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Application of Nanoparticles for Chemical Enhanced Oil Recovery

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Abstract

In this paper, the potentials of using particles, especially nanoparticles, in enhanced oil recovery is investigated. The effect of different nanoparticles on wettability alteration, which is an important method to increase oil recovery from oil-wet reservoirs, is reviewed. The effect of different kinds of particles, namely solid inorganic particles, hydrophilic or hydrophobic nanoparticles, and amphiphilic nanohybrids on emulsion formation (which is cited as a contributing factor in crude oil recovery) and emulsion stability is described. The potential of nanohybrids for simultaneously acting as emulsion stabilizers and transporters for catalytic species of in situ reactions in reservoirs is also reviewed. Finally, the application of nanoparticles in core flooding experiments is classified based on the dominant mechanism which causes an increase in oil recovery from cores. However, the preparation of homogeneous suspensions of nanoparticles is a technical challenge when using nanoparticles in enhanced oil recovery (EOR). Future researches need to focus on finding out the proper functionalities of nanoparticles to improve their stability under harsh conditions of reservoirs.

Keywords: Amphiphilic Nanohybrids, Enhance Oil Recovery, Nanoparticle, Pickering Emulsions, Porous Media, Wettability Alteration

1. Introduction

There is an increasing concern about the dependency of the developed countries on the fossil fuel reserves as a primary energy source. Oil reserves are limited, and oil prices have increased in recent years. There is a grave need to enhance the recovery of petroleum from oil wells, especially stripper and mature oil wells (Amani et al., 2013).

Oil recovery processes have been defined as primary, secondary, and tertiary processes. The primary process produces oil by natural energy when the reservoir is opened to the lower pressure of a producing well. Recovery factor during the primary recovery stage is typically 15-20%. The well pressure will decrease gradually, and, at some points, there will be inadequate underground pressure to force the oil to the surface. Secondary recovery techniques increase the pressure of the reservoirs by water injection or natural gas reinjection. Typical recovery factor from water-flood operations is about 30-40% and occasionally as high as 50% depending on the properties of oil and the characteristics of the reservoir rock.

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Tertiary, or enhanced, oil recovery methods increase the mobility of the oil in order to increase extraction. Tertiary recovery begins when secondary oil recovery is not enough to continue adequate extraction, but only when the oil can still be extracted profitably (Simon, 1981). It is well known that EOR projects have been strongly influenced by economics and crude oil prices (Alvarado and Manrique, 2010). Current enhanced oil recovery strategies are varied and include both thermal and nonthermal methods. Thermal approaches involve heating the formation to reduce oil viscosity and improve its mobility (Afzal et al., 2014). Nonthermal methods are either chemical or microbial. Chemical technologies generally involve synthetic surfactants to aid with oil solubility and mobility or use polymers that alter floodwater viscosity and enhance injected water sweep efficiency (Zhu et al., 2013). In polymer flooding, the apparent viscosity of water is increased, but its relative permeability is decreased (Hematpour et al., 2011).

The flow of oil through a porous medium is governed by viscous, gravity, and capillary forces (Zhang et al., 2007). Poor oil recovery from the existing oil producing wells can be due to several factors. The low permeability of some reservoirs or the high viscosity of the oil is the main factor which results in poor mobility. High interfacial tensions between the water and oil may also result in high capillary forces, retaining the oil in the reservoir rock (Amani et al., 2013)

Two major variables that may have a direct impact on the EOR process and can be modified by the addition of different chemicals and particles are the capillary number (N_c) and the mobility ratio (MR). The capillary number (N_c) is defined as $N_c=\mu.v/\sigma$; where v is Darcy velocity (fluid flux per unit of area), and μ represents the viscosity of the mobilizing fluid (water); σ is the interfacial tension (IFT) between the oil and the water. As mentioned before, decreasing the IFT results in increasing capillary number, and subsequently larger amounts of oil displacement from pores will occur. The mobility ratio (MR) is a function of the relative permeability (k_i) of the porous media toward oil and water respectively, and the viscosity (μ_i) of the oil and the mobilizing fluid (water). To achieve the displacement of oil by water, MR must be lower than unity. This condition can be obtained by increasing the viscosity of the sweeping fluid, relative to that of the oil (Drexler et al., 2012).

The increasing energy demands of the growing population cannot be provided by the conventional methods of oil exploration and production. Nanotechnology suggests some unique solutions for these challenges; nanotechnology, especially using nanoparticles, has the potential to improve EOR mechanism and processes (Suleimanov et al., 2011). When nanoparticles are injected into porous media, four phenomena will occur: adsorption, desorption, blocking, and migration with flowing fluid. When the force between the nanoparticles and pore walls is attractive, it, in turn, leads to the adsorption of nanoparticles on the pore wall. Otherwise, the desorption of nanoparticle from the pore wall will occur due to repulsion. The dynamic equilibrium of adsorption and desorption is controlled by the force type between particles and pore wall. Blocking will take place if the diameter of nanoparticles is larger than the size of the pore throat, or when several nanoparticles are smaller than the pore size bridge at the pore throat. The migration of nanoparticles in porous media is governed by diffusion and convection (Ju et al., 2012). Nanoparticles may affect the adsorption behavior of surfactant onto rock surface. In this way, Ahmadi and Shadizadeh (Ahmadi and Shadizadeh, 2013) reported that hydrophobic silica nanoparticles are more effective than hydrophilic silica nanoparticles to inhibit adsorption losses of a kind of natural derived surfactant (*Zyziphus spina-christi*) onto shale sandstone.

The aim of this study is to overview the application of nanoparticles in different EOR processes. Wettability alteration by different nanoparticles is extensively discussed. The role of emulsions, especially emulsions stabilized by nanoparticles and nanohybrids, in EOR applications is also reviewed. The potential of using reactions conducted by nanohybrid catalysts at the water-oil interface for enhancing oil recovery is another topic. Finally, a number of the studies about nanofluid flooding are reviewed and classified based on the effective mechanism which causes an increase in oil recovery.

