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COMPARISON STUDY OF DOLOMITE SURFACE WETTABILITY ALTERATION BY Al_2O_3 AND ZrO_2

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ABSTRACT

Nanoparticles have been used widely in oil and gas industry. Many researchers have identified nanoparticles as a good agent to enhance oil recovery due to its characteristics and properties. Therefore, this research was conducted experimentally to investigate the efficiency of Al_2O_3 and $ZrO_2$to alter the wettability of oil-wet dolomite rock. In this experiment, nanofluids were obtained by dispersing nanoparticles in cationic surfactant with the presence of sodium salt. The investigation was conducted by measuring contact angle reduction of dolomite surface after treatment with nanofluids. Field emission scanning electron microscopy (FESEM) images were used to observe the rock surface before and after the application of nanofluids. Meanwhile, energy-dispersive x-ray (EDX) data was used to verify the adsorption of nanoparticles on the rock surface. Interfacial tension and surface tension of surfactant were also studied in order to examine the ability of the surfactant to increase the mobility of oil in the pore throat. Other than that, core displacement test was conducted to determine oil recovery after injection of nanofluids into the system and the efficiency of nanofluids to alter wettability of oil-wet dolomite rock is observed. From the testing, it was found that, reduction of contact angle was greater at below critical micelles concentration of the surfactant. After the addition of nanoparticles into the surfactant, the contact angle of the rock has become more reduced. Moreover, the effect of nanofluids injection on the rock to alter the wettability was assessed by core displacement test result. It was discovered that about 55 % and 64 % oil can be recovered by water flooding for sand pack 1 and sand pack 2 respectively. The remaining oil trapped in the rock was recovered with the injection of Al_2O_3 and ZrO_2 nanofluids in sand pack 1 and 2 respectively. About 20 % and 16.7 % more oil can be recovered from sand pack 1 and sand pack 2 after the injection of 2 PV of nanofluids into the system. As a conclusion, this experimental works proves that, Al_2O_3 and ZrO_2can act as enhanced oil recovery agent by altering the wettability of the rock system from oil-wet condition to a more water-wet condition.

Keywords: wettability, nanoparticles, surfactant, enhanced oil recovery, dolomite.

1. INTRODUCTION

Wettability plays an important role in oil productions. Wettability of clean solid surface can be modified by the introduction of surface active compounds such as resins and asphaltene. These surface active compounds have carboxylic groups and when in contact with brine, it will become negatively charged and will be adsorbed onto the rock surface [1]. The adsorption of carboxylic component on rock surface will change the wettability of the rock into a more oil-wet condition. In two immiscible fluid system, wettability is defined as the measure of the preferential tendency of one fluid to spread or adhere to the surface of porous medium in the presence of other fluid [2]. The interaction of oil-water system on solid surface was explained by Young's Law,

$$\cos\theta = \frac{\sigma sw - \sigma so}{\sigma wo} \quad (1)$$

where θ is contact angle and σ value indicate the interfacial tension among solid-water (σsw), solid-oil (σso), and water-oil (σwo) interfaces. The Young's equation has been widely used in order to understand the contact angle in term of interfacial tension. In order to derive the Young's equation, few assumptions have been made which are if the solid surface is rigid, flat, insoluble, chemically homogenous and smooth. Figure-1 demonstrates the inhibition of oil drop on solid surface in the presence of other immiscible fluid.

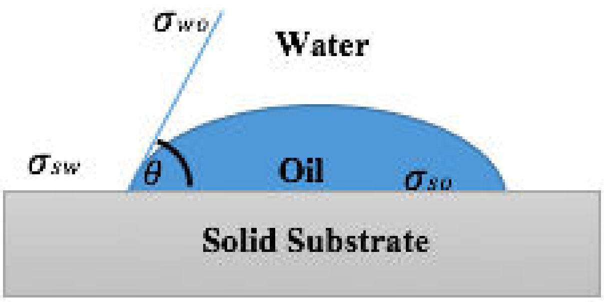

Figure-1. Illustration of contact angle in oil-water-rock system.

