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Chapter

Nanotechnology Application in Chemical Enhanced Oil Recovery: Current Opinion and Recent Advances

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Abstract

Chemical enhanced oil recovery (EOR) has been adjudged as an efficient oil recovery technique to recover bypassed oil and residual oil trapped in the reservoir. This EOR method relies on the injection of chemicals to boost oil recovery. Recently, due to the limitations of the application of chemical EOR methods to reservoirs having elevated temperatures and high salinity and hardness concentrations, nanotechnology have been applied to enhance its efficiency and improve oil productivity. The synergistic combination of nanoparticles and conventional EOR chemicals has opened new routes for the synthesis and application of novel materials with sterling and fascinating properties. In this chapter, an up-to-date synopsis of nanotechnology applications in chemical EOR is discussed. A detailed explanation of the mechanism and applications of these novel methods for oil recovery are appraised and analyzed. Finally, experimental and laboratory results were outlined. This overview presents extensive information about new frontiers in chemical EOR applications for sustainable energy production.

Keywords: chemical enhanced oil recovery, nanotechnology, surfactant, polymer, nanoparticles

1. Introduction

Crude oil has remained the major source of world energy supply despite considerable efforts on other sources of energy [1]. Due to rapid industrialization, there is an increase in world energy demand leading the need to produce increasing volume of crude oil to support this demand. Meanwhile, the oil and gas industry is concerned with the shortage of new conventional oil reserves and low production from existing conventional reservoirs. On average, one-third of conventional reservoirs can be recovered through primary and secondary (i.e. waterflooding) oil recovery processes. The remaining oil-in-place is the target for enhanced oil recovery (EOR). Several EOR methods have been developed to recover bypassed and residual oil in the reservoir. These are majorly categorized into thermal and non-thermal EOR methods. Thermal EOR are unsuitable for reservoirs with great depth

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or thin pay zones. Hence, non-thermal EOR methods such as gas flooding, chemical flooding and microbial methods have received important attention over the last decades for oil recovery processes [2–4].

Of the numerous EOR methods, chemical EOR has been considered as the most promising because of its high efficiency, technical and economic feasibilities. Chemical EOR methods increase the efficiency of oil production by increasing the volumetric sweep efficiency of the injected waterflood. By tuning the efficiency of the injected chemical floods, the microscopic (pore scale) displacement efficiency and/or macroscopic (sweep) efficiency of the reservoir is increased leading to an increase in oil production. Chemicals for injection include alkali, surfactants, and polymers. Alkali and surfactants increase oil recovery by improving microscopic displacement at the pore scale; while polymers enhance the volumetric sweep efficiency of the reservoir [5].

Despite its highly reported efficiency and widely acclaimed potentials, chemical EOR has several limitations. The chemicals injected degrade and/or precipitate in the presence of resident reservoir brines and elevated temperature conditions. Besides, retention of the chemicals occurs during their flow in porous media which decreases it process efficiency and may lead to formation damage. To overcome this shortcoming, new salt and temperature-tolerant chemicals of various kinds have been developed and tested for their EOR potentials. Nonetheless, most of the newly developed chemicals have been jettisoned as they were found to increase the cost of the overall EOR process.

Nanotechnology is the application of nanoparticles characterized by a size ranging from 1 to 100 nm (see **Figure 1**) [6, 7]. In the oil and gas industry, applications of nanotechnology ranges from drilling processes, flow assurance, hydraulic fracturing, cementing, to EOR [8]. For EOR process, the engineered nanomaterials are mixed with fluids that are injected into the reservoir to boost oil production [9].

Nanoparticles and conventional EOR chemicals blends have been reported to possess important properties that are not observed in the individual chemical or nanoparticle [10]. For example, surfactant nanofluids (or nanosurfactant), a blend of nanoparticle and surfactant were reported to improve the efficiency of the surfactant at lowering the interfacial tension (IFT) of oil/water (o/w) interface and lower their adsorption during their transport in porous media [11]. Besides, emulsions and foams stabilized by nanoparticles are found to be thermodynamically

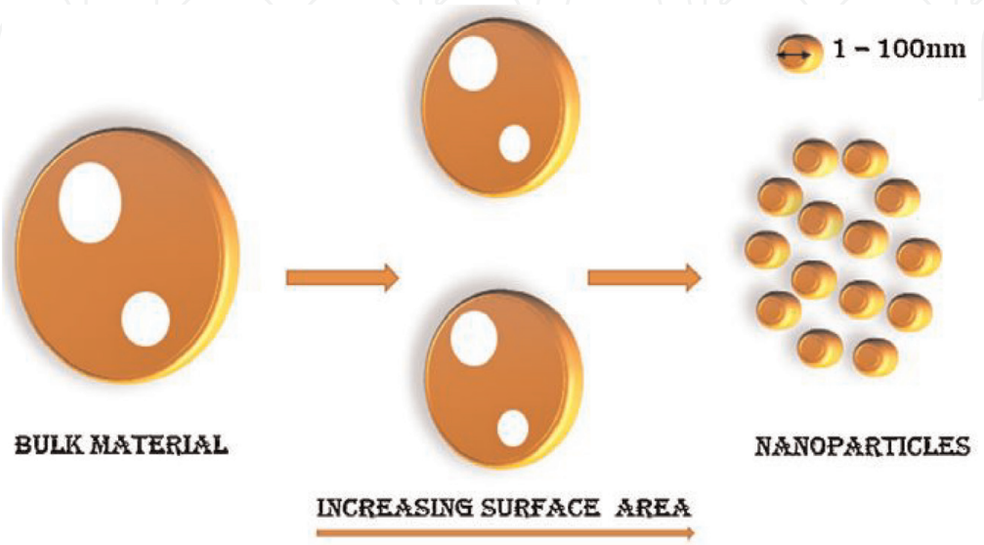


Figure 1.
Schematic of increasing surface area of nanoparticle with decreasing particle size [6].

