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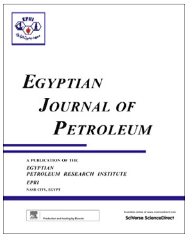

FULL LENGTH ARTICLE

An evaluation of modified silica nanoparticles' efficiency in enhancing oil recovery of light and intermediate oil reservoirs

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KEYWORDS

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Nano fluid;
Oil recovery;
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Wettability

Abstract The role of nanoparticles in enhancing oil recovery from oil reservoirs is an increasingly important topic of research. Nanoparticles have the properties that are potentially useful for enhanced oil recovery processes, as they are solid and two orders of magnitude smaller than colloidal particles. This paper presents a comparison between the efficiency of modified silica nanoparticles in enhancing oil recovery from two different Iranian light and intermediate oil reservoirs. The mechanisms used to recover additional oil would be oil–water interfacial tension reduction and wettability alteration. Oil phase contact angles and oil–water interfacial tensions were measured in the absence and the presence of nano fluids' different concentrations (1–4 g/L). Results showed that the interfacial tension reduces dramatically in the presence of nanoparticles for both light and intermediate oil. In addition oil phase contact angle results showed a transformation of rock wettability from water-wet toward oil-wet condition. However, these nanoparticles are more capable in the reduction of the interfacial tension and the alteration of wettability in the case of light oil reservoir. A comparison between recovery results indicated that these nanoparticles are more efficient in light oil reservoirs and produce more incremental amount of oil after primary and secondary processes.

1. Introduction

More than 50% of the original oil in place is trapped in the rock due to high capillary forces that prevent oil from flowing through the rock [1]. Capillary pressure which influenced by wettability and oil–water interfacial tension is the force necessary to squeeze a hydrocarbon droplet through a pore throat [2]. Reservoir wettability plays an important role in oil recovery processes and can cause drastic changes in displacement mechanisms [3]. In addition, oil–water interfacial tension governs capillary forces, deformation of oil droplets, oil mobiliza-

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tion and oil recovery [4,5]. Recently, nano materials have attracted many researchers' attention in the field of enhancing oil recovery due to their unique properties [6–14]. The capability of silica nanoparticles to alter the wettability of the reservoir rock and reduce the interfacial tension between crude oil and brine phases has recently been actively investigated to find implementation in enhanced oil recovery. In the last decade, some studies had been done for the application of silica nanoparticles in water-wet sandstone [14–18]. However, from the view of the literature in this field, there is a lack of fundamental understanding about the efficiency of modified silica nanoparticles in enhancing oil recovery of different oil reservoirs (i.e. light and intermediate oil reservoirs). Modified silica nanoparticles which are chosen for this study, have a great potential for increasing pore scale displacement efficiency through the reduction of interfacial tension and wettability alteration. This paper presents a comparison between the efficiency of these nanoparticles in enhancing oil recovery from two different Iranian light and intermediate oil reservoirs.

2. Materials and experimental method

2.1. Material

Core plugs used for this study are sandstone rocks obtained from one of the Iranian oil producing formations. These core plugs had a diameter of 38.4 mm and the lengths ranged from 68.0 to 68.5 mm, with a porosity and average water permeability equal to 18.5% and 102 md, respectively. The composition of the brine used in all experiments was 5 wt.% NaCl. NaCl with a purity of 99.5% was provided by the Merck Company. The density and viscosity of the brine were 1.05 g/cm^3 and 1.09 cp at room temperature (23 °C), respectively. Two types of degassed oil used for the experiment obtained from different formations of one of the Iranian oil reservoirs in the Dezful embayment (i.e. Asmary and Sarvak formations). They contain little amount of asphaltene (1–3 wt.%). Also, they had a viscosity of 11.014 and 29.364 cp at 20 °C and API gravity of 33.53 and 27.43 respectively. The partially hydrophobic fumed silica (AEROSIL R 816) was used in this study provided by Evonik Degussa GmbH. AEROSIL R 816 is a fumed silica after-treated with hexadecylsilane based on AEROSIL 200. The physical properties of AEROSIL R816 are shown in Table 1. As shown in Fig. 1, the shape of a nanoparticle looks like an approximate sphere when observed under a TEM. Different concentrations of the nano fluid (1–4 g/L) were used in this study prepared by sonication of nanoparticles in ethanol for 30 min (600 W, 20 kHz). After nano fluid preparation, the solutions were placed for one week in a closed transparent bottle away from degrading factors such as light and heat to ensure its homogeneity and stability. (Fig. 2)

Table 1 Properties of modified silica nanoparticles.

