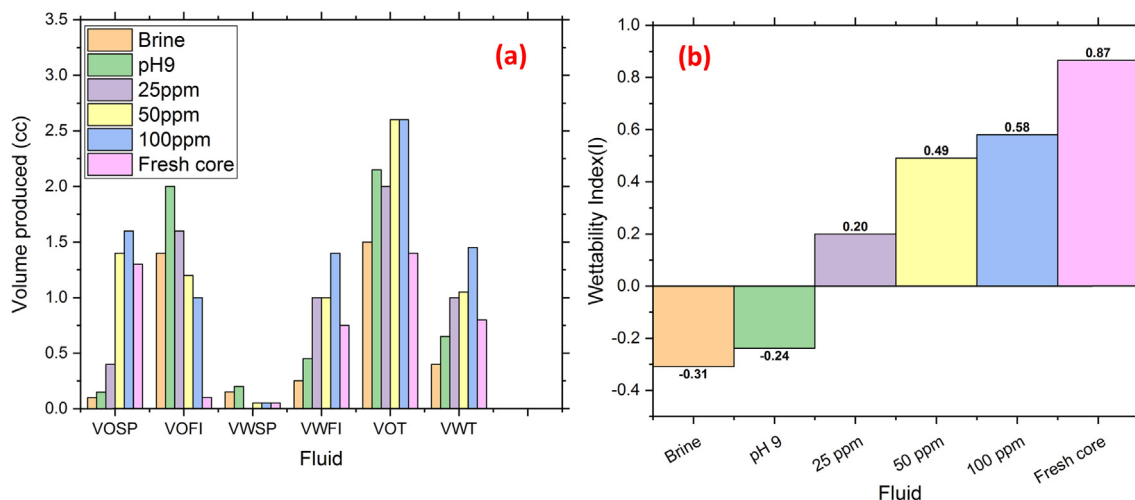


Fig. 8. Wettability index for different measured fluids.

strongly oil-wet. However, the induction time according to Marrow and Mason [57] is not clearly understood but the authors related it to the time required for water pathways to be established. Standnes and Austad [33] observed that during the aging period, an organic layer or a stronger coating is deposited at the rock surface which makes the rock surface more oil-wet than the center of the core hence extending the induction time especially in presence of brine alone. However, in the presence of the nanofluids, it is clear that the induction time could be reduced as the nanoparticle concentration increased due to diffusion and possibly desorption of the asphaltene from the core surface thus, oil could start to be produced. Nanoparticles adsorb on the rock surface and create a detaching force or disjoining force that acts to change the rock wettability to strong water-wet, therefore water can spontaneously imbibe into the core due to positive capillary pressure [16,35].

3.8. Effect of irreducible water saturation on wettability alteration and imbibition

Ideally, reservoirs contain connate water with various ions (monovalent and divalent) [58]. Therefore, it is imperative to investigate the effect of this connate water and composition on wettability alteration and its effect on imbibition in the presence of nanofluids. Experiments performed in the laboratory without initial water saturation do not represent actual reservoir conditions. To also properly understand the role of asphaltene in wettability alteration in the presence of initial water saturation and the impact of nanoparticles, we first investigated their interaction with the rock interface. Several studies have documented a strong interaction between asphaltenes and solids, especially

clays [59,60]. Moreover, the presence of water due to its higher dielectric constant ($\epsilon = 78.5$) has been postulated to contribute to greater ionic interaction strength between the solid and fluid [61]. To establish the irreducible water saturation, the cores were flooded with oil in each direction and the volume of produced water from the core after oil saturation was used to estimate the oil in place. After that, the cores were aged for 4 weeks at 90 °C with a similar oil heptane mixture used previously. In the presence of initial water saturation, a longer period of aging and a higher temperature was desirable. For cores without initial water saturation, adsorption of polar components on the rock surface is faster because there is no barrier (water film) for the interaction to take place. However, in the presence of initial water saturation, the polar ends must pass the water barrier and adsorb at the sandstone surface then reorganize in the pore structure. As such, to get closer to the required thermodynamic state, and speed up the process, the aging time and temperature were increased higher than the previous temperature (without initial water) for laboratory applications even though this does not guarantee a thermodynamically stable system. Asphaltenes are not soluble in water, however, brine with a significant concentration was found to dissolve in crude oil and the presence of initial water saturation increased the intermolecular interactions between crude oil and the solid surface [61]. Other authors, on the contrary, have reported that the presence of initial water saturation reduced the asphaltene adsorption [11,60]. In their study, they concluded however that asphaltene adsorption also depends on the initial water saturation ratio. As the initial water saturation increases, it can act as a shield and prevent the direct interaction of the surface with asphaltenes. Also, depending on the DLVO forces that affect film