stable and easily transported in reservoirs [12]. Meanwhile, polymeric nanofluids demonstrated to have improved rheological behavior and stability at characteristic reservoir temperature and salinity conditions [4]. This chapter presents an overview of nanotechnology applications in chemical EOR. First, the challenges of chemical EOR are briefly discussed. Subsequently, the mechanism and efficiency of nanotechnology application in chemical EOR is discussed. Finally, the experimental and laboratory studies of the newly devised EOR technique are outlined.

2. Challenges of chemical EOR methods

2.1 Degradation and precipitation

An oil reservoir exists at a specific temperature, salinity, and pH. The prevailing conditions of the reservoir influence the efficiency of the injected chemicals and consequently of the EOR process [13]. Most injected chemicals degrade and become unstable at high salinity, elevated temperature, and low pH conditions [14]. For polymers, under saline conditions, screening of the charged polymer molecules by cations contained in the reservoir brine occurs. This reduces the hydrodynamic radius and polymer chain entanglement causing the contraction of the macromolecules that ultimately results in the loss of polymer solution viscosity [15, 16]. Meanwhile, high temperature causes hydrolysis of the polymer and its precipitation in the presence of divalent ions [17]. In the case of surfactant and alkali solutions, depending on the rock type, precipitation of the chemicals occurs in the presence of divalent cations [18]. Low pH reservoir conditions might interact and acidify injected chemical solutions [15].

2.2 Adsorption and retention

Depending on the type of chemical injected into the reservoir, adsorption and retention of chemical occur during flow through porous media, which negatively affects the efficiency of the EOR process [19]. Chemicals react with the rock surface through electrostatic attraction, steric interaction, and van der Waal forces that

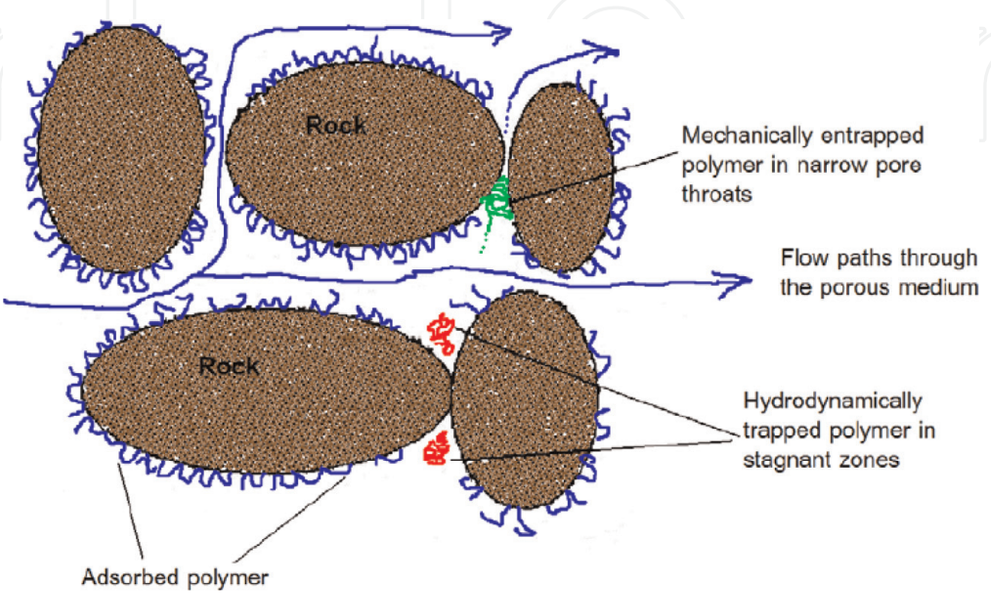


Figure 2.
Retention of polymers in porous media. Sourced from [19].

reduces the concentration of the injected chemical solutions. Adsorption is prevalent for surfactant and alkali chemicals, while polymer is mainly retained due to mechanical entrapment because of the size of the polymer macromolecules [3, 18, 20]. The adsorption process occurs when the interface is energetically favored by the surfactant and/or alkali in comparison to the bulk phase. Thus, the adsorption at the solid–liquid interface takes place by the transfer of the molecule of the chemical to the solid–liquid interface from the bulk solution phase [21]. Meanwhile, polymer retention and inaccessible pore volume dictates the propagation of polymer flow in the reservoir [22]. Retention of polymer is alluded to any mechanism that leads to reduction or removal of polymer molecules from transported aqueous phase. The nature of polymer retention in reservoir rock is depicted in **Figure 2**. Overall, adsorption and/or retention of chemicals in porous media governs the efficiency and economic viability of the EOR process. Several factors affecting adsorption or retention of chemical EOR includes; electrolyte concentration (salinity), temperature, pH, composition of reservoir fluids, and the presence of clay mineral content [21, 23].