Appearance	Fluffy white powder
BET-Surface Area (m^2/g)	190 ± 20
Average primary particle size (nm)	12
Tapped density (g/l)	40
SiO_2 (wt.%)	$\geqslant$99.8
Al_2O_3 (wt.%)	$\leqslant$0.05
Fe_2O_3 (wt.%)	$\leqslant$0.01
TiO_2 (wt.%)	$\leqslant$0.03
HCl (wt.%)	$\leqslant$0.025
Wettability	Partially hydrophilic

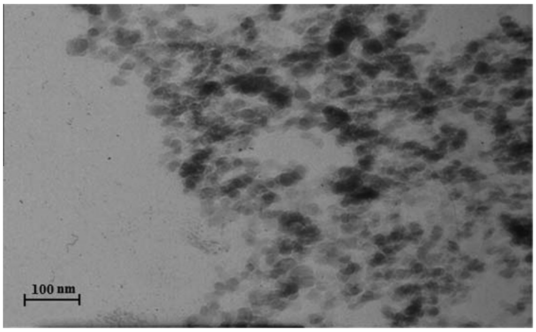

Figure 1 The image of modified SiO_2 nanoparticles observed under TEM.

2.2. Experimental method

Four different concentrations of nano fluid were considered for contact angle and interfacial tension measurements. The concentration yielding the highest change in contact angle and the lowest value for interfacial tension was considered the ideal concentration and employed in nano fluid injection processes. In order to observe the impact of nanoparticles on wettability alteration, two sets of plates were sawed from samples, polished and laid vertically in nano fluid at room temperature (23 °C). Then, side images of oil drops on the sandstone plates were taken using a microscopic camera and the contact angles were measured (Fig. 3). The volume of the drops was manually tuned with a precision syringe in order to obtain the smallest possible size. In addition, oil–water interfacial tension was measured before and after the application of nano fluids' different concentrations at ambient pressure and room temperature by pendant drop method [19]. To perform interfacial tension measurement, images of oil droplets surrounded by brine and different concentrations of nano fluid were taken by a microscopic camera. The drop parameters were measured from the drop dimension. The IFT was calculated based on the Eq. (1):

$$\sigma = (gd_e/) * (\rho o - \rho w) \tag{1}$$

where ρ_o and ρ_w are oil and water density (gr/cm^3), g is the gravitational constant at the point of measurement (cm/s^2), is a shape factor based on the ratio of $K = d_s/d_e$, d_e is the maximum horizontal diameter of the drop (cm) and d_s is the diameter of the drop measured at the height d_e above the bottom of the drop. For coreflood test, first core plug was saturated with light oil and the second one was saturated with intermediate oil. Then, coreflood experiments were performed under ambient pressure and at room temperature with a flow rate of 60 cc/h. Plugs were flooded with two pore volumes (1 PV = 14.56 cc) of brine to mimic primary and secondary recovery processes. Afterward, they were flooded with two PV of nano fluid and lastly with another two PV of brine to sweep nano fluid from the core samples.