Wettability of a rock surface can be determined using qualitative and quantitative method. Quantitative methods are used to determine the wettability of rock surface including contact angle measurement, spontaneous imbibition, and wettability indexes determination using Amott, Amott-Hervey and USBM method. In contrast, qualitative methods used are relative permeability measurement, and core flooding.

Oil recovery by water flooding is about less than half of the original oil in place in non-fractured carbonate, and it is much lesser in fractured carbonate reservoirs [3]. Low recovery in these reservoirs is primarily because of fractured reservoir and oil-wet rocks. Wettability alteration from oil-wet to more water-wet conditions of the reservoirs has great impact on oil flow to increase oil recovery. Alteration of rock's wettability can be done using thermal, chemical i.e. surfactants, low salinity brine and selective ions.

Apparently there is an increasing interest in using chemical to alter wettability of the rocks. In numerous articles, wettability alteration of rock by surfactant was studied and the usage of ionic surfactant has been considered as a feasible method [4, 5, 6, 7]. It is noted that effectiveness of wettability alteration is influenced by the type of surfactant. The mechanism involved in wettability alteration of oil-wet carbonate rock by cationic surfactant is the formation of ion pairs. These cationic surfactants are able to desorb the negative charged component of the crude oil and change the surface of carbonate rock to more water-wet. Meanwhile, wettability alteration of carbonate rocks by anionic surfactant is through the formation of monolayer between surfactant molecules tails and crude oil components that was adsorbed on the rock surface. The interaction that is responsible for the layer is hydrophobic interaction and it is weaker compared to ion-pairs interaction [8].

Nanoparticles have received a great attention in the petroleum industry. It has great potentials to solve or manage several problems in the petroleum industry. One of the application of nanoparticles in oil and gas industries is the enhanced oil recovery (EOR). It is reported that, nanoparticles can alter certain factors in the formations and in oil properties. Two leading factors that make nanoparticles unique to oil and gas exploration and production are their size and ability to adjust their behavior [9]. Mechanism for nanoparticles to alter wettability of rock surface is by forming a continuous wedge film at contact line of oil/water/rock system. The driving forces that are responsible for the spreading of the nanoparticles is the structural disjoining pressure [10]. Despite all the reported studies, there are still not many research that has been conducted on the application of nanoparticles dispersed in cationic surfactant to alter the wettability of carbonate rock. In this paper, alteration of oil-wet carbonate rock to more water-wet condition is studied using nanoparticles that are dispersed in cationic surfactant with the presence of sodium salt.

2. MATERIAL AND METHOD

2.1 Material. Characterization of crude oil

The crude oil from reservoir located at Sarawak, Malaysia was used. The characterization of the crude oil was conducted to determine its density, viscosity, API gravity and total acid number. Physical properties of the crude were listed in Table-1. FTIR analysis was also conducted to determine the functional group that is present in the crude.

Table-1. Physical properties of the crude oil.

Asphaltene content (wt %)	0.01
Resins content (wt %)	6.26
Kinematic viscosity at 25°C (mm2/s)	2.016
Density at 25°C (g/mL)	0.8283
° API gravity	37.7
Total acid number (mg KOH/g)	0.06

Nanoparticle, NPs: Two commercial type of nanoparticles, namely Al_2O_3 (20 nm, purity 99+%, and specific surface area >138 m^2/g) and ZrO_2 (40 nm, purity 99+%, and specific surface area 20-40 m^2/g) were purchased from US Research Nanomaterials, Inc (Houston, TX).

Fluids: Sodium Chloride (NaCl), from Qrëc (Asia) SdnBhd was used as salts to make synthetic brine (20 g/L) and Cetyltrimethylammonium Bromide (CTAB) from Fisher Scientific UK Ltd was used as cationic surfactant. Nanofluids with weight concentration 0.05 wt % were prepared by using high speed stirrer and were stirred for 10 minutes at 500 rpm. A homogenous suspension was later obtained by treating the mixture in ultrasonic apparatus for 1-hour prior the test was conducted.