3. Application of Nanotechnology in chemical EOR

Nanotechnology application in chemical EOR is used to overcome the shortcomings and improve the process efficiency of chemical EOR methods. Though most works are still at the laboratory scale, the synergic application of nanoparticles and chemicals have led to the formation of novel nanomaterials with exceptional qualities [6]. Recently, field trials have been reported in Columbia oilfield [24]. Depending on the nanoparticle type and chemical used, the formulated nanomaterials have demonstrated better stability and superior quality which enhances their performance during simulated reservoir conditions. So far, the most common nano-chemical studies are polymeric nanofluids and surfactant nanofluids.

3.1 Surfactant nanofluid

Surfactant nanofluid, a combination of nanoparticle and surfactant, increases the microscopic displacement efficiency through the mechanisms of IFT reduction and wettability alteration [11, 25, 26]. This nanofluid could be used for the generation or formation of stable foams and emulsions in the reservoir. Stable foams ensure fluid diversion from thief zones to lower permeability regions in the reservoir, while emulsions ensure conformance efficiency of the injectant [27, 28]. Furthermore, surfactant nanofluids have been reported to have lower adsorption onto rock surface compared to ordinary surfactant solutions [29, 30].

IFT and wettability are major parameters for quantifying fluids distribution and movement in the reservoir [31]. After secondary oil recovery, a portion of the oil is trapped in the reservoir due to capillary forces. This capillary force is measured by a dimensionless capillary number defined as [32]:

$$N_c = \frac{\mu v}{\sigma . \cos\theta} \tag{1}$$

Where μ is the displacing fluid viscosity, v is the displacing Darcy velocity, θ is the contact angle, and σ is the IFT between the displacing fluid (water) and the displaced fluid (oil). N_c is closely related to residual oil saturation and oil recovery. N_C increases as residual oil saturation decreases. Consequently, a higher N_c will result in a higher oil recovery [32, 33]. The capillary trapped oil can be released by either lowering the IFT of the o/w interface or through the wettability alteration

mechanism [33]. Surfactant molecules due to their amphiphilic nature lowers IFT and alters wettability of porous media by adsorbing at the o/w interface [5, 32]. Nanoparticles also performs the same task in similitude to surfactant molecules, though at a different efficiency. The synergic effect of blending nanoparticles and surfactants have been shown to enhance the surfactant flooding process by lowering IFT and altering the wettability more efficiently than the individual nanoparticle or surfactant solution. On the other hand, the surfactant enhances the stability of the nanoparticles, thus, increasing the efficiency [11].

Driven primarily by electrostatic interaction, the surfactant adsorbs on the nanoparticles surface forming surfactant-coated nanoparticles [11]. Nonetheless, the relative concentration of nanoparticles and surfactant in the solution determines the properties of the mixture. A lower concentration ratio of surfactant to nanoparticle in the mixture means that only a small fraction of the nanoparticle surface will be coated by surfactant. Conversely, a higher concentration ratio of surfactant to nanoparticles implies the surfactant molecules will form a bilayer on the particle surface [11, 34]. A single-chain surfactant on nanoparticle is required to form maximum nanoparticle flocculation and hydrophobic nature required for an optimal performance.

3.1.1 IFT reduction

To quantify the performance of surfactant nanofluid on IFT of o/w interface, Le et al. evaluated the impact of silica (SiO_2) nanoparticles and anionic surfactant for IFT reduction using a spinning drop tensiometer. Their results indicated that at a total concentration of 1000 ppm and at a surfactant to SiO_2 ratio of 8:2, a four-fold IFT reduction was achieved by the nanosurfactant. Hence, they proposed the application of surfactant nanofluids for EOR in high temperature and high salinity (HTHS) conditions [35]. Mohajeri et al. evaluated the effect of zirconium oxide (ZrO_2) nanoparticles on anionic sodium dodecyl sulfate (SDS) surfactant and cationic cetyltrimethylammonium bromide (CTAB) surfactant [25]. They reported that the contribution of ZrO_2/SDS yielded an IFT reduction of 81% while ZrO_2/CTAB decreased the IFT of o/w interface by 70%. Zargartalebi et al. probed the effect of SiO_2 nanoparticles and anionic SDS to quantify the effect of the nanoparticle on IFT, adsorption and oil recovery potential of the surfactant molecules. They observed that nanoparticles effectively improve surfactant performance by enhancing the governing mechanism. Furthermore, flooding results shows that oil recovery increased significantly due to the inclusion of nanoparticles in the surfactant solution [26].

The mechanisms of nanosurfactant for reducing IFT at o/w interface has been explored. Researchers noted that the adsorption of the surfactant on the nanoparticle surface occurs as a result of the mix, leading to a hydrophobic character of the nanoparticle surface. Due to their Brownian motion, the nanoparticle acts as carriers for the surfactant molecules from the bulk of the fluid to the interface. At the interface, the minimization of the interfacial energy by the nanosurfactant leads to IFT reduction. As compared to ordinary surfactant whose molecule desorbs from the interface after some time, the nanoparticle prevents desorption of surfactant molecules from the interface, hence, better IFT reduction [11].

3.1.2 Wettability alteration

The reduction of interfacial energy at the rock/oil/brine interface by nanosurfactant also results in higher wettability alteration. Besides, the relative permeability curves of oil and water also changes after contact with the surfactant

nanofluid; the relative permeability to water and oil decreases and increases respectively [34]. Mohajeri et al. studied the effect of ZrO_2/surfactants on wettability alteration in a fractured micromodel. The sessile drop experiments and wettability alteration measurements showed that coating the micromodel with heavy oil makes an oil-wet surface. Moreover, coating of the oil-wet micromodel with surfactant or nanoparticle altered the wettability of the surface to water-wet condition, while coating the surface with the blend ZrO_2/surfactant altered the wettability to strongly water-wet condition [25].