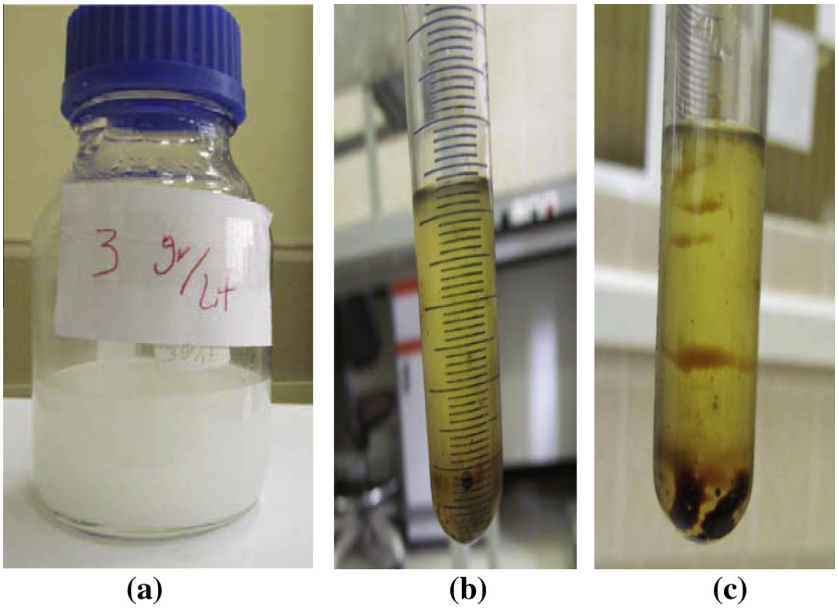

Figure 2 The prepared modified SiO_2 nano fluid (a) and the effluent produced after nano fluid injection into core plugs that were saturated by light (b) and intermediate (c) oil.

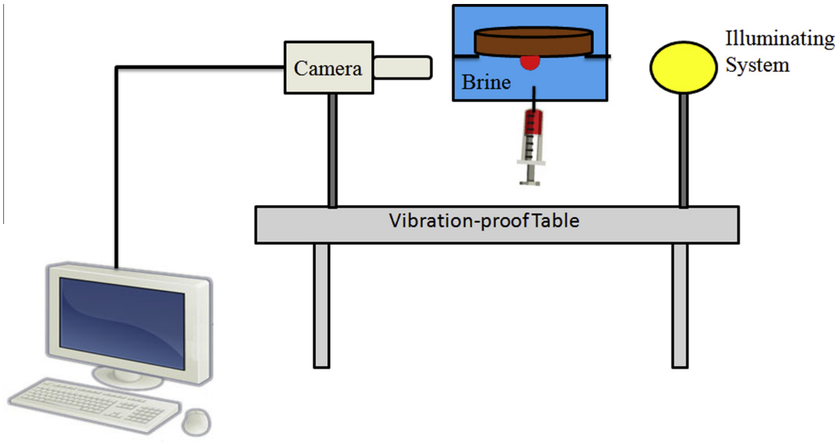

Figure 3 A schematic diagram of contact angle measurement setup.

3. Results and discussion

3.1. Contact angle and interfacial tension measurement

Wettability conditions were estimated before and after the surface treatment with nanoparticles by measuring the oil phase contact angle in the presence of water. As mentioned before, oil phase contact angles of nano fluids' at different concentrations (1–4 g/L) were examined to determine the optimum concentration of nano fluid for injection in core samples. Oil phase contact angles of the untreated sandstone plates were about 135.5° and 130° respectively in the first and second set of core plates (Figs. 4 and 5) implying water-wet characteristic of the rock surfaces. These measurements were performed by using light and intermediate oil for the first and second sets of core plates respectively. On the other hand, contact angles on the surface treated plates with different concentrations of

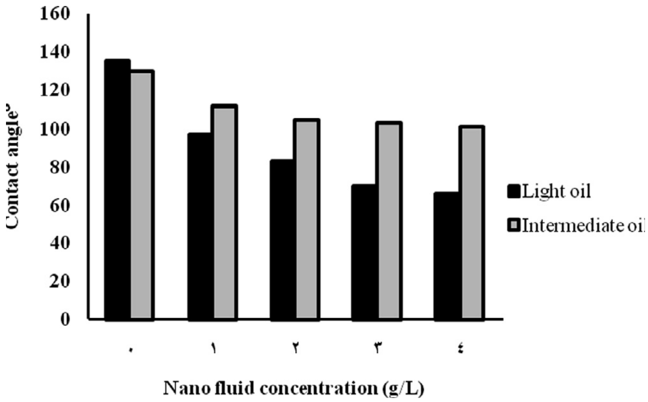

Figure 4 Measured water/crude oil contact angle of the water-wet samples aged in different concentrations of nano fluid.