Preparation of Porous media: Carbonate dolomite were obtained from Kocurek Industries INC, (Caldwell, TX). The core was first cut into small plate (3mm thickness and 38.1 mm diameter) using trimming machine and is polished to obtain a flat and smooth surface. For displacement test, the core was crushed and sieved. Grain-sized crushed dolomite was selected at a range of 50-300 µm. Then, the grain was packed in the cylindrical shape of a perspex tube.

2.2 Measurement of surface tension and interfacial tension

Surface tension measurement was used to determine critical micelle concentration (CMC) of the surfactant. Interfacial tension (IFT) of nanofluids/oil system was determined. In this measurement, Kruss Easy Dynetensiometer was used under ambient pressure and temperature with Du Noüy method by Harkins and Jordan correction. The ring was cleaned thoroughly with toluene and dried using the bunsen burner before each measurement.

2.3 Measurement of contact angle

Contact angle is one of the easiest way to measure the wettability of a rock surface. It is a quantitative method and the contact angle was measured through a denser fluid. In oil/water/rock system, contact angle was measured through water. For contact angle measurement, oil-wet dolomite substrate was submerged in different test solutions. The substrates were placed vertically in the test solution in room temperature for 48 hours. Then, oil was injected onto the rock surface and side image of oil drops were taken using a camera and the contact angle was determined. Figure-2 is the schematic diagram for contact angle measurement.

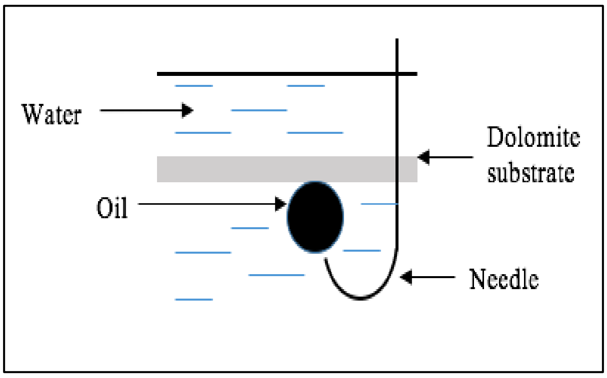

Figure-2. Schematic diagram for measuring contact angle.

2.4 Core displacement test

Core flooding was conducted in order to study the performance of wettability alteration on oil recovery. Unconsolidated sand packs were prepared for displacement test with the length of 43.8cm and 3.4cm diameter to stimulate reservoir formation. The packs were placed vertically for saturation brine (single phase flow) to determine the porosity and permeability with injection rate of 2 cc/min. After that, oil was injected into the pack until no more water is produced at the outlet. Water flooding was conducted at the injection rate of 2 cc/min until the is no more production of oil. Oil recovery from water flooding was then recorded. The injection was continued with nanofluids at 2 cc/min as tertiary recovery mode. Oil recovery from tertiary mode was recorded and evaluated.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of crude oil

Fourier transform infrared spectroscopy (FTIR) was used to determine the chemical groups that are present in the crude oil. FTIR spectrum for the crude oil employed in this research is shown in Figure-3. The spectra were recorded at wavelength between 500 and 4000 cm^{-1}. From Figure-3, it can be seen that, adsorption at 1820-1670 $cm^{-1}$is due to C=O stretching meanwhile at 3000-3600 $cm^{-1}$is due to O-H functional group. Hence, the presence of carboxylic acid in the crude is confirmed by FTIR analysis and the total acid number of the crude oil is 0.06 mg KOH/g which supported the FTIR analysis. Another major functional groups that exist in the crude oil are alkanes groups i.e. CH_3 and CH_2 at wave number of 2920 cm^{-1}. The peak at 1373 $cm^{-1}$and 1454 cm^{-1}indicate deformation of $CH_3$and deformation of CH_2. The adsorption at peak 745 $cm^{-1}$is due to vibration of alkyl halide stretching.