2. Nanoparticles for wettability alteration

It is well known that the oil recovery is affected by wettability of porous medium; wettability is the tendency of the reservoir rock surface to preferentially contact a particular fluid in a multiphase or two-phase fluid system. Surface wettability is considered by measuring the contact angle of a liquid drop with a particular surface. When the contact angle is greater than 90, the liquid does not wet the surface, and when the contact angle is less than 90, the liquid wets the surface. Hence, a water-wet reservoir rock will be wetted by water, and an oil-wet reservoir rock will be wetted by oil (Maghzi et al., 2012b).

Ju et al. (Ju et al., 2006) has analyzed the mechanism of enhanced oil recovery using lipophobic and hydrophilic polysilicon (LHP) nanoparticles ranging in size from 10 to 500 nm for changing the wettability of porous media. The results showed that LHP can be adsorbed on pore walls. It can increase the blockage of pores, leading to a change in the wettability of rock surfaces. Porosity and permeability will decline due to the retention of LHP. The change of the wettability of reservoir rock from hydrophobic to hydrophilic is responsible for enhancing oil recovery. It was suggested that an LHP concentration ranging from 0.02 to 0.03 should be desirable to enhance oil recovery.

To visualize the effect of wettability on the behavior of two-phase flow in porous media, Maghzi et al. (Maghzi et al., 2012a) constructed a five-spot glass micromodel and used it as a porous medium. To examine the effect of nanoparticles on wettability during water flooding, silica nanoparticles were used as a dispersed phase in water (DSNW flooding). The significant enhancement of ultimate oil recovery was observed by DSNW flooding. The pore-scale visualization of media wettability showed that the hydrophilic nature of silica nanoparticles causes a wettability alteration of the micromodel from oil-wet to water-wet (Figure 1); contact angle measurements also confirmed this fact. A reduction in absolute permeability is observed because of the adsorption of silica nanoparticles on the glass surface in pores and throats. The results of this work suggest the silica nanoparticles for an additive to water for the improvement of oil recovery during water flooding instead of or before the implementation of other suitable EOR schemes.

In another similar study, Maghzi et al. (Maghzi et al., 2012b) investigated the effect of dispersed silica nanoparticles in polyacrylamide (DSNP) solution on the wettability of crude oil on a microscopic scale. Two types of flooding tests, namely flooding by a polyacrylamide solution and by a DSNP solution, were performed. Because of wettability alteration from oil-wet to water-wet by silica nanoparticles, oil recovery after DSNP solution flooding caused more of the pore space to become saturated with the DSNP solution, which resulted in 10% higher oil recovery compared to polymer flooding alone. They concluded that, in polymer flooding, adding silica nanoparticles to polymer solution can be an acceptable method to enhance oil recovery because in addition to increasing sweep efficiency by means of polymer, nanoparticles, which are present in polymer solution, can alter the surface wettability.

Hendraningrat et al. reported that the LHP silica nanoparticles suspension seems potentially interesting for EOR in water-wet sandstone at certain nanofluid concentrations. Based on this particular study, the 0.05 wt.% silica nanofluid is the best in terms of oil recovery among other concentrations for both low–medium and high permeability water-wet Berea sandstone (Hendraningrat et al., 2013).

a) b)

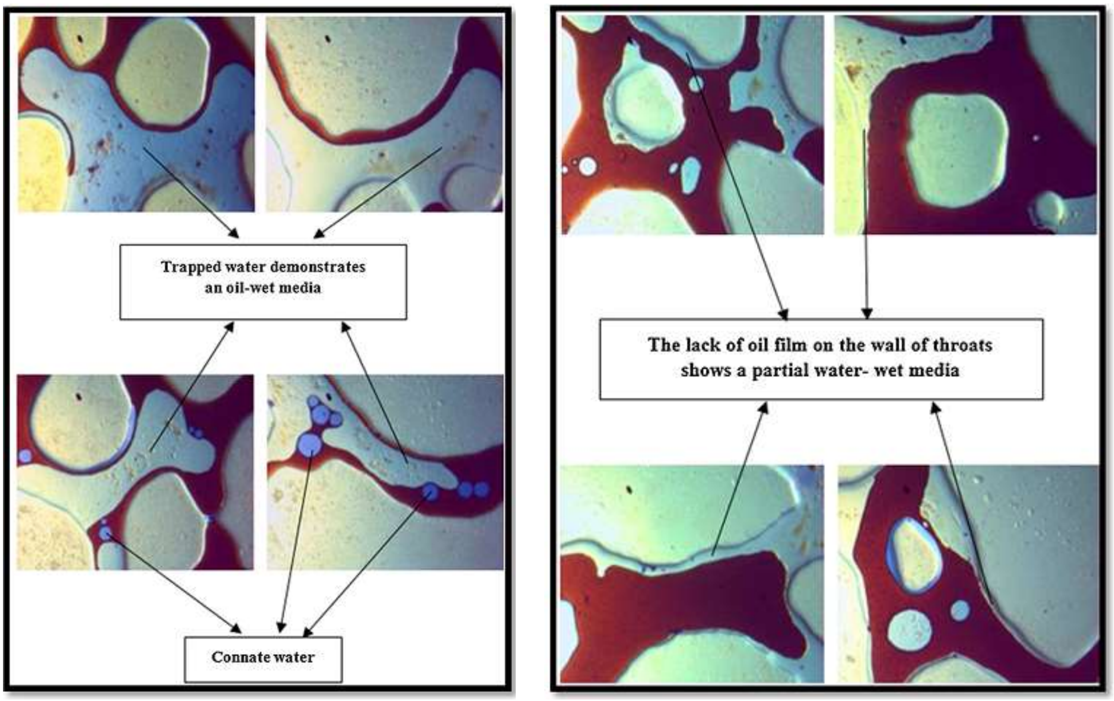

Figure 1
Pore-scale visualization of media wettability during a) water and b) DSNW flooding (Maghzi et al., 2012a).