Additionally, the use of nanosurfactants as wettability alteration agents have proved useful for improving oil recovery from carbonates reservoir, which are characterized by poor oil recovery owing to its inherent natural fractures and hydrophobic nature that makes water imbibition into its rock matrix difficult, because of capillary pressure effects. Nwidee et al. assessed the effect of nanosurfactant formulation for wettability alteration of oil-wet limestone over a wide range of temperatures (0–70°*C*). ZrO_2 and nickel oxide (NiO) were used as the nanoparticles while CTAB and triton X-100 were used as surfactants for the formulation. Due to their strong electrostatic interaction, ZrO_2/CTAB and NiO/CTAB display greater affinity for the rock surface and demonstrated better wettability alteration efficiency for all temperature conditions considered in this study [36].

Surfactant nanofluids have also been used to improve wettability alteration of sandstone cores to boost oil recovery. Giraldo et al. tested alumina-surfactant nanofluid to improve oil recovery in sandstone cores via wettability alteration using contact angle and imbibition tests. Their results show that the effectiveness of surfactant as wettability modifier was improved with the addition of 100 ppm of alumina nanoparticles. Additionally, the effective oil permeability increased by 33%, and consequently, a higher oil recovery was recorded [37]. Huibers et al. measured changes in wettability of sandstone cores of saturated with light and heavy crude oil using surfactant nanofluid composed of SiO_2 nanoparticle and Tween 20 nonionic surfactant in Berea and Boise sandstone cores. Using direct imaging and contact angle measurements, 0.001 wt.% SiO_2 nanoparticles yielded an increase in contact angle of 101.6% for light oil saturated cores, while the optimum concentration for heavy oil was not ascertained at the nanoparticle concentration range investigated [38].

3.1.3 Adsorption reduction

One of the major challenges of surfactant EOR is the loss of surfactant molecules to adsorption onto the formation rock during the flooding process. Surfactant adsorption can make the chemical EOR process economically unfeasible. Therefore, reducing the surfactant adsorption improves the oil recovery process. Previous studies have investigated the use of polymers such as sodium polyacrylate as sacrificial agent to reduce surfactant adsorption during flow in porous media [39]. Recently, the adsorption reduction effect of nanoparticles has been investigated during the co-injection of nanoparticles with surfactant for oil recovery. Nanoparticles showed good potential for inhibiting surfactant adsorption via competitive adsorption mechanism by blocking the active site of the porous media while the surfactant flows through the porous media contacting the resident fluids in the reservoir. Yekeen et al. observed that the presence of SiO_2 and Al_2O_3 nanoparticles decreased surfactant adsorption on kaolinite in the presence of reservoir brines. The addition of Al_2O_3 nanoparticles reduced the SDS adsorption on kaolinite by 38%, while the addition of SiO_2 nanoparticles reduced the SDS adsorption by 75% [40].

Wu et al. conducted static and dynamic adsorption experiments to investigate the inhibition mechanism of SiO_2 nanoparticle during co-injection with surfactant. An optimum aging time, solid–liquid ratio, nanoparticle concentration, and surfactant concentration were determined for the adsorption process. Static adsorption experiments showed that 0.5 wt.% of SiO_2 nanoparticle concentration reduced the adsorption of SDS from 2.84 to 1.61 mg/g. Dynamic adsorption experiments conducted at 20°*C* showed that the adsorption and dynamic retention of single SDS solution were 1.16 and 0.30 mg/g respectively. The addition of 0.3 wt.% SiO_2 nanoparticle concentration reduced the adsorption and dynamic retention of the surfactant by 43.6% to 0.66 and 0.06 mg/g, respectively. Furthermore, oil recovery displacement experiments in sand packs using a nanosurfactant solution showed a 4.68% incremental oil recovery factor over the oil recovery attained by the injection of conventional surfactant solution [29]. Suresh et al. extended the adsorption studies on nanosurfactant to higher salinity and elevated temperature (80°*C*) conditions using thermogravimetric analysis (TGA) to determine the surfactant concentration in the produced fluids. The dynamic adsorption of the surfactant was calculated from the difference between injected and effluent concentration of the surfactant. Results showed that the addition of 0.5 wt.% SiO_2 nanoparticle to the surfactant solution reduced the surfactant adsorption by a factor of 3 times from 0.810 to 0.265 mg/g [30].

3.1.4 Foam and emulsion stability

Foams used for oil recovery are generated by co-injecting a gas (e.g., carbon dioxide, nitrogen or air) and a foaming agent containing liquid into the reservoir [41]. In the porous media, foams act as a dispersion of gas in liquid separated by a lamella, with the gas phase residing in the upper side while the bulk liquid is located at the bottom of the foam structure [42]. They perform two diverse roles in the reservoir namely; (1) mobility control, (2) fluid diversion. These mechanisms aid foam to overcome the challenges of gas EOR such as gravity override and viscous fingering phenomena. The liquids used as conventional foaming agents includes surfactants, polymers, and proteins. When used with polymers, foams are used to plug high permeability areas, while the polymer is diverted to lower permeability regions, thus, improving the volumetric sweep efficiency of the reservoir. In the case of surfactant-stabilized foams, a stable foam is formed due to a decrease in the required energy to form the gas–liquid interface [43]. Moreover, the synergic combination with surfactant lowers the interfacial tension of the capillary trapped oil, hence, facilitates oil displacement [44, 45]. Conventional foams have been shown to be thermodynamically unstable in the presence of oil and resident reservoir brines. This implies that the foam coalesces leading to of the reduced efficacy of the process. The addition of nanoparticles to the surfactant solution seems to generate more stable foams with longer half-life and ability to withstand harsh reservoir conditions [43]. Due to the solid nature of nanoparticles, the foams they stabilize are highly resistant to unfavorable reservoir conditions. Nanoparticles adsorb at the lamellae interface of the foam with a strong adhesion energy that makes their attachment irreversible (see **Figure 3**) [41, 46].