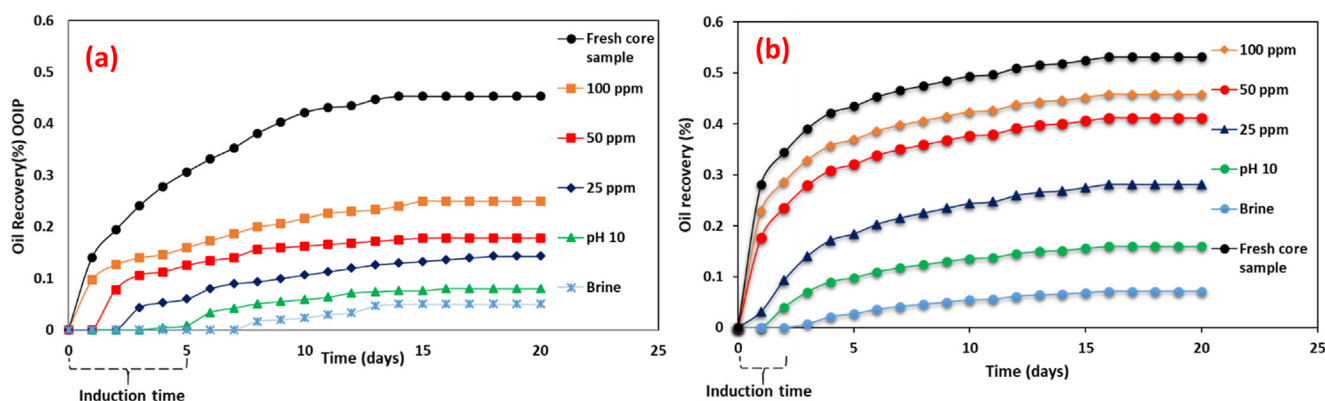


Fig. 9. Spontaneous imbibition of various fluids without initial water saturation (a) and in the presence of initial water saturation (b) at 60 °C.

stability, water in thin films may prevent or promote the interaction of the asphaltene and the rock surface. From this current study, based on the brine concentration used, the obtained wettability index (I) for the core plug under brine alone after aging was -0.31 . This clearly indicates that in the presence of only monovalent ions in the initial water saturation, core plug did not result in a strongly oil-wet state due to weak interaction between the rock and asphaltene in the presence of water film. Cuiec [62] postulated that a system is intermediate-wet when $-0.3 \leq I \leq 0.3$. Therefore, the results of brine/oil-rock interaction from this study were found to result in a mixed-wet of either patchy sort, dalmatian, or of interconnected water-wet and non-water wet pathways. This is consistent with what was reported by Salathiel [63]. The effect of initial water saturation on wettability alteration might be negative or positive depending on its ratio. In fact, in the presence of initial water saturation, only areas that are contacted with crude oil undergo changes in the wetting that is significant to the displacement process. This was reflected in the recovered oil during the spontaneous imbibition of brine alone (Fig. 9b). A very slow spontaneous imbibition was observed even after 20 days resulting in 7.14% of oil recovered, while during forced imbibition still with brine almost 40% of OIIP was recovered. The slow recovery during spontaneous imbibition may be attributed to the strong interaction of the asphaltene and the rock surface that resulted in strong oil wetness at the surface hence water could not easily create pathways to access the pores. Also, possibly because of the saturation end effects during the establishment of the irreducible water saturation. However, when nanofluids were applied with increasing concentrations, oil could be easily recovered due to nanoparticle diffusion that could result in the preferentially strong water-wet surface.