It is obvious that many researchers used SiO_2 nanoparticles. The stability of this nanoparticle in different conditions is an important factor. In this way, Esmaeeli Azadgoleh et al. (Esmaeeli Azadgoleh et al., 2014) studied the effect of some important factors such as electrolyte concentration and temperature on the stability of two kinds of hydrophilic silica nanoparticle dispersions. They used several methods such as direct observation, optical absorption measurement, and nanoparticle effective diameter in different periods of time. Their results showed that the critical salt concentration (CSC) of potassium chloride (KCl) is less than that of sodium chloride (NaCl), and it decreases as nanoparticle concentration and temperature increase. Moreover, an anionic surfactant increases the CSC, while a nonionic surfactant leads to the instability of dispersion even at low electrolyte concentrations.

The effect of ZrO_2-based nanofluids on the wettability alteration of a carbonate reservoir rock was experimentally investigated by Karimi et al. (Karimi et al., 2012); to this end, several nanofluids were made; the nanofluids were composed of ZrO_2 nanoparticles and mixtures of nonionic surfactants. It was observed that these nanofluids could significantly change the wettability of the rock from a strongly oil-wet to a strongly water-wet condition. Scanning electron microscopy (SEM) images confirmed the adsorption of ZrO_2 nanoparticles on the surface and the consequent formation of nanostructured ribbons. This causes changes in the wetting properties of the new developed surface. Use of the nanofluids in free imbibition tests showed the strong ability of these new agents for oil recovery from hydrocarbon reservoirs.

Tajmiri et al. (Tajmiri et al., 2015) introduced the new concept of adding ZnO nanoparticles to alter the wettability of cores. The experiments were conducted through spontaneous imbibition tests. The experimental results showed that when nanoparticles were added, the oil recovery for three sandstone cores changed from 20.74, 4.3, and 3.5% of original oil in place (OOIP) to 36.2, 17.57, and 20.68% of OOIP respectively; also, for the carbonate core, the recovery changed from zero to 8.89% of OOIP by adding nanoparticles. Relative permeability curves showed that, the crossover-point of the curves shifted to the right for both sandstone and carbonate cores in the presence of nanoparticles, which meant wettability was altered to water-wet.

Radnia et al. (Radnia et al., 2017) investigated the interaction of graphene oxide with sandstone. Their results showed that the adsorption of graphene oxide onto sandstone was a function of graphene oxide concentration, pH, and salinity. The contact angle measurements of the rock surface treated in a graphene oxide solution showed that the wettability of the sandstone was altered from strongly oil wet to intermediate conditions.

3. Particles stabilized water and crude oil emulsions

All enhanced oil recovery processes (EOR) involve the formation and flow of emulsions. In most cases, emulsions are formed in porous media as a result of oil-water interactions, possibly assisted by heat and clay minerals and influenced by the chemicals present in the connate water and those in the injected fluids. Fluid flow, in particular the flow of gas, as well as the tortuosity of the pore channels provided any needed agitation. Emulsions may also be formed externally and may be intentionally injected (Kumar et al., 2010). If water droplets are of a size similar or larger than typical pore-throats, then capillary pressure will trap water droplets and block further displacement, which causes water flow to deviate to other unswept areas of the porous media (Alvarado et al., 2011). Oil/water emulsions stabilized by surfactants are frequently used in the oil industry (Chen et al., 2013; Iglauer et al., 2009; Kang et al., 2011).

Pickering emulsions are the emulsions of any type, namely oil in water (O/W), water in oil (W/O), or even multiple, which are stabilized by solid particles. The solid particles adsorbed at the oil–water interface in place of the surfactant molecules and subsequently stabilize the droplets as shown in Figure 2. Pickering emulsions are named after S.U. Pickering paper is considered as the first report of O/W emulsions stabilized by solid particles adsorbed at the surface of oil droplets (Chevalier and Bolzinger, 2013).

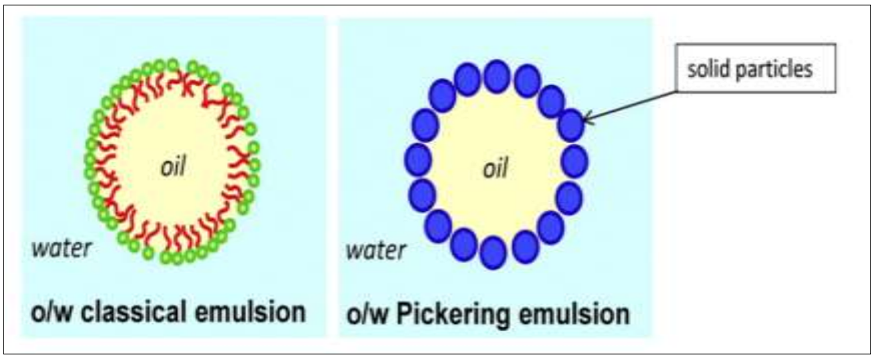

Figure 2
A sketch of a Pickering emulsion and a surfactant-based emulsion (Chevalier and Bolzinger, 2013).

The properties of the solid particles, such as their concentration, wettability, shape, size, and the interactions between the particles, play a main role in the Pickering behavior. The wettability of the particle has been established as a key factor in the type and the properties of Pickering emulsions (He et al., 2013)

Pickering emulsions have a number of advantages over conventional surfactant-stabilized emulsions in that they can reduce tissue irritation and their viscosity can be easily adjusted by solid content and/or solid type (Zoppe et al., 2012). Another benefit of Pickering by solid emulsions is the availability of stable millimeter-sized emulsions with respect to classical emulsions; this possibility is due to their high stability against coalescence (Chevalier and Bolzinger, 2013).

Formation of emulsions can help or hinder oil recovery depending on circumstances. If the emulsion-dispersed phase drops are formed and displaced in such a manner that they effectively block the flow of the injected fluid in the more permeable paths and force it to flow through the upswept regions, the overall oil displacement and sweep efficiencies will increases, which in turn leads to an increase in oil recovery.