Sun et al. studied the influence of nanoparticles on the generation, propagation, and stability of SiO_2/SDS-stabilized foam in micromodels and sandpack porous media [47]. In the case of the SDS-stabilized foam, the shape of the oil droplet could not be changed by the foam because the microforce acting on the oil droplet was small. This subsequently leads to bubbles rupture and coalescence leaving a substantial amount of oil trapped in the porous media. In the case of SiO_2/SDS foam, a

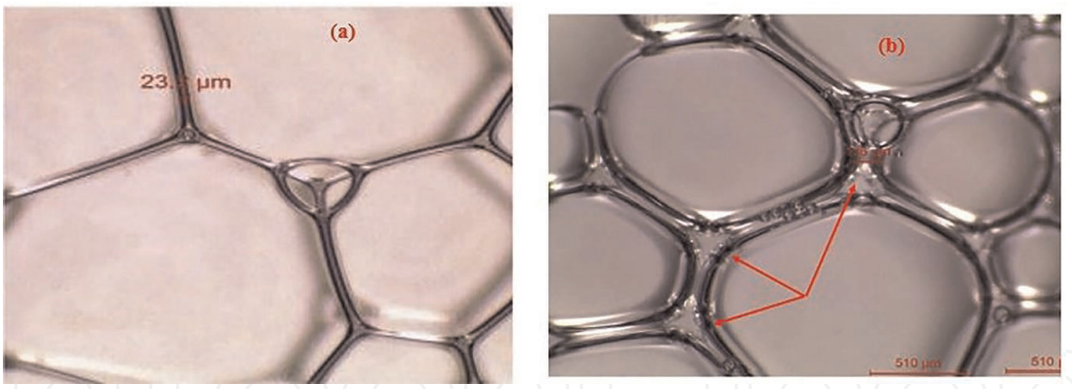


Figure 3.
Foams stabilized (a) without nanoparticles showing signs of foam drainage, (b) with nanoparticles stabilizing the lamellae [46].

large amount of oil was displaced by the foam due to the higher microforce acting on the oil droplet. The higher microforce was attributed to the enhanced viscoelasticity of the bubble surface by the attached nanoparticles. Yekeen et al. studied the influence of SiO_2 and Al_2O_3 nanoparticles on surfactant-foam stability and propagation in the presence of oil. They noted that the presence of nanoparticle increases foam half-life. Additionally, the SiO_2-SDS and Al_2O_3-SDS foam achieved nearly 100% microscopic efficiency even in the presence of oil. Finally, they identified mechanisms of foam flow as lamellae division and bubble-to-multiple bubble lamellae division, while the dominant mechanism of oil displacement and residual oil saturation are direct displacement and emulsification of oil [40]. **Tables 1** and **2** summarizes laboratory and experimental results of nanoparticles-stabilized and nanoparticle-surfactant stabilized foams.

On the other hand, the interactions of surfactants with oil during flow through porous media may generate emulsions. Emulsions generated *in situ* have potential for mobility and conformance control in the reservoir, which are desirable properties for improving the oil recovery process. Further, the feasibility of injecting emulsions has also been explored, exhibiting appropriate potential for oil recovery. Nonetheless, conventional emulsions show poor stability at high pressure and high temperature conditions. As temperature increases, the average droplet size of the dispersed phase increases which eventually plug pore throats in the reservoir [75]. Recently, the binary mix of nanosurfactant with oil have been evaluated for emulsion generation showing better stability performance in the reservoir for oil recovery applications. Besides, the presence of nanoparticle significantly improved the stability and mobility of the emulsions.

Pei et al. investigated the synergetic effect of SiO_2 nanoparticle and CTAB for o/w emulsions applications. Phase behavior testing, rheology evaluation, and microvisualization studies showed that nano-surfactant-stabilized emulsion demonstrated a high bulk viscosity and desirable mobility for recovering heavy oil [50]. Kumar et al. synthesized a Pickering emulsion stabilized by SiO_2 nanoparticle and sodium dodecylbenzene sulfonate (SDBS) surfactant. The synthesized Pickering emulsion displayed better thermal stability at the high pressure (0–5 MPa) and high temperature (30–100°C) conditions investigated, and showed a higher oil recovery when injected into the sandpack [75].

3.2 Polymeric nanofluids

Depending on the method of preparation, polymeric nanofluids are categorized into two types; polymer-coated nanoparticles and polymer nanoparticles.