3.9. Effect of solution pH during wettability alteration

We conducted a simple bottle test to better understand the effect of pH on wettability alteration in the presence of monovalent ions. pH affects the stability of water film in the presence of various salts. The sandstone surface in the presence of monovalent aqueous solutions is negatively charged when the pH is above 2. Over a wide range of pH values, crude oil/brine and rock interface can have charged sites that are either positive or negatively charged. The DLVO theory can be used to predict if the water film that is initially in contact with the surface will remain stable using the ionizable site models of the oil/brine interface [12]. For low ionic strength in the presence of mainly monovalent ions, especially NaCl, the water film remains stable at higher pH and unstable at low pH [64]. If the water film breaks, oil can contact and adsorb on the rock surface, resulting in a weakly water-wet, intermediate-wet or oil-wet surface. Since pH depends on zeta potential, we investigated its effect and the wettability implications in the presence of brine with monovalent ions. Zeta potential measurements were also conducted to determine the surface sign charge at the brine/mineral or oil/brine interface at various pH values. The measurements indicated that the surface charges were negative. However, Dubey et al. [37] postulated that the surface charge of sandstone due to the presence of various traces of aluminosilicate minerals (field spar and clay) may show diverse behavior. They also concluded that the overall zeta potential magnitude and charge mainly depends on the brine pH. Oil is positively charged at low pH, as the pH increases the zeta potential decays to zero at the isoelectric point (pH less than 2) and then becomes strongly negative [37]. Fig. 10 shows the measured values of zeta potential against pH at 25 °C for the Berea sand in brine. It can be observed that zeta potential increased towards more negative as the pH increased. Small changes in pH imposed significant changes in the surface charge of the rock. When the pH increases, the electrical charges shift from positive to negative at the rock/brine interface, also, the forces changed from attractive to electrostatic repulsive between the rock and oil which makes the rock more water-wet due to double layer expansion and stabilization of the water film surrounding the

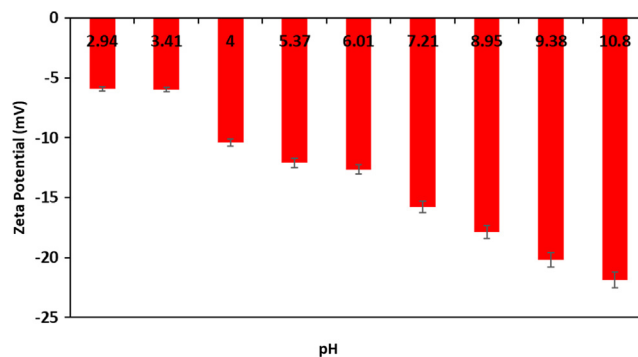


Fig. 10. Zeta potential for the Berea sandstone in brine at various pH.

rock. Moreover, the measured wettability index in the presence of pH 10 alone showed a shift from -0.31 to -0.22 , indicating the significance of pH in changing wettability, which is consistent with zeta potential measured results. Also based on the bottle test Fig. S3 in the Supporting Information, as the pH increased more clear sand could be seen indicating stronger water wet. This could explain the additional oil recovery of 4.37% obtained when a brine alone at pH 10 was injected in the core at the tertiary stage. Therefore, adjusting the nanofluids pH to 10 not only improves their stability and dispersity but also enhances the ability of nanofluids to change the rock wettability towards more water-wet.

3.10. Core flooding experiments

The effect of different nanopyroxene-based nanofluids concentrations on EOR after brine injection was investigated through core flooding experiments using four displacement tests. A summary of results is shown in Table 4. The effects of the injected nanoparticle concentrations on tertiary recovery for the injected fluids can be seen in Fig. 11. The additional oil recovered after brine injection increased as the concentration of the nanoparticles increased. It should be noted that prior to the injection, pH of the nanofluids was adjusted to 10 to improve their stability. Therefore, for comparison, brine alone with pH adjusted to 10 was used to investigate its effect on EOR. Brine with pH 10 was injected into the porous medium after the initial brine flooding (WF1) and allowed to soak for 24 h comparable to what was performed in the case of nanofluid injection. An additional 4.31% was recovered with brine pH 10 after WF1. Fig. 11 shows the oil recovery before and after nanopyroxene injection of various nanofluid concentrations in comparison to pH 10. The additional oil recovery for pH 10 brine can be attributed to the change in pH for the medium that makes the system more strongly water-wet. Also, based on the bottle test Fig. S3 in the Supporting Information shows that with increasing pH the system becomes more water-wet.