3.1. Inorganic solid particles

Small inorganic particles present in crude oil reservoirs strongly enhance water crude oil emulsion when interactions with asphaltenes promote particle adsorption at the oil water interface. For emulsions encountered in the petroleum industry, some possible important parameters are the size and surface energy of the stabilizing particles and the state of asphaltene aggregation. Emulsions stabilized with particles and asphaltenes can be much more stable than those stabilized only by asphaltenes alone (Langevin et al., 2004).

Sztukowski and Yarranto (Sztukowski and Yarranton, 2005) reported that fine solids, i.e., platelet-shaped particles ranging from 50 to 500 nm, compete with asphaltenes to be adsorbed on the interface. These solids are adsorbed flat on the interface and expected to form a partial barrier to water bridging between droplets. A combination of asphaltenes and fine solids at the water/oil interface at a 2:1 fractional area ratio creates a maximum in emulsion stability. If there are too few solids, there is insufficient surface coverage to provide extra stability, whereas too many solids results in an interface that is not rigid enough to maintain stability.

Sullivan et al. studied (Sullivan and Kilpatrick, 2002) a variety of particle types (montmorillonite, kaolin, Fe_2O_3, and Ca(OH)) to investigate the factors controlling particle-stabilization effectiveness. The effect of the size, concentration, and type of inorganic solid particles on crude oil emulsion stability was shown. All the particles used were hydrophilic. If these hydrophilic particles were small enough, they form oil-in-water emulsions due to their interfacial activity. The particles stabilized water-in-oil emulsions when they were dried and exposed to asphaltene-containing oil phases. A decrease in the size of oil-wet particles causes an increase in water-in-oil emulsion stability. The similarity of the effects of inorganic solid particles in crude and model oil emulsion systems is a good sign that resin and asphaltene fractions are responsible for the effectiveness of solid particles in crude oil emulsion stabilization. The effectiveness of solid stabilization of water-in-oil emulsions is dictated by the extent of asphaltene aggregation. Aggregation can be controlled with the aromatic/aliphatic ratio of the solvent or the concentration of resin.

In another research, Wang and Alvarado (Wang and Alvarado, 2011) showed that particle suspension improved emulsion stability. This is cited as a contributing factor in crude oil recovery by low-salinity water flooding. For this purpose, kaolinite and silica particle dispersions were characterized at different brine salinities. Their results showed that both kaolinite and silica increased emulsion stability. At the same weight fraction, kaolinite with a smaller size can better stabilize water-in-oil emulsions because smaller kaolinite (roughly 1 µm in size) has a larger specific surface area, and larger coverage on the water droplets occurs. In this case, neutral conditions are more promising for the formation of stable emulsion than acid conditions. For silica-stabilized emulsions, the opposite result is obtained. Larger silica particles (5 µm) are better stabilizing agents than the smaller ones due to the stabilizing mechanism via steric repulsion in particle dispersion. Moreover, silica stabilizes emulsions better in an acidic pH conditions than in a neutral pH conditions, which is opposed to emulsions stabilized by kaolinite particles.

An overview of the development and field testing of a nonthermal, viscous oil recovery technology which injects an external solid stabilized emulsion (SSE) fluid as a displacement fluid into a reservoir oil is given by Kaminsky et al. (Kaminsky et al., 2010). Emulsion is generated on site using crude oil and water. Small amounts of mineral fines were added to enhance the performance of naturally present surface active components in the oil. Gas was dissolved into oil to alter the viscosity of the injected emulsion to be similar to the viscosity of the in situ oil. SSE fluid moves viscous oil (viscosities of up to 3000 cP) in a miscible-like manner with satisfactory mobility, which leads to improved displacement and recovery.

A series of laboratory tests were conducted to check the effectiveness of solid stabilized emulsions as displacing agents. Also, special core floods were used to perform process understanding and to determine displacement efficiencies. Then, a field pilot of SSE process was designed, constructed, and operated for the investigation of the ability to generate and sustain the injection of a solid stabilized emulsion in the field and to spread stabilized emulsions in a reservoir. The pilot demonstrated that SSE fluids could be adequately generated and injected over a long time period. The emulsion was reasonably stable as it flowed through the reservoir; it was also observed that much improved oil recovery was possible.

3.2. Nanoparticles

Nanoparticles-stabilized emulsions have attracted many researchers' attention in oil industry in recent years, particularly in enhanced oil recovery processes. This is due to their specific characteristics and advantages over conventional emulsions stabilized by surfactants or by colloidal particles (Yoon et al., 2013). For example, solid colloidal particles are micron sized and easily trapped in the rock pores, but nanoparticles are two times smaller than colloidal particles. The nanoparticle-stabilized emulsions droplets are small enough to pass through pores without much retention. They also remain stable in harsh conditions of reservoirs due to the irreversible adsorption of nanoparticles on their droplet surface. The large viscosity of nanoparticle-stabilized emulsions can also help to manage the mobility ratio during flooding.

The most commonly used nanoparticles are spherical silica particles. Their wettability is managed by the covering extent of silanol groups on their surface. They can be made hydrophilic (90% silanol groups) forming oil-in-water emulsions, can be made hydrophobic (10% silanol groups) forming water-in-oil emulsions, or have intermediate hydrophobicity (70%). In the latter case, the stable emulsion type is dependent on the oil polarity (O/W for nonpolar oils and W/O in polar oils) (Zhang et al., 2010) (Figure 3).

Zhang et al. (Zhang et al., 2010) investigated the emulsion stability stabilized by both hydrophobic and hydrophilic silica nanoparticles. They reported that very stable emulsions could be made at a silica nanoparticle concentration of 0.5 wt.% or higher. An increase in nanoparticle concentration led to more of dispersed phase emulsification, and subsequently the average droplet diameter decreased. Increasing viscosity resulted in an increase in apparent viscosity of the oil-in-water emulsions, while the opposite trend was observed for water-in-oil emulsions. The emulsion rheology was strongly shear-thinning and emulsions had very high apparent viscosities at very low shear rates. The rheological characteristics have the potential to facilitate the conformance control during oil recovery.