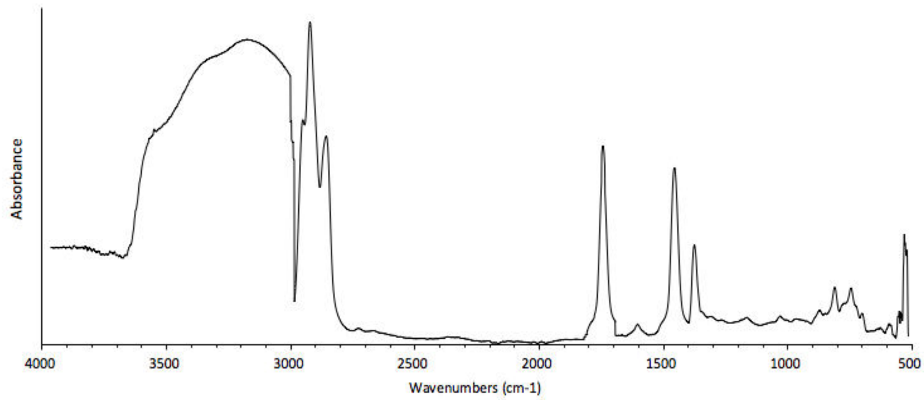

Figure-3. FTIR spectra for the crude oil.

3.2 Surface tension and interfacial tension reduction by surfactant

The surface tension of water can be reduced by the addition of surfactant in a solution. The surface tension value also can be used to determine the critical micelle concentration (CMC) of a surfactant. CMC is the concentration of surfactant at which the surfactant solution begins to form micelles in large amounts. The surface tension of CTAB surfactant in brine was measured at different concentrations. A graph of surface tension versus surfactant concentration was plotted in Figure-4(a). The lowest surface tension value for CTAB surfactant is 31.75 mN/m. CMC is measured at the inflection point of the curve and based on this figure, the CMC value for this surfactant is 1200 ppm. Meanwhile, interfacial tension (IFT) was measured between two immiscible fluids and in this system IFT was measured between crude oil and surfactant solution. The IFT value at zero surfactant concentration is 16.23 mN/m and after the addition of 0.1 wt% of surfactant, the value reduces significantly to 8.60 mN/m as shown in Figure-4(b). The results also showed that, at below CMC for a fixed salinity, the IFT value decreases with the increase of surfactant concentrations. However, above the CMC value, the reduction of IFT was not significant with the increase of surfactant concentration. The reduction of IFT value shows the efficiency of the surfactant to reduce capillary pressure in the pore throat to increase oil mobilization.

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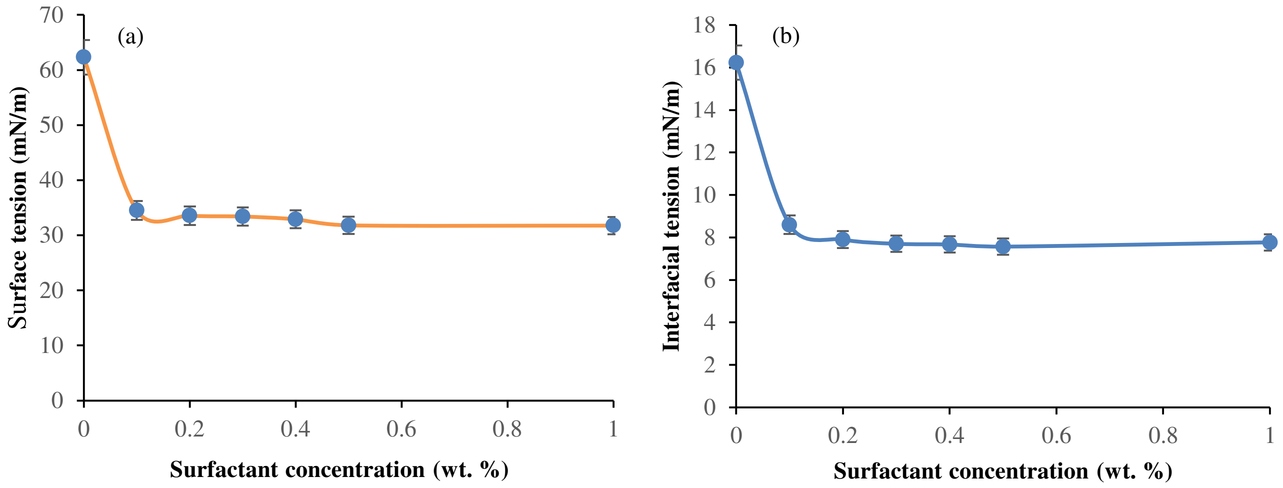