Nanoparticle	Surfactant	NP conc. (wt.%)	Surfactant conc.	Base fluid	Oil type	Porous media type	Mechanism of recovery	RF	Ref.
SiO_2	SDS	0.1–0.5	0.2 wt.%	Deionized water	Crude oil	Quartz sand	IFT, competitive adsorption	4.68% IO	[29]
SiO_2	Alfoterra, Soloterra	0.1–0.8	0.005–0.2 wt.%	Brine	Crude oil	Dolomite, Limestone	IFT, WA	37–45% OOIP	[48]
SiO_2	TX-100	0.1	0.1 wt.%	Brine	Crude oil + kerosene	Sandstone	IFT, WA	8% IO	[49]
SiO_2	CTAB	0.05–0.5	0.1 wt.%	Brine	Heavy oil	Micromodel	ES	17.4–38% OOIP	[50]
SiO_2	SDS	0.25	1 wt.%	Brine	Heavy oil	Mircomodel	IFT, ES	5% IO	[51]
SiO_2	Non-ionic Tween 20	2–4	0.74 wt.%	Deionized water	Heavy oil	Micromodel	IFT, ES	18–39%	[52]
SiO_2	CTAB	0–5	0.09 mM	Distilled water	Heptane	—	IFT	—	[53]
Hydrophilic and hydrophobic SiO_2	SDS	0.1	0.01–0.6 wt.%	Deionized water	—	Sandstone	IFT, Adsorption reduction	—	[54]
Non-ferrous metal	Sulphanole	0.001	0.0078–0.05 wt.%	—	Heavy oil	—	IFT, WA	12–22% IO	[55]
Al_2O_3	PRNS	0.001–1		Distilled water	Heavy oil	Sandstone	WA	33% IO	[37]
Fumed SiO_2 Hydrophobic SiO_2	Zyziphus Spina Christi	0.05–0.2	0.1–8 wt.%	Deionized water	—	Shale sandstone	Adsorption reduction	—	[56]
ZrO_2	SDS, CTAB	0.01	0.1–0.4 wt.%	Distilled water	Heavy oil	Micromodel	IFT, WA	—	[25]
ZrO_2, NiO	TX-100, CTAB	0.004–0.05	0.1–3.2 wt.%	Deionized water	—	Limestone	WA	—	[36]
SiO_2	SDS, PAM	0.5–2.0	0.14 wt.%	Deionized water	Medium oil	Sandstone	IFT, WA	60% OOIP	[57]

Table 1.
Laboratory results of oil recovery applications by nanosurfactant.

Ref.	NP type	NP size (nm)	NP Conc.	Surfactant	Temperature	Pressure	Salinity	Foam generator	Oil recovery
[58]	SiO_2, Al_2O_3, CuO, TiO_2	10–40	0.002–0.1 wt.%	—	27°C	—	NaCl (0.3 wt%)	Sandpack	5.1–17.4% OOIP[a]
[59]	PEG coated-SiO_2	5	0.01–0.1 wt.%	—	21.1–90°C	1350–1400 psia	NaCl (2–4 wt.%)	Glass beads pack, Capillary tube	—
[60]	SiO_2	100–150	0 – 5 wt.%	—	25°C, 60°C	1200 – 2000psia	NaCl (0.5, 2.0, 5.0%)	Sapphire observation tube	—
[61]	AlOOH	10–100	1 wt.%	SC (0–100 mM)	60°C	6 mPa	NaCl (10–600 mM), $CaCl_2$ (10–200 mM)	Sanpack	~20% OOIP[a]
[62]	SiO_2	17	0.01–0.5 wt.%	—	25°C	1200 psig, 1500 psig	NaCl (2.0%)	Berea sandstone core	—
[63]	SiO_2	100–200	0.05–3.0% w/v	PEG, Tergitol 15-S-20, DCDMS	35°C, 50°C	1200–3000 psia	—	Glassbead pack	—
[64]	APTES – SiO_2	20–30	0.01 wt.%	SDS (0.4 wt.%)	25°C	14.7 psi	—	Glassbead pack	18% OOIP[a]
[65]	PECNP	—	1.0 wt.%	Surfonic N120	40°C	1300 psi, 1800 psi	KCl (2.0 wt.%)	Indiana limestone	10.71% OOIP[b]
[66]	TTFA	80	0.5 wt.%	Cationic, anionic and non-ionic surfactant (0.2 wt.%)	25°C	1300 psi (backpressure)	NaCl (1.0 wt.%)	Berea sandstone	—
[67]	PEG coatedSiO_2	10 (20)	0.5 wt.%	AOS (0–0.5 wt.%)	25°C	100 psi (backpressure)	NaCl (1–10 wt.%), API Brine	Berea sandstone	10% OOIP[a]
[68]	SiO_2, Al_2O_3, CuO, TiO_2	10–40	0.1–1.0 wt.%	AOS (O.5 wt.%)	Room temperature	—	NaCl (2 wt.%)	Sandpack models	5–14% OOIP[a]
[69]	FA	100–200	< 0.05 wt. %	AOS (0.0315 wt.%)	—	—	NaCl (1.0–5.0 wt.%), $CaCl_2$ (0–9.5 wt.%)	Bentheimer sandstone	—
[70]	SiO_2	5, 12, 25, 80	0.5–10 wt. %	—	70°C	2200 psi	NaCl (8.0 wt.%), $CaCl_2$ (2.0 wt.%)	Biose sandstone, Sandpack	—