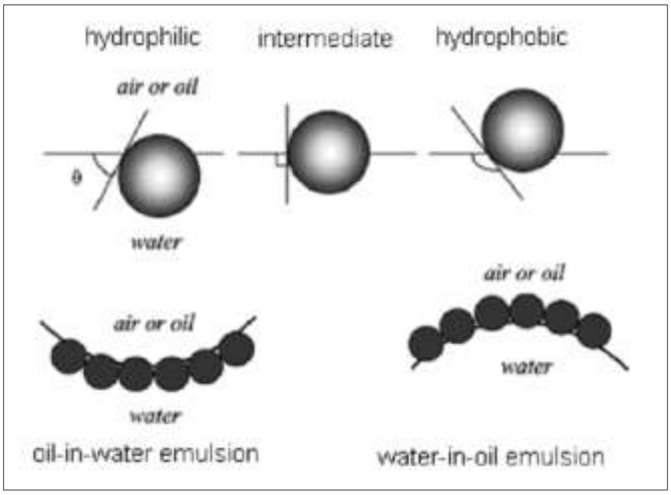

Figure 3
Contact angle on particle surface and its relation with emulsion structure (Zhang et al., 2010).

Khosravani et al. prepared γ-Al_2O_3 nanostructures with different morphologies and surface areas by a wet chemical method which is very simple and economic. The as-prepared γ-Al_2O_3 nanostructures were used for emulsion preparation with other agents such as water, suitable surfactant, n-decane, and 2-propanol. They suggested that the as-prepared O/W emulsion can be applied to chemical enhanced oil recovery (C-EOR), especially for the carbonate reservoirs (Khosravani et al., 2013).

3.3. Amphiphilic nanohybrids

Shen and Resasco (Shen and Resasco, 2009) anticipated that the SWNT-silica combination offers a unique structure. The structure and transmission electron microscopy (TEM) image of single-walled carbon nanotubes (SWNT)-silica nanohybrid is represented in Figure 4.

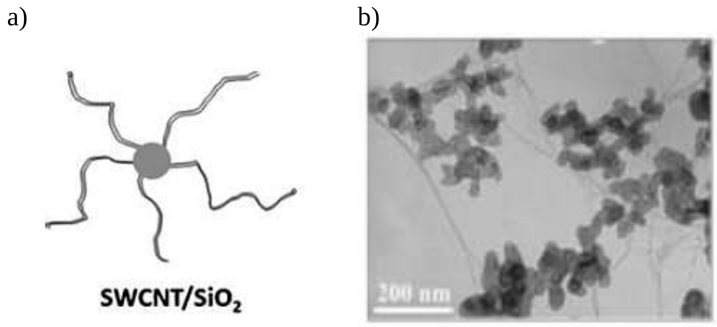

Figure 4
a) structure (Ruiz et al., 2011) and b) TEM image of (Shen and Resasco, 2009) SWNT-silica nanohybrid.

This unique structure can offer great flexibility in controlling the surface wettability by adjusting the carbon/silica ratio, silica particle size, nanotube length, and surface functionalities, which in turn can be varied by varying reaction conditions and surface treatments. Thus, it is possible to modify the distributions of partitioning coefficients between oil and water. In this contribution, they reported the preparation of water-in-oil and oil-in-water emulsions with variable fractions of emulsion volume using the carbon nanotube-silica nanohybrids as stabilizers.

The resulting emulsions exhibit good resistance to coalescence and sedimentation. This novel way to prepare emulsions by supported SWNT shows great advantage in achieving a high emulsion volume compared with using only SWNT, and has opened new opportunities for utilizing these materials as supports for heterogeneous catalysis to be used in biphasic systems. Furthermore, these nanohybrids are a very promising material that could be used for enhanced oil recovery because of their interfacial activity.

A patent concerning nanohybrid preparation methods and compositions has been deposited, focusing on the usage of these structures as emulsion stabilizers for chemical enhanced oil recovery (C-EOR) (Khosravani et al., 2015). Two main steps are mentioned in this patent for using these structures in C-EOR; first, modifying multi-walled carbon nanotubes (MWCNT's) and second inserting inorganic nanoparticles into the modified MWCNT's with special techniques. These nanohybrids are used for preparing nanofluids. These nanofluids can decrease the oil surface tension and may alter the wettability of reservoir from oil-wet to water-wet.

Bornaee et al. (Bornaee et al., 2013) synthesized functionalized multi-walled carbon nanotube (MWCNT)/silica nanohybrid. This nanohybrid was suggested as a stabilizer for oil-in-water Pickering emulsion. The emulsion formation time was investigated, and the effect of the type of the cation in water on the emulsion properties was studied. The hydrophilic–lipophilic balance changed more intensely by bivalent cations such as magnesium and calcium rather than by the sodium univalent cation.

Tajik et al. (Tajik et al., 2016) synthesized a novel silica-graphene nanohybrid through a simple and one step chemical vapor deposition of acetylene on silica surface. The characterizations confirm that graphene sheets were successfully grown. The stability of silica-graphene nanohybrid was considered by zeta potential test. The value of zeta potential was found to be about -21 mV. The nanohybrid was used for preparing the decalin/water emulsion. The effects of particle concentration, migration time of nanoparticles to the interface, sonication time, type of oil, and type of surfactant on emulsion droplets diameter were investigated. A Taguchi L_{16} array was used for designing the experiments. Among the mentioned parameters, types of surfactant, type of oil, and nanohybrid concentration were the most effective factors affecting the emulsion droplet size. In another study, they modified the surface of silica-graphene nanohybrid through treatment with a mixture of nitric and sulfuric acid vapors. In this way, they produced a novel stabilizer which was able to stabilize decalin-water emulsions. They reported that the formed emulsion average droplet size decreased by increasing the nanohybrid concentration (Tajik et al., 2017).