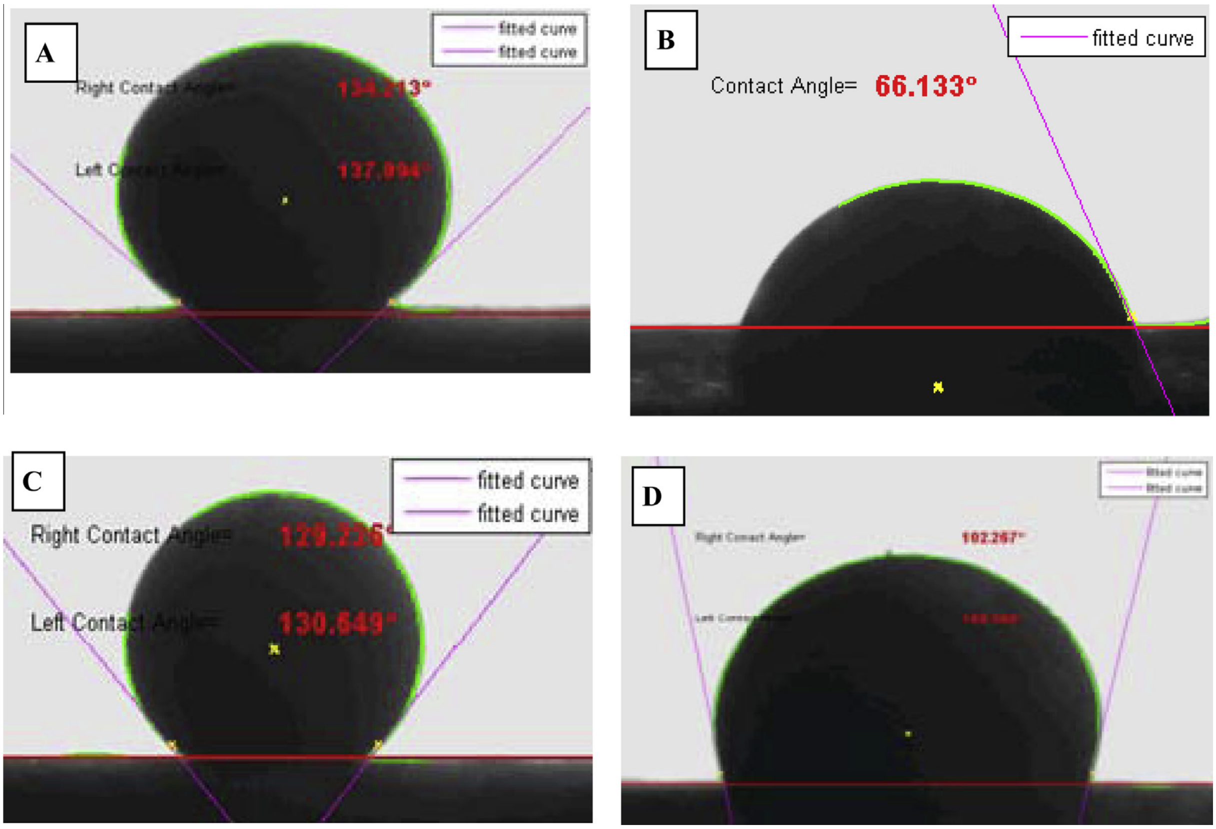

Figure 5 Wetting condition of sandstone slices (water/crude oil) before and after surface treatment with nanoparticles in the case of light (A and B) oil and intermediate oil (C and D).