Ref.	NP type	NP size (nm)	NP Conc.	Surfactant	Temperature	Pressure	Salinity	Foam generator	Oil recovery
[71]	Al_2O_3 – coated SiO_2	20	1–5 wt.%	Triton CG-110 AOS, PG (0.1–0.5 wt.%	Room temperature	100 psi (backpressure)	—	Berea sandstone	14.8–20.6% OOIP[a]
[72]	MWCNT	10	0.01 wt.%	Tergitol 15-s-40, AOS	25°C	—	NaCl (2.4 wt.%), $CaCl_2$ (0.6 wt.%)	Ottawa sandpack	—
[73]	PEG coated SiO_2	5 (10)	0.3 wt.%	AOS (0.5 wt.%	55, 75°C	110 psi (backpressure)	NaCl (1–8 wt.%)	Heterogeneous sandpack	34.4% OOIP[a] 9% OOIP[b]
[46]	SiO_2 Al_2O_3	12–20	0.05–5.0 wt%	SDS (0.03 wt.%)	25°C	—	NaCl (0.5 wt.%)	Hele-shaw cell	—
[74]	PEG-SiO_2, GLYMO-SiO_2	12, 20	0.5 wt.%	AOS	25, 60, 80°C	110 psi (backpressure)	NaCl (8 wt.%), $CaCl_2$ (2 wt.%)	Sandpack	29.0–43.3% OOIP[a]

[a]*Incremental oil recovery over waterflood.*
[b]*Incremental oil recovery over surfactant-stabilized foam.*

Table 2.
Laboratory and experimental investigation of nanoparticle/nanoparticle-surfactant stabilized foams.

Polymer-coated nanoparticles were developed due to overcome the aggregation and agglomeration problems of nanoparticles at reservoir conditions. It involves grafting polymers onto the surface of nanoparticles to improve dispersibility. In addition, their properties can be customized for particular applications [34]. Meanwhile, polymer nanoparticles are prepared by the hybrid dispersion of nanoparticles in polymer solutions. These polymer nanoparticles emerged as a means of inhibiting polymer degradation in typical reservoir conditions [4]. The mechanisms of polymeric nanofluids performance during EOR applications include improved rheology and stability, wettability alteration, and lower polymer adsorption [6].

3.2.1 Improved rheology and stability for mobility control

Rheology is defined as the study of flow and deformation behaviors of fluids under stress [76]. For EOR applications, an improved rheological behavior of injectant is required to inhibit viscous fingering phenomena and maintain a suitable mobility ratio in the reservoir; which requires that the displacing fluid maintain its viscosity and chemical integrity in the presence of resident reservoir brines [77]. Polymer and nanoparticles undergo degradation in the presence of reservoir brines. The cations present in the brine interact with the carboxylate and amide groups in the polymer molecule resulting in viscosity loss [78]. In the case of nanoparticles, the electrostatic attraction among nanoparticles are increased in the presence of brine fostering their aggregation and agglomeration; which implies the loss of surface functionality that is required for EOR [79]. However, the combination of polymer and nanoparticles results in a synergistic effect that improves the rheology of the polymer and the stability of the nanoparticle [4].

The preparation of polymer-nanoparticles blends involves the mixing of the nanoparticle and the polymer solution or grafting of the polymer on the nanoparticle [80, 81]. Subsequently, interactions occur between the nanoparticle and the carboxylate and amide group in the polymer molecules. Therefore, nanoparticles act as physical crosslinkers among the polymer chains forming three-dimensional network of stable flocs that increases the viscosity of the suspension [82]. At high temperature, polymer-nanoparticles blends exhibit better rheological performance due to the enhanced bridging induced flocculation [82, 83]. Furthermore, in the presence of reservoir brines, nanoparticles shield the polymer backbone from the cations of the brine by inducing ion-dipole interactions that inhibit the degradation of the polymer molecules [81].

Lai et al. noted that the shear and mechanical resistance of acrylamide polymer solution can be increased by adding modified nano-SiO_2, because the presence of SiO_2-NP caused a reduction of the hydrodynamic radius of the polymer molecules [84]. Hu et al. studied the rheological properties on an oilfield polyacrylamide (HPAM) -SiO_2 NP under different aging times, salinity, and temperature conditions. The results demonstrated that the presence of the SiO_2-NP significantly improved the viscosity and viscoelastic properties of the HPAM under high temperature and high salinity (HTHS) conditions [80]. Haruna et al. grafted HPAM molecules with graphene oxide (GO) nanosheets and evaluated the rheological and stability properties of the formulated polymeric nanofluid. They reported enhancement of the suspension viscosity behavior, as well as high-temperature stability and improved elastic properties of the dispersion [85].

As for polymer-coated nanoparticles, depending on the grafting method, the polymeric chains protrude from the nanoparticle surface. Hence, hydrodynamic interactions occur between the grafted nanoparticle when subjected to shear. Besides, polymeric chains grafted on the surface of the nanoparticle overlap with another polymer chain adsorbed on another nanoparticle. The overlapping of

several grafted nanoparticles results in the strengthening of the network structure of the polymer -nanoparticle system. Consequently, hydro clusters are formed, which results in an increase of stability and viscosity [86]. Liu et al. grafted a layer of amphiphilic-polymeric chains on nano-SiO_2 core shell via a facile water-free radical polymerization and evaluated its rheological properties and oil recovery performance. The synthesized polymer-coated nanoparticle formed a three-dimensional microstructure and intermolecular associations characterized by long-term stability and better rheological properties than the individual polymer or nanoparticles. Furthermore, a 20% incremental oil recovery was recorded after flooding the polymer-coated nanoparticle solution at a concentration of 1500 mg/L in sandstone cores [87]. **Table 3** summarizes some laboratory and experimental studies of improved rheological properties and oil displacement properties of polymeric nanofluids.