Figure-4. (a) Surface tension of the surfactant (b) Interfacial tension of the surfactant.

3.3 Factors influencing contact angle

Contact angle of the substrate was determined by measuring oil droplet on dolomite substrate surface in synthetic brine. The measurement was conducted in room temperature and at atmospheric pressure. In order to observe wettability alteration, initial contact angle was determined. In the first part, wettability alteration due to effect of changing surfactant concentration was observed; the salinity was fixed at 2 wt %. Figure-5 shows the relationship between contact angle and surfactant concentration. From the graph, it revealed that, for the surfactant employed in this study, contact angle decreases with the increase of surfactant concentration. It is noted that dolomite rock has positive surface charge value; therefore the negative charged component from crude oil will strongly be adsorbed on the rock surface. The mechanism involved in wettability alteration of dolomite rock by cationic surfactant is the formation of ion pairs between the cationic head of surfactant and the acidic components of the crude adsorbed on the rock surface. From the experiment, it can be observed that the changes were more significant at concentration below CMC, meanwhile at concentration above CMC value, contact angle reduction was not much. This is because, at concentration above CMC, surfactant start to form micelles and the monomer activity of the surfactant becomes relatively constant [11]. In addition, the adsorption of surfactant also did not experience any changes hence, the contact angle also remained slightly unchanged or the reduction is not significant.

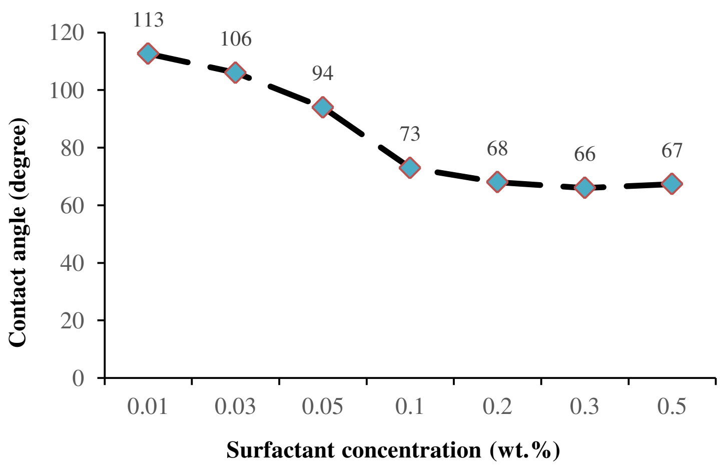

Figure-5. Effect of surfactant concentration on the contact angle of dolomite substrate.

Introduction of nanoparticles into the solution also helps to reduce the contact angle. In this study, $Al_2O_3$and ZrO_2 nanoparticles were employed. Nanoparticles with each concentration of 0.05 wt % was dispersed into 0.12 wt % CTAB surfactant at salinity of 2 wt %. Each nanosolution was stirred for 10 minutes and ultrasonicated for 30 minutes prior testing to get a homogenous and stable solution. After the introduction of nanofluids to oil wet dolomite, the contact angle reduced significantly. In the event of Al_2O_3nanofluid, the contact angle decreases from 130º to 52º, meanwhile in the case of ZrO_2nanofluid, the contact angle reduces from 128º to 60º.