nanoparticles decreases to 66° in the first set of core plates while, it dips to 101° in the second one. Therefore, an alteration was observed in the rock wettability after surface treatment with modified silica nanoparticles. It is well known that the wettability of a solid surface was related directly to the solid–fluids and fluid–fluid interactions. Maybe, the adsorption of nanoparticles on plate surface and consequently the change of free surface energy is the reason behind the alteration of wettability to more water-wetting conditions. This can be considered as the role of solid–fluids interaction. In addition, fluid–fluid interaction in the presence of nanoparticles can be another reason for such an alteration in rock wettability. The interfacial forces in a three-phase system were related to one another in a famous equation known as the Young's law,

$$\mathrm{Cos}\,\theta = (\sigma^{sw} - \sigma^{os})/\sigma^{wo} \qquad (2)$$

where θ is the oil phase contact angle and σ denotes interfacial tension. Superscripts sw, so, and wo represent the solid–water, solid–oil, and water–oil interfaces, respectively. The presence of nanoparticles at the oil–water interface provides a decrease in oil–water interfacial tension. Therefore, according to Eq. (2), Cosθ increases linearly as the oil–water interfacial tension decreased and consequently the oil phase contact angle (θ) decreased, implying transformation of the system toward oil-wet condition. A comparison between the contact angle measurements for different concentrations of nano fluids revealed that the concentration of 3 g/L had been more capable of changing the wettability for both systems. In addition, nanoparticles have greater capability on wettability alteration in the case of light oil reservoirs.

It should be noted that in this study only the role nanoparticles' adsorption on wettability alteration of the rock surface was investigated, because slices were placed vertically in nano fluids during the surface treatment process.

The reduction of interfacial tension between oil and water is very important, thus allowing the recovery of oil trapped in smaller pores and part of the residual oil remained in the pores after water flooding and it will lead to a reduction of the capillary pressure within the pores. As Fig. 6 illustrates, employing nano fluid lowers oil–water interfacial tension from 26.5 mN/m to less than 1.95 mN/m for the light oil system and from 28.3 mN/m to 7.3 mN/m in the case of the intermediate one. Oil–water interfacial tension was reduced with an increase in the concentration of nano fluid. According to interfacial tension measurement results for different concentrations of nano fluid, a concentration of 3 g/L showed the significant share of interfacial tension reduction in proportion to its concentration. It was considered as the optimum concentration and was employed in coreflood experiments. Reduction of interfacial tension demonstrated the nano fluids' potential to mobilize immobile oil and improve oil recovery [5]. This leads to easy flow of the trapped oil, because it reduces the work of deformation needed for oil droplets to move through the pore throat [4]. A comparison between the amount of interfacial tension reduction in the case of light and intermediate oil showed that these nanoparticles had stronger impact on the reduction of interfacial tension in light oil reservoir. The

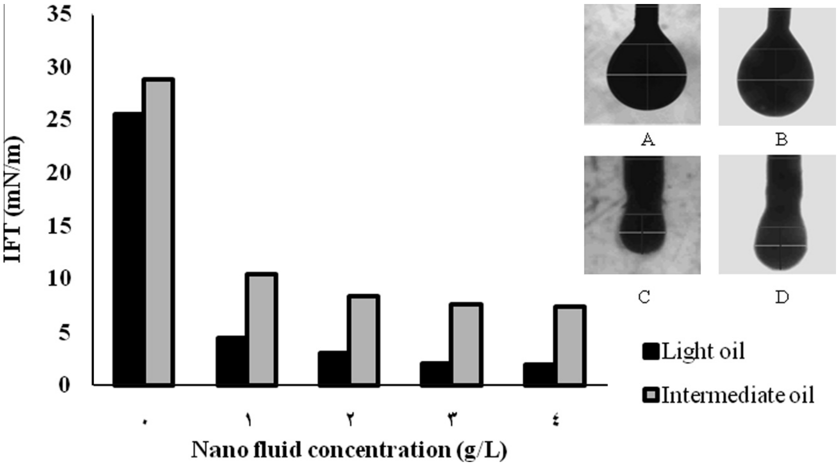

Figure 6 Oil–water interfacial tension before and after the application of Nano fluids' different concentrations for light (A and C) and intermediate (B and D) oil.