3.2.2 Adsorption inhibition

Polymeric nanofluids also show reduced adsorption onto porous media due to the synergic interaction between the polymer and nanoparticles. Foster et al. used the grafting through approach to tether tuneable quantities of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) and poly([3-(methacryloxylamino)propyl] dimethyl(3-sulfopropyl)ammoniumhydroxide)(PMPDSA) homopolymer (PMPDSA) onto iron oxide nanoparticle surfaces. Steric stabilization of the synthesized polymer-coated nanoparticle was observed which remained stable at HTHS conditions. Moreover, adsorption experiments on crushed Berea sandstone cores showed that the adsorption of polymer-coated iron oxide nanoparticles was

References	NP type	Polymer/ copolymer type	PNF conc. (ppm)	Brine/conc.	Temp. (°C)	Porous media type	Incremental oil recovery (%)
[88]	SiO_2	PEOMA	10,000	1.0 wt.% NaCl	30	Berea sandstone	19.5
[89]	SiO_2	AMPS	50,000	—	80	Quartz sand	23.22
[90]	SiO_2	PEG	10,000	—	80	Glass micromodel	20.0
[87]	SiO_2	$MeDiC_8AM$	1500	12 wt.% (NaCl & $CaCl_2$)	82.3	Sandstone	20.0
[91]	SiO_2	$AMC_{12}S$	1100	18 wt.%	110	Sandstone	24.0
[92]	SiO_2	AA/AM	2000	2 wt.% NaCl, 0.18 wt.% $CaCl_2$	65	Sandstone	20.1
[93]	SiO_2	AM/AA	1500	—	—	—	18.84
[94]	SiO_2	HPAM	1000	2.4 wt.% (NaCl, $CaCl_2$, $MgCl_2$)	25	Glass micromodel	10.0
[95]	SiO_2	HPAM	800	3 wt.% NaCl	—	Glass micromodel	10.0
[76]	MMT clay	HPAM	1000	10 wt.% (NaCl, $CaCl_2$, $MgCl_2$)	90	Quartz sand	33.0

Table 3.
Laboratory results of oil recovery applications by polymeric nanofluid [6].

infinitesimal and almost negligible [96]. Cheraghian et al. performed static adsorption experiments to investigate the impact of nano-SiO_2 and nanoclay on the adsorption inhibition of polyacrylamide onto sandstone rocks. Polymer nanoparticles containing SiO_2 nanoparticle showed lower adsorption onto sandstone rock surface compared to the polymer containing nanoclay [97].

3.2.3 Wettability alteration

Wettability alteration plays a vital role in enhancing the microscopic displacement efficiency. In the case of polymeric nanofluids, an interplay of electrostatic repulsive forces occur at the interface of the nanoparticles., Two-dimension layered structure of nanoparticles occur due to Brownian motion when brought into contact with an oil-wet solid surface, creating a wedge film because of the ordering of nanoparticles at the three-phase (solid-oil–water) contact region. This results in an increase of the disjoining pressure,which causes the spreading of the nanofluid phase at the wedge of the vertex, altering the wettability of the surface [6]. Maurya et al. grafted polyacrylamide on the surface of SiO_2 using the free radical polymerization approach and investigated its wettability potential on an oil-wet sandstone rock surface. They indicated that the polymer grafted nanoparticle altered the wettability of the sandstone surface to a more water-wet condition [86]. Maghzi et al. performed wettability alteration studies employing polymer nanoparticles consisting of SiO_2 nanoparticle and polyacrylamide polymer solution in a five-spot glass micromodel. The polymer nanoparticle altered the surface of the micromodel from an average contact angle of 112° (oil-wet) to 20° (water-wet). More details of wettability alteration by polymeric nanofluids can be found in the literature [6, 34].

4. Conclusions

This chapter summarizes some of the recent advances in the application of nanotechnology in chemical EOR processes to boost oil production. The mechanisms of oil recovery through nanotechnology were reviewed. Several experimental studies were summarized and discussed. Results of various experiments shows that the incorporation of nanotechnology with chemical EOR shows good potential to improve pore scale mechanisms in the case of surfactant. Adsorption of surfactant on rock pores is inhibited while greater IFT reduction and better wettability alteration were achieved. Furthermore, nanotechnology improved the rheological properties of polymer and stability of emulsions and foams indicating the good potentials of improving sweep efficiency of injected chemicals especially in the presence of harsh reservoir conditions. Finally, future research should focus on modeling the flow behavior of nanomaterials through porous media, which is required for the designing and field implementation of nano-chemicals EOR.

Nomenclature

AA	acrylic acid
AlOOH	aluminum hydroxide
AM	acrylamide
AMPS	2-acrylamido-2-methyl-1-propanesulfonic acid
$AMC_{12}S$	2-acrylamido-dodecylsulfonate
APTES	(3-aminopropyl)triethoxysilane

AOS	alpha olefin sulfonate
$CaCl_2$	calcium chloride
CuO	copper oxide
DCDMS	dichlorodimethylsilane
ES	emulsion stability
FA	fly ash
GLYMO	(3-glycidyloxypropyl)trimethoxysilane
HPAM	hydrolysed polyacrylamide
IO	incremental oil
KCl	potassium chloride
PAM	polyacrylamide
PECNP	polyelectrolyte composite nanoparticle
PEG	polyethylene glycol
PEOMA	poly(oligo(ethylene oxide) mono methyl ether methacrylate)
$MeDiC_8AM$	2-methyl-N,N-dioctyl-acrylamide
MWCNT	multiwall carbon nanotube
$MgCl_2$	magnesium chloride
MMT	montmorillonite
NaCl	sodium chloride
NiO	nickel oxide
NP	nanoparticle
OOIP	original-oil-in-place
RF	recovery factor
SC	sodium cumenesulfonate
TTFA	thermally treated fly ash
WA	wettability alteration

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