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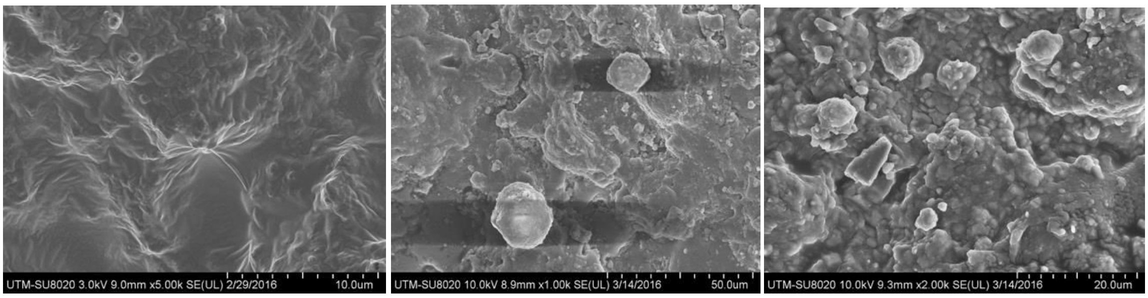
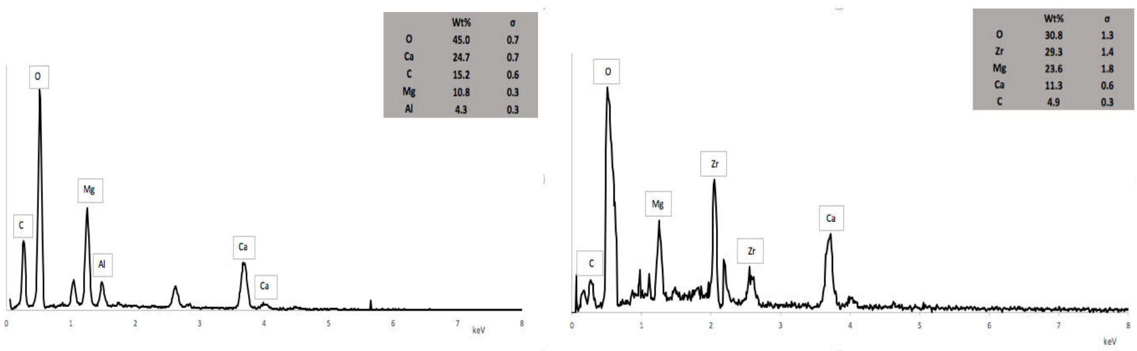
Figure-5 shows the FESEM images of the dolomite substrate. From figure 6(a), it can be observed that, the dolomite has smooth surface after aging in crude oil and it indicates oil wet condition. Meanwhile, figure 6(b) and 6(c) shows the adsorption of nanoparticles on dolomite rock surface. The adsorption of nanoparticles on rock surface was verified by EDX spectrum analysis. Dolomite was mainly composed from oxygen, carbon, magnesium and calcium element only. After the substrates were submerged in $Al_2O_3$and ZrO_2nanofluids respectively, the EDX analysis was shown in Figures 7(a) and 7(b). The presence of Al and Zr on the aged dolomite surface proves that nanoparticles were adsorbed onto the rock surface and seconded the FESEM images.



(a) (b) (c)

Figure-6. FESEM images of dolomite substrate: (a) after aging in crude oil; (b) after aging in ZrO_2nanosolution; (c) after aging in Al_2O_3nanosolution.



(a) (b)

Figure-7. EDXmeasurement (a) after aging in Al_2O_3nanofluid (b) after aging in ZrO_2nanofluid.