AfzaliTabar et al. (AfzaliTabar et al., 2017b) prepared nanohybrids with different carbon structures using SiO_2 nanoparticles through a sol-gel method. The nanohybrids were utilized to prepare Pickering emulsions. A mixture of SDBS, 2-propanol, and n-decane was used as the oil phase. The results demonstrated that the best sample was the 70% MWCNT/SiO_2 nanohybrid which could well stabilize Pickering emulsions for one month. The prepared nanohybrid could also alter the wettability of the carbonate rock from oil-wet to water-wet and could decrease the interfacial tension between aqueous and organic phases. In another research (AfzaliTabar et al., 2017a), they proposed a very simple and economic preparation method for nanoporous graphene/silica nanohybrid using the same sol–gel method. They used this nanohybrid for preparing Pickering emulsions. The results showed that the nanoporous graphene/SiO_2 nanohybrids Pickering emulsion had superior properties to the MWCNT/SiO_2 nanohybrids Pickering emulsion presented in their previous research. This nanohybrid could also improve the rheological properties of polymer suspensions which were used for polymer flooding.

Villamizar et al. (Villamizar et al., 2012) examined the feasibility of producing a stable dispersion of the targeted nanoparticles to deliver these particles to the oil and water (O/W) interface in different porous media. Their results showed that the oxidized SWNT-Si nanohybrid particle dispersion in an aqueous solution could flow through both glass beads and crushed Berea sand packed columns. The dispersed nanohybrid particles did adsorb onto the crushed Berea sand surface as well as at the oil/water interface. The adsorption of the nanohybrid particle onto the oil/water interface supports the application of this type of particle for enhanced oil recovery by interfacially active catalytic reaction in the oil reservoir. It was understood that injecting the emulsion stabilized by oxidized SWNT-Si nanohybrid particles requires a tremendous amount of energy to propagate and penetrate through the porous media.

4. Amphiphilic nanohybrid catalysts for reactions at the water/oil interface

A novel technique is suggested for application in oil reservoirs. The technique uses amphiphilic nanoparticles in the water injection. These hybrid nanoparticles can simultaneously act as emulsion stabilizers and carriers for catalytic species, e.g. metals. In contrast to homogeneous catalysts previously used, the solid particles can be recovered (Faria et al., 2010). The advantage of the novel procedure is that the amphiphilic nanohybrids stabilize a high interfacial area, which results in higher conversions, and they do not require the use of a liquid surfactant that could not be separated from the reaction mixture. In contrast to homogeneous catalysts previously used, the recoverable solid stabilizes a water-in-oil emulsion and catalyzes reactions (Crossley et al., 2009; Faria et al., 2010). They can be active for in situ partial oxidation or hydrogenation. These reactions may result in changes in rheological and interfacial properties of the oil, along with adapting the wettability of the walls. These changes might be efficiently used to improve the oil recovery process (Drexler et al., 2012).

Ruiz et al. (Ruiz et al., 2011) prepared a series of different amphiphilic nanohybrids based on SWCNT's and MWCNT's (the hydrophobic side) fused to different metal oxide particles (the hydrophilic side) as stabilizers of water/oil emulsions and supports for metal clusters that catalyze reactions at the water/oil interface in emulsion systems. The catalytic performances of the different nanohybrids (SWCNT–SiO_2, "onion-like" carbon–SiO_2, and MWCNT–Al_2O_3) doped with palladium were compared in three different reactions: 1) hydrogenation of phenanthrene; 2) hydrogenation of glutaraldehyde and benzaldehyde; 3) partial oxidation of tetrahydronaphthalene (Figure 5). These materials have been selected as a model compound representing the complex mixtures typically found in crude oil to simplify the experimental procedures required to analyze the results of the reactions. The following advantages for these novel catalysts are presented: higher interfacial area, enhanced mass transfer of compounds between the two phases, effective product separation by differences in solubility, and most importantly recoverability and recyclability after reaction.

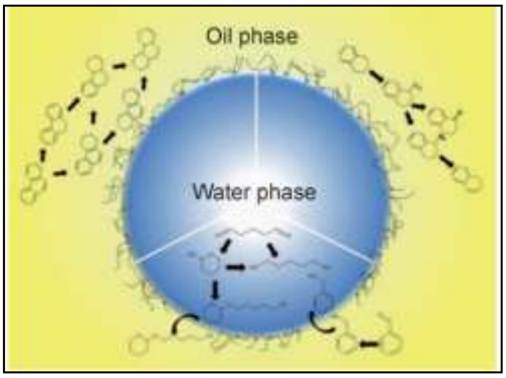

Figure 5
Nanostructured carbon metal oxide hybrids as an amphiphilic emulsion stabilizer and catalyst (Ruiz et al., 2011).

Drexler et al. (Drexler et al., 2012) investigated the above reactions in another concept. They reported changes in interfacial tension after the partial oxidation of tetrahydronaphthalene (tetralin). The addition of small amounts of tetralone, which is a product of this reaction, generates a considerable decrease in interfacial tension. This decrease is caused by the enrichment of the polar compound at the oil/water interface, because of a higher affinity of the polar compound to water compared to the nonpolar bulk phase. Although the reduction in IFT does not reach the typical reductions that one would expect for EOR techniques, it serves as an initial proof of concept for this application. If the oxidation reactions were carried out to convert molecules with polarity lower than that of tetralin, as a long-chain olefin, the impact on the IFT reduction would be increased.