During nanofluid injection, rock wettability may change towards strong water-wet. This affects the oil relative permeability hence the displacement efficiency increases as the nanofluid concentration increases. Because of a post flush WF2 after soaking with 1 PV, any modification due to the interaction between the rock and nanoparticles results in a piston-like flow through a porous medium. Moreover, during nanofluid injection, as shown in Fig. 12a, there was a slight differential pressures increment along the core which is attributed to the deposited nanoparticle on the rock surface that tend to cause pressure increase as the oil is detached/washed from the core during the post flushing stage with additional water injection after soaking with the nanofluids. Altering the rock wettability results in increasing the microscopic displacement efficiency (ED) and this was slightly a function of nanoparticle concentration. ED increased as the nanoparticle concentration increased as shown in Fig. 12b. Altering the wettability to strong water-wet as the nanoparticle concentration

Table 4
EOR Scenarios and Experimental Conditions.

Core no	Initial oil saturation (OIP)	Injection rate (cm ³ /min)	Nanoparticle concentration (ppm)	Water flood recovery (%)	Tertiary recovery (%)	Final recovery (%)
1	0.61	0.2	100	62.43	14.28	76.71
2	0.64	0.2	50	62.92	13.54	76.46
3	0.62	0.2	25	60.01	12.57	72.76
4	0.61	0.2	Brine at pH 10	60.15	4.31	64.46

increases shifts the relative permeability to the right, the relative permeability to oil also increases while that for water decreases which ultimately results in more residual oil being remobilized [25]. The displacement efficiency was estimated from Eq. (2), the detailed calculations for the required parameters are provided in the Supporting Information Table S6.

$$E_D = 1 - \frac{SO_{r2}}{SO_{r1}} \tag{2}$$

where,

- E_D = displacement efficiency
- SO_{r1} = residual oil saturation after brine flooding
- SO_{r2} = residual oil saturation after nanofluid flooding

4. Conclusion

In the current study, an investigation of the mechanism(s) of EOR with completely hydroxylated nanopyroxene by varying the concentrations was evaluated. Interfacial tension (IFT), asphaltene aggregation and wettability measurements were performed by contact angle measurements, imbibition experiments and wettability index to understand the underlying mechanism(s). From this study, IFT reduction was noticeable but not significant for remobilizing trapped oil since it was not in an ultra-low range. A chemical mechanism for adsorption and desorption of asphaltene in the crude oil deposited on the sandstone surface was suggested that involved co-adsorption/disaggregation of asphaltenes from the oil/mixed-wet sites using nanopyroxene with and without initial water saturation. The results showed that partially hydrophobic nanopyroxene have higher affinity for adsorbing asphaltenes in oil and reduce their aggregate size, however, there is an optimum concentration beyond which the asphaltenes size reduction may be negligible and insignificant to EOR. Treatment of sandstone cores that are initially strongly water wet with heptane/oil mixtures results in a mixed wet of either patchy sort, dalmatian, or of interconnected water-wet and non-water wet pathways or intermediate-wet as shown by the relative index measurements. Moreover, nanopyroxene nanoparticles significantly affect the contact angle, imbibition and wettability index, as they increase as the nanoparticle concentration increases. In the presence of only monovalent ions, wettability alteration depends on the composition and pH of brine in the initial irreducible water saturation. Furthermore, adjusting the nanofluid pH to 10 not

only improved the nanofluid stability and dispersibility but also had a substantial impact on EOR, almost 4.03% of the residual oil could be recovered possibly due to the shift in the zeta potential that makes the rock surface more water-wet. Core flooding experiments showed that nanopyroxene-based nanofluid injection can recover an addition of ~12–14.5% after waterflooding.

CRediT authorship contribution statement

Farad Sagala: Conceptualization, Methodology, Visualization, Investigation, Data curation, Writing - original draft. **Afif Hethnawi:** Methodology, Investigation, Data curation, Validation. **Nashaat N. Nassar:** Conceptualization, Supervision, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2020.117462>.