mechanistic reason for this reduction in oil–water interfacial tension is unknown to us, though it is certainly related to the interactions between oil phase/nano fluid and aqueous phase/nano fluid. However, as nanoparticles are found energetically favorable to adsorb to a fluid–fluid interface, adsorption of nanoparticle-ethanol complex at the interface can be a possible explanation for the observed phenomena. In fact, when the nanoparticles-ethanol complexes replace water and/or oil molecules of the original interface, the interaction across the interface is now between the hydrophilic part of the complexes and water molecules on one side of the interface and between the hydrophobic part of the complexes and oil molecules on the other side of the interface. Since these interactions are now much stronger than the original interaction between the highly dissimilar oil and water molecules, the tension across the interface is reduced by the presence of the nanoparticle- ethanol complexes [20].

3.2. Oil recovery

The total oil recovery was increased after the application of modified silica nano fluid in both first and second core samples (Fig. 7 and 8). As can be clearly seen, waterflooding recovery of the first core plug, which was saturated by light oil is 54.01% and that of the second one which was saturated by intermediate oil is 41.65%. However, the oil recovery was increased by 25.43% and 14.55% respectively in first and second core samples after the injection of nano fluid. A comparison between the recovery results revealed that nano fluid can produce a significant amount of oil after primary and secondary recovery processes. However, the capability of nano fluid in enhancing oil recovery depended on the oil type and varies for different oil reservoirs. According to results of the interfacial tension and contact angle measurement, when nanoparticles are introduced to the porous media, some of them may adsorb on the rock surface and others react with the immobile oil droplets and mobilize them to flow. In both samples, the interfacial tension reduction and wettability alteration played an essential role in enhancing oil recovery. However, these mechanisms are more effective in enhancing oil recovery from light oil reservoirs. Furthermore, the effect of ethanol itself as a surfactant was investigated for both samples and the results obtained indicated that about 14.21% and 9.33% of the trapped oil was produced after the injection of ethanol respectively in

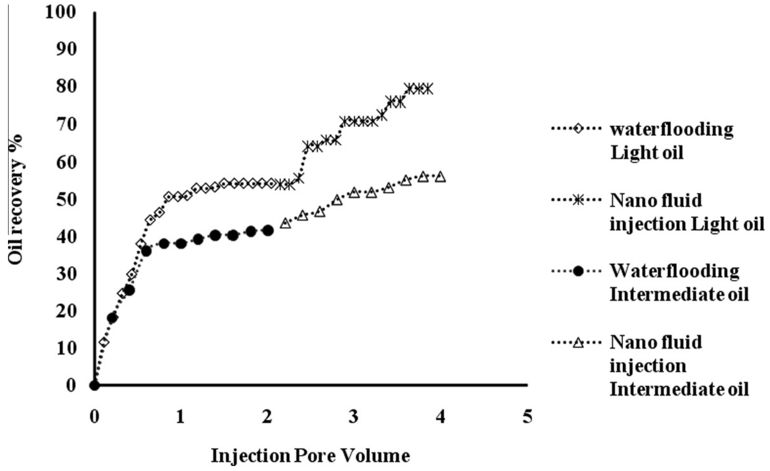

Figure 7 Oil recovery results for waterflooding and nano fluid injection in first and second core samples.

