EFFECT OF MAGNETIC IRON CORE-CARBON SHELL NANOPARTICLES IN CHEMICAL ENHANCED OIL RECOVERY FOR ULTRA-LOW INTERFACIAL TENSION REGION

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Abstract

Some of advantages of the simultaneous use of surfactants and nanoparticles in EOR processes are the increase in the efficiency of injection fluid for sweeping, the reduction of the adsorption of surfactant onto reservoir rock, the alteration of wettability and the reduction of water/crude oil interfacial tension. However, a large amount of nanoparticles required in chemical enhanced oil recovery (CEOR) processes might limit their application. Therefore, the main objective of this work is to synthesize, characterize and evaluate magnetic iron core-carbon shell nanoparticles that can be recovered and its impact on the reduction of surfactant adsorption on the porous media, and oil recovery at reservoir conditions. The additional benefit of the proposed method is that these nanoparticles can be recovered and re-used after the application due to its magnetic properties. The magnetic iron core-carbon shell nanoparticles were obtained following a new one-pot hydrothermal procedure and were carbonized at 900 °C using a teflon-lined autoclave. The core-shell nanoparticles were characterized using scanning electron microscopy (SEM), dynamic light scattering (DLS), N_2 physisorption at -196 °C, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and magnetometry measurements. Magnetic iron core-carbon shell nanoparticles with an average particle size of 60 nm were obtained. The XPS spectrum corroborated that magnetic Fe (0) of the core was adequately coated with a carbon shell. The interfacial tension (IFT) was measured using a spinning drop tensiometer for a medium viscosity crude oil and a surfactant mixture. The minimum IFT reached was approximately 1×10^{-4} mN m^{-1} at a nanoparticles concentration of 100 mg L^{-1}. At this concentration, the dynamic adsorption tests demonstrated that the nanoparticles reduce 33% the adsorption of the surfactant mixture in the porous media. The simultaneous effect of core-shell nanoparticles and the surfactant mixture was evaluated in a displacement test at reservoir conditions obtaining a final oil recovery of 98%.

Keywords: enhanced oil recovery; nanoparticles; surfactant

Resumen

Algunas de las ventajas del uso simultáneo de tensioactivos y nanopartículas en procesos EOR son el aumento de la eficiencia del fluido de inyección para barrido, la reducción de la adsorción del tensioactivo en la roca del yacimiento, la alteración de la humectabilidad y la reducción de la tensión interfacial agua/petróleo crudo. Sin embargo, una gran cantidad de nanopartículas necesarias en los procesos de recuperación mejorada de petróleo (CEOR) podría limitar su aplicación. Por lo tanto, el objetivo principal de este trabajo es sintetizar, caracterizar y evaluar las nanopartículas magnéticas de núcleo de hierro-carbono que pueden ser recuperadas y su impacto en la reducción de la adsorción de surfactante en el medio poroso, y la recuperación de aceite en condiciones de yacimiento. El beneficio adicional del método propuesto es que estas nanopartículas pueden ser recuperadas y reutilizadas después de la aplicación debido a sus propiedades magnéticas. Las nanopartículas magnéticas de núcleo de hierro-carbono se obtuvieron mediante un nuevo procedimiento hidrotérmico de una olla y se carbonizaron a 900 °C utilizando un autoclave revestido de teflón. Las nanopartículas del núcleo se caracterizaron mediante microscopía electrónica de barrido (SEM), dispersión dinámica de la luz (DLS), fisisorción de N2 a -196 °C, difracción de rayos X (DRX), espectroscopía de fotoelectrones de rayos X (XPS) y mediciones magnetométricas. Se obtuvieron nanopartículas magnéticas de núcleo de hierro-carbono con un tamaño medio de partícula de 60 nm. El espectro XPS corroboró que el Fe magnético (0) del núcleo estaba adecuadamente recubierto con una capa de carbono. La tensión interfacial (IFT) se midió utilizando un tensiómetro de gota giratoria para un crudo de viscosidad media y una mezcla de surfactantes. El IFT mínimo alcanzado fue de aproximadamente 1×10-4 mN m-1 a una concentración de nanopartículas de 100 mg L-1. A esta concentración, los ensayos de adsorción dinámica demostraron que las nanopartículas reducen en un 33% la adsorción de la mezcla tensioactiva en