3.4 Oil recovery by nanofluids

The performance of both nanoparticles were further tested by core flooding experiment. The prepared sand packs were saturated with oil and after that, water was injected into the packs to measure oil recovery due to water flooding. The injection of water was continued until no more oil was recovered. Oil recovery by water flooding was recorded and the injection was continued with nanofluids to recover more oil due to enhanced oil recovery. Figure 8 shows oil recovered by water flooding and enhanced oil recovery. From Figure-8(a), the results revealed that, total oil that can be recovered by water flooding is 55 % and 64 % for sand pack 1 and 2 respectively after injection of 1.5 pore volumes. The remaining oil in the pore cannot be recovered by water injection, thus injection of nanofluids into the reservoirs was used as tertiary recovery. In this research, Al_2O_3 nanofluids was injected into the first sand pack meanwhile ZrO_2 was injected into the second sand pack. After the injection of 2 pore volumes of nanofluids, additional 20 % oil can be recovered from sand pack 1 meanwhile about 16.7 % more oil can be recovered from sand pack 2. A correlation between total oil recovery after injection of Al_2O_3 nanofluids and ZrO_2nanofluids revealed that both nanoparticles can enhance more oil after secondary recovery. In addition, it can be concluded that, oil recovery by $Al_2O_3$was higher in comparison with oil recovery by ZrO_2nanofluids. The mechanisms involved in displacement by nanoparticles was explained by Abdelrahman (2015). In his paper, it is mentioned that, nanoparticles are using disjoining pressure mechanisms. The particles will form a wedge-shaped film at the contact line of oil/water/rock system. The film will separate the oil from the formation rock and thus recovers more oil. The energy that drives this mechanism is called as Brownian motion and electrostatic repulsion between nanoparticles [13].

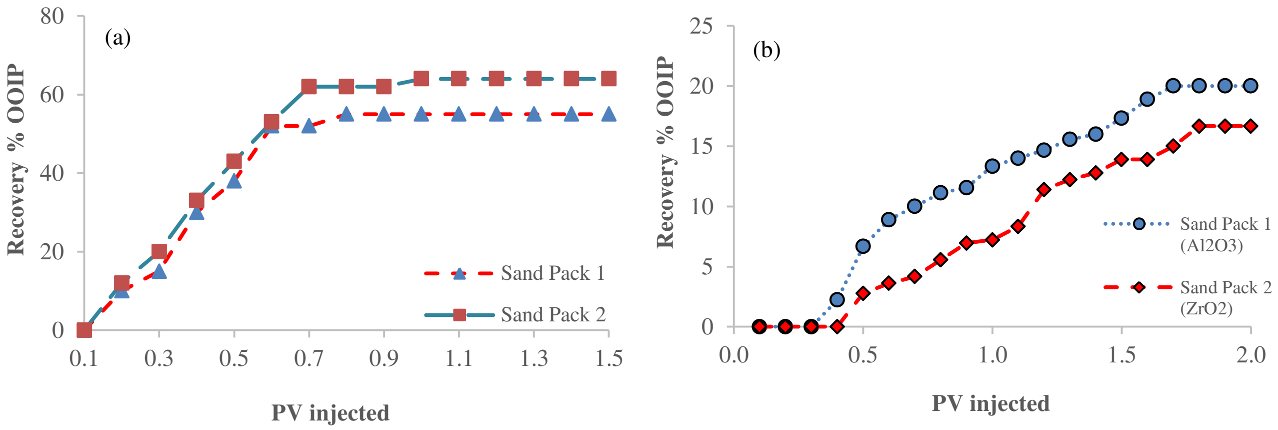


Figure-8. (a) Result of oil recovery by water flooding (b) Result of oil recovery after injection of nanofluids.

4. CONCLUSIONS

Based on this experimental work, few conclusions can be drawn. Cationic surfactant has been a good wettability alteration agent for carbonate rock. In this case, the effect of surfactant concentration has been studied and the results revealed that, as the concentration of surfactant increases, the contact angle of dolomite rock decreases at concentration below CMC value. However, at above CMC value, as the concentration of surfactant increases, reduction of contact angle is not significant. Other than that, this study gives comparison between Al_2O_3 and ZrO_2 nanoparticles as wettability alteration agent on oil-wet dolomite rock for enhanced oil recovery. Both nanoparticles can change the wettability of dolomite rock from oil-wet to more water-wet condition. However, Al_2O_3has higher influence on reduction of dolomite substrate contact angle. Furthermore, core displacement test results revealed that injection of nanofluids into the system will increase production of oil. Therefore, Al_2O_3 and ZrO_2can be considered as a good EOR agent and further tests need to be conducted for field application.

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