One of the possible effects of hydrogenation on rheological properties could be associated with the increased flexibility of the polyaromatic molecules when the aromaticity is broken. This interesting effect could explain the change of the state of matter observed when the phenanthrene (which is a solid at room temperature) is selectively hydrogenated toward the 9,10- dihydrophenanthrene (which is a liquid at room temperature). Hence, based on this observation, Drexler et al (Drexler et al., 2012) decided to study the effect of the extent of hydrogenation of the polyaromatic molecules on the dynamic viscosity (μ). For this analysis, they employed the known approach of combining experimental data with quantitative structure property relationship (QSPR) software. Their results showed that the partial oxidation of organic compounds lowered the water-oil interfacial tension. This led to an increase in the capillary number (N_c). Alternatively, the partial hydrogenation of polynuclear aromatics can enhance the viscosity of the oil phase in the emulsion. In other words, it improves the mobility ratio (MR). As a result, partial hydrogenation can be an effective pretreatment of the oil to favor the subsequent partial oxidation (Drexler et al., 2012).

5. Application of nanofluids in core flooding experiments

Many studies have used nanoparticles in water flooding as a chemical method to increase oil recovery. A number of these studies are classified here based on the effective mechanisms which cause an increase in oil recovery during core flood experiments. Table 1 shows a number of related researches using nanoparticles in core flood experiments. In this table, the proposed mechanism and the amount of increase in oil recovery due to nanofluid flooding are tabulated.

Table 1

Nanoparticles and different mechanisms for enhanced oil recovery in core flood experiments.

Reference	Nanoparticle	Core	Mechanism	Increase in oil recovery
(Roustaei and Bagherzadeh, 2015)	SiO_2	Carbonate	Wettability alteration	9-12 %
(Seid Mohammadi et al., 2014)	γ-Al_2O_3	Carbonate	Wettability alteration	11.25%
(Ahmadi et al., 2016)	SiO_2	Carbonate	IFT reduction	25%
(Hendraningrat and Torsæter, 2015)	Al_2O_3, SiO_2, TiO_2	Berea sandstone	Wettability alteration-IFT reduction	0.4-11%
(Luo et al., 2016)	Graphene-based amphiphilic Janus nanosheets	Sandstone	IFT reduction	15.2%
(Hendraningrat et al., 2013)	SiO_2	Berea sandstone	Wettability alteration-IFT reduction	0-6.14%

Reference	**Nanoparticle**	**Core**	**Mechanism**	**Increase in oil recovery**
(Joonaki and Ghanaatian, 2014)	Al_2O_3, Fe_2O_3, SiO_2	Sandstone	Wettability alteration-IFT reduction	17.3-22.5%
(Sharma et al., 2015)	SiO_2	Berea sandstone	Pickering emulsion formation	4-21%
(Yoon et al., 2016)	SiO_2	Berea sandstone	Pickering emulsion formation	4%
(Pei et al., 2015)	SiO_2	N.A.	Pickering emulsion formation	~10-30 %

Some studies have emphasized that wettability alteration is the dominant mechanism which causes an increase in oil recovery during water flood experiments. Roustaei and Bagherzadeh (Roustaei and Bagherzadeh, 2015) studied the effect of SiO_2 nanoparticles on the wettability properties of a carbonate rock. Their results showed that the wettability of the treated rock changed from strongly oil-wet to strongly water-wet condition due to the adsorption of nanoparticles on the rock surface. The core flood experiments showed that a considerable amount of oil can be recovered right after the start of water injection to the core plug aged with nanofluid. Mortazavi et al. (Mortazavi et al., 2016) made a chemical additive by a combination of polymer, alkaline, and silica nanoparticles. This mixture was used to control the relative permeability curves and oil recovery. The experimental observations emphasized that using the suitable chemical additives changed the relative permeability of the phases towards higher oil relative permeability values; this resulted in oil recovery. In another study, Seid Mohammadi et al. (Seid Mohammadi et al., 2014) investigated the effect of γ-Al_2O_3 on the wettability alteration of one of Iran carbonate reservoirs. The results showed that the wettability of the calcite surface changed from oil-wet to water-wet due to the adsorption of γ-Al_2O_3 nanoparticles on the surface of rock. The optimum concentration of γ-Al_2O_3 was 0.5 wt.% at which the maximum change in the contact angle was observed. At this concentration, the oil recovery increased by 11.25%. In another study, Kiani et al. (Kiani et al., 2016) synthesized γ-Al_2O_3 for preparing a nanofluid at various salinities. The nanofluid was used for water-flooding experiments on sandstone rock. The ultimately optimum recoveries of using 2000, 20,000, and 200,000 ppm nanofluid in injections were obtained as 56.95, 64.78, and 71.48% respectively. It was found that these oil recoveries strongly depended upon the concentration of salinities, and they were increased by decreasing salinity.

The increase in oil recovery during water flooding experiments may be attributed to a decrease in interfacial tension (IFT reduction). Ahmadi et al. (Ahmadi et al., 2016) investigated the ability of hydrophobic nanoparticles of SiO_2 in a core flooding process for carbonate rock samples. Their results showed that the IFT between water and oil phase decreased with an increase in nanoparticle concentration, and consequently the oil recovery increased. However, silica nanoparticle can increase oil recovery through other mechanisms. Ahmadi and Shadizadeh (Ahmadi and Shadizadeh, 2014) reported that using silica with a particle size of 12 nm could increase the oil recovery from carbonate rock. They mentioned that an increase in the viscosity of the injection fluid was the reason for an increase in the oil recovery. Similar results were obtained using combination of hydrophilic nano-silica and extracted surfactants from the leaves of *Ziziphus-spina-christi* as an injected fluid in core displacement experiments (Ahmadi and Shadizadeh, 2017).

Hendraningrat and Torsæter (Hendraningrat and Torsæter, 2015) reported that the mixture of metal oxide nanofluids and dispersant improved the oil recovery to a larger extent compared to either silica-based nanofluid or dispersant alone in all wettability systems. It was observed that metal oxide-based nanofluids altered the quartz plates to become more water-wet. In addition, the presence of nanoparticles and dispersant reduced the IFT. These results were consistent with those of the core flood experiment. In a study, Luo et al. (Luo et al., 2016) designed and produced a nanofluid of graphene-based amphiphilic nanosheets. These nanosheets spontaneously approached the oil–water interface and reduced the interfacial tension. A climbing film appeared and grew in moderate hydrodynamic conditions. This film could encapsulate the oil phase and subsequently could rapidly separate oil phase from rock surface.