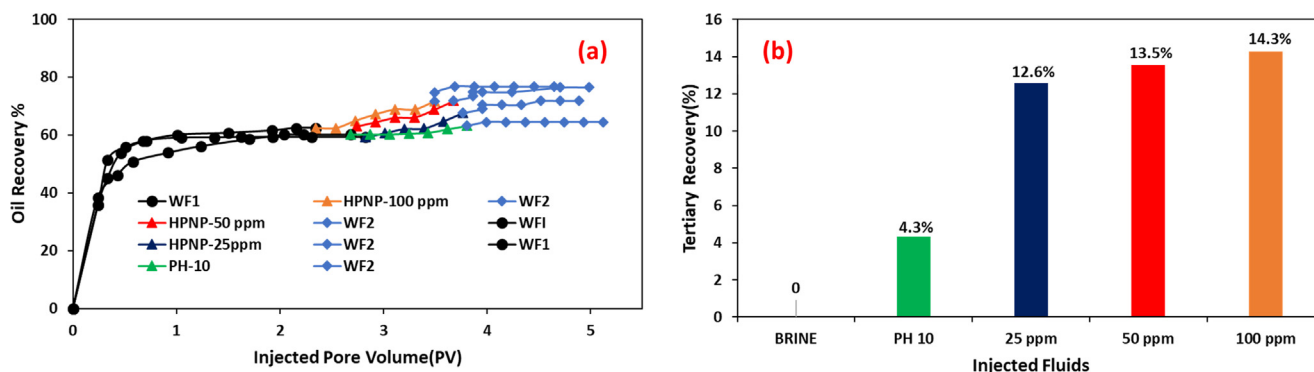


Fig. 11. Oil recovery (a) and additional tertiary recovery (b) against injected PV for the considered fluids.

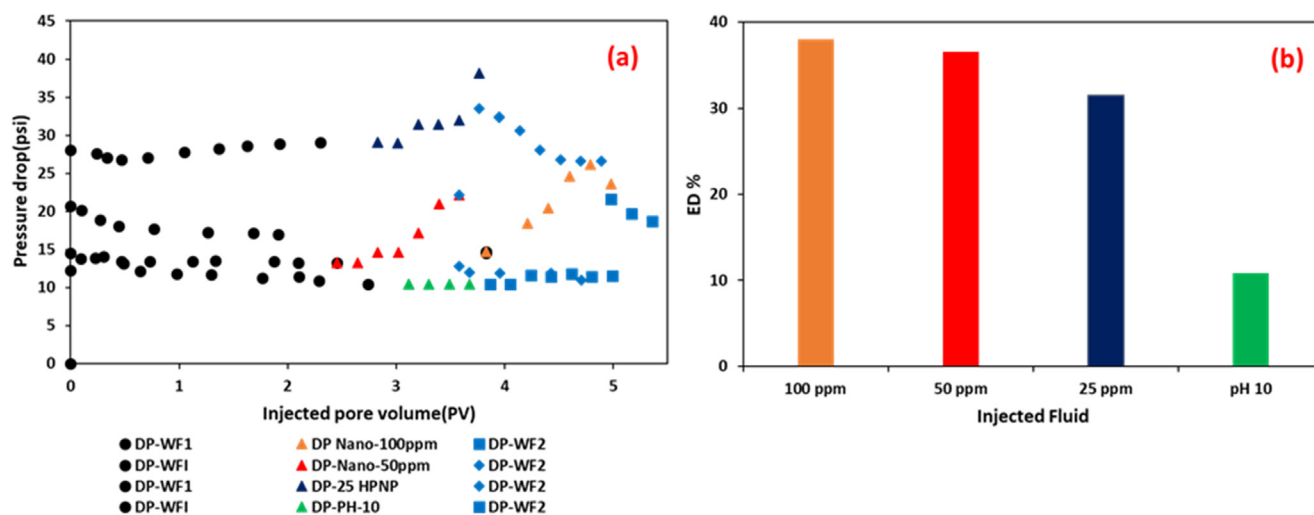


Fig. 12. (a) Pressure profiles for the first brine flooding (WFI), brine with nanofluids or brine at pH 10 and subsequent brine WF2 and (b) for displacement efficiency during tertiary recovery.

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