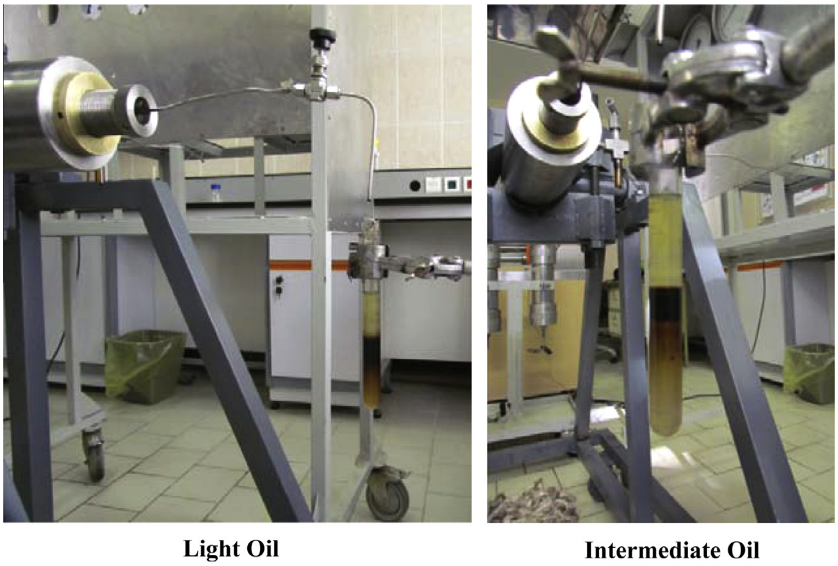

Figure 8 A schematic of produced oil after injection of nano fluid into core samples.

the first and second core samples. Therefore, partition coefficient of nanoparticles (the ratio of recovered oil by nanoparticles to recovered oil by nano fluid) would be 44.29% and 35.87% for first and second samples and the efficiency of nanoparticles in oil recovery is supported by these results.

3.3. Effluent fluids

Nano fluid has a different color before and after injection into core samples (Fig. 2). As can be clearly seen, the color of the nano fluid produced as effluent fluid from the core plugs turns from a white cloudy solution to pale greenish yellow in both samples. Difference in the color of nano fluid before and after injection into core sample revealed that a reaction may take place between the nano fluid and the reservoir oil or between the rock and the nano fluid. According to contact angle and interfacial tension variations (Figs. 5 and 6), it may be concluded that both reactions are probable for the samples, and nano fluid reacted with both rock and reservoir oil.

3.4. Mechanism

After waterflooding, almost all the remaining oil is immobile. The discontinuous residual oil which is the target of the nano fluid exists in the form of small spherical globules behind pore throats and cannot pass through them [21]. The presence of nano fluid in porous media enhanced oil recovery through two main mechanisms of interfacial tension reduction and wettability alteration from water-wet toward oil-wet condition. Reduction of interfacial tension decreased the work of deformation needed for oil droplets to move through the pore throat [4]. Therefore, the trapped oil packets are mobilized and can pass through the pore throat easily. In addition, capillary pressure acts as a barrier in pore throat for the displacement of mobilized oil from one pore to another (Fig. 9). However, wettability alteration changed the role of capillary force from a barrier to a driving force. In fact, the direction of capillary force was turned when the wettability of the system was transformed from water-wet toward oil-wet condition (Fig. 9b and c).

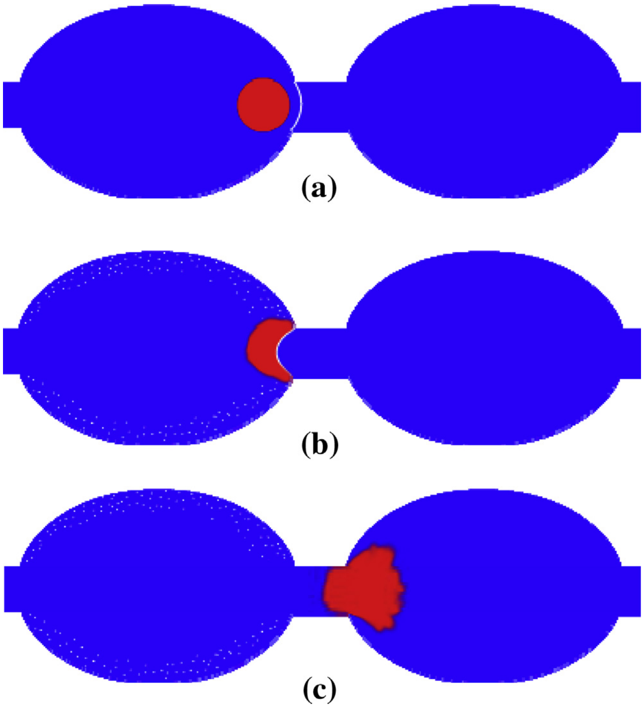

Figure 9 Role of nanoparticles in wettability alteration and consequently direction of capillary curvature in the pore throat before (a) and after surface modification with nanoparticles (b and c).