In some reported studies, wettability alteration along with the IFT reduction is responsible for an increase in oil recovery during water flooding experiments. Hendraningrat et al. (Hendraningrat et al., 2013) performed laboratory core flood experiments in water-wet Berea sand stone core plugs with permeability in range of 9–400 mD. They used different concentrations of hydrophilic lipophilic SiO_2 nanoparticles as the flooding fluid. Their results showed that a decrease in both IFT and contact angle is responsible for an increase in oil recovery. They reported that interfacial tension and contact angle decreased as the nanofluid concentration increased, but there was no guarantee that additional oil recovery was obtained in low–medium permeability water-wet Berea sandstone at higher nanofluid concentrations. The reason may be attributed to pore network blockage at higher concentrations of nanofluid (e.g. 0.1 wt.% or higher). Joonaki and Ghanaatian (Joonaki and Ghanaatian, 2014) used Al_2O_3, Fe_2O_3, and SiO_2 as EOR agents during a flooding process. The experiment results showed that the nanofluids could decrease the IFT between water and oil phases and could make the solid surface more neutral wet. Their results indicate that aluminum oxide and silicon oxide treated by saline were good agents for enhanced oil recovery.

Formation of Pickering emulsions may also cause an increase in oil recovery during water flooding experiments. Some researches indicate that the Pickering emulsion provides significant improvements to conventional EOR techniques, indicating their suitable use for oilfield applications. Sharma et al. (Sharma et al., 2015) formulated novel Pickering emulsion stabilized using polyacrylamide (PAM) and nanoparticles (SiO_2 and clay) in the presence of surfactant. Nanoparticle-stabilized Pickering emulsion enhanced oil recovery by about 80% at elevated temperatures compared to conventional surfactant polymer (SP) flood. In another study, Yoon et al. (Yoon et al., 2016) designed a complex colloidal layer consisting of silica nanoparticles, dodecyl tri-methyl ammonium bromide (DTAB), and poly 4-styrenesulfonic acid-*co*-maleic acid sodium salt (PSS-*co*-MA). This complex colloidal dispersion fluid was injected into the Berea sandstone for a core flooding experiment. The result revealed that the colloidal dispersion significantly increased the oil recovery by ~4% compared to the case of flooding water. This means that the emulsion drops in situ produced in the core could readily flow through the rock pores. Pei et al. (Pei et al., 2015) conducted an experimental study for investigating the synergistic effect of nanoparticles and surfactants in stabilizing oil-in-water (O/W) emulsions for improved heavy oil recovery. The emulsion stability and rheology properties were studied. The results showed that the addition of nanoparticles could improve the stability of the emulsion and could increase the bulk viscosity of the emulsion. The core flooding conducted with the nanoparticle-surfactant stabilized emulsion showed a marked improvement in oil recovery compared to the surfactant-stabilized emulsions. In this case, the tertiary oil recovery can reach over 40% of the initial oil in place.

6. Remarks and directions for future research

Increasing world request for energy requires a rise in extracting the crude oil from reservoirs. Many novel enhanced oil recovery (EOR) methods have been utilized to increase oil recovery in oil fields, and some studies have been reported the role of nanoparticles in EOR operations. Particles can be injected with water or other chemicals; they can alter the wettability from oil-wet condition to water-wet conditions. Formation and flow of emulsions can also enhance oil recovery processes; emulsions may be formed externally and may be intentionally injected. Spontaneous emulsification is also known to occur under favorable conditions. Clay minerals can assist the formation of emulsions, and hydrophobic or hydrophilic nanoparticles, particularly silica particles, can be used. A unique technique that can potentially be used in oil reservoirs is adding amphiphilic nanoparticles into the water injection. These hybrid nanoparticles can act as emulsion stabilizers and as carriers for catalytic species. They can be applied to in situ reactions such as partial oxidation and hydrogenation. These reactions may result in altering the wettability of the walls and may lead to changes in rheological and interfacial properties of oil. The mentioned mechanisms can cause an increase in oil recovery during core flooding experiments reviewed in this paper.

The preparation of homogeneous suspension of nanoparticles remains a technical challenge since the nanoparticles form aggregates due to high attractive forces. However, future researches need to focus on finding out proper functionalities for nanoparticles. These functional groups should reduce the energy required for the adsorption of nanoparticles at the oil-water interface. Furthermore, they should facilitate nanoparticle propagation through a reservoir under harsh conditions of temperature and salinity. A proper stabilizing functional group should be able to stabilize the nanoparticle in both static and dynamic conditions. The functional groups should also minimize the adsorption of nanoparticles on the rock. The long-term chemical stability of functional groups along with low production cost is another challenge which should be taken into consideration.

Nomenclature

C-EOR	Chemical enhanced oil recovery
CSC	Critical salt concentration
DSNP	Dispersed silica nanoparticles in polyacrylamide
DSNW	Dispersed silica nanoparticles in water
DTAB	Dodecyl tri-methyl ammonium bromide
EOR	Enhanced oil recovery
k_i	Relative permeability of the porous media
SSE	Solid stabilized emulsion
IFT	Interfacial tension
LHP	Lipophobic and hydrophilic polysilicon
MR	Mobility ratio
MWCNT	Multi-walled carbon nanotubes
N_c	Capillary number
OOIP	Original oil in place
O/W	Oil in water
SEM	Scanning electron microscopy
SWNT	Single-walled carbon nanotubes
TEM	Transmission electron microscopy
W/O	Water in oil
Greek symbols	
μ	Viscosity
σ	Interfacial tension (IFT)

v	Darcy velocity (fluid flux per unit of area)

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