4. Conclusion

In this work, we present a comparison between the efficiency of modified silica nano fluid in enhancing oil recovery from two different Iranian light and intermediate oil reservoirs.

Based on the obtained results the following conclusions can be drawn:

(1) Modified silica nano fluid improved oil recovery through major mechanisms of interfacial tension reduction and wettability alteration toward oil-wet condition.
(2) Based on contact angle and interfacial experiments, the concentration of 3 g/L showed a significant share of interfacial tension reduction and high capability in the transformation of wettability toward oil-wet condition. It was considered as the optimum concentration and was employed in coreflood experiments for both light and intermediate oil systems.
(3) Modified silica nanoparticles are more capable in the reduction of interfacial tension and the alteration of wettability in the case of light oil reservoir.
(4) Oil recovery was improved after the application of nano fluid in the first and second core samples. However, these nanoparticles are more efficient in light oil reservoirs.

References

[1] Y. Wu, P.J. Shuler, M. Blanco, Y. Tang, W.A. Goddard, SPE J. 13 (2008) 26.
[2] J. Bear, Dynamics of Fluids in Porous Media, Dover Publ. Inc., New York, 1988.
[3] Y. Wang, H. Xu, W. Yu, B. Bai, X. Song, J. Zhang, Pet. Sci. 8 (2011) 463.
[4] E.C. Donaldson, G.V. Chilingarian, T.F. Yen, Enhanced Oil Recovery II, Processes and Operations, Elsevier Science Publ. Co., New York, 1989.
[5] A. Samanta, K. Ojha, A. Sarkar, A. Mandal, Adv. Pet. Explor. Dev. 2 (2011) 13.
[6] N.Y. Le Thi, D. kh Pham, K.H. Le, Ph.T. Nguyen, Adv. Nat. Sci. Nanosci. Nanotechnol. 2 (2011) 035013.
[7] T. Skauge, S. Hetland, K. Spildo, A. Skauge, Paper SPE 129933 presented at the SPE Improved Recovery (IOR) Symposium, Tulsa, Oklahoma, 24–28 April 2010.
[8] K. Sefiane, J. Skilling, J. MacGillivray, Adv. Colloid Interface Sci. 138 (2008) 101.
[9] T.N. Hunter, R.J. Pugh, G.V. Frank, G.J. Jameson, Adv. Colloid Interface Sci. 137 (2008) 57.
[10] B.P. Bink, C.P. Whitby, Colloids Surf. A 253 (2005) 105.
[11] T. Zhang, A. Davidson, S.L. Bryant, C. Huh, Paper SPE 129885-MS presented at the SPE Improved Oil Recovery (IOR) Symposium, Tulsa, Oklahoma, 24–28 April 2010.
[12] H. Fan, D.E. Resasco, A. Striolo, Langmuir 27 (2011) 5264.
[13] S. Drexler, J. Faria, M.P. Ruiz, J.H. Harwell, D.E. Resasco, Energy Fuels 26 (2012) 2231.
[14] B. Ju, Sh. Dai, Zh. Luan, Paper SPE 77938 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Melbourne, Australia, 8–10 October 2002.
[15] B. Ju, T. Fan, M. Ma, China Particuol. 4 (2006) 41.
[16] B. Ju, T. Fan, Powder Technol. 192 (2009) 195.
[17] K. Wang, C. Wang, S. Lijing, F. Yi, Paper presented at the Power and Energy Engineering Conference (APPEEC), Asia-Pacific, 28–31 March 2010.
[18] M. Onyekonwu, N. Ologo, Paper SPE 140744 presented at the SPE Nigeria Annual Conference, Tinapa-Calapar, Nigeria, 31 July–7 August 2010.
[19] J.M. Andreas, E.A. Hauser, W.B. Tucker, 50th Colloid Symposium, Cambridge, MA, June 1938.
[20] M.J. Rosen, Surfactants and Interfacial Phenomena, John Wily and Sons Inc., New York, USA, 1978.
[21] W.G. Anderson, JPT 39 (1987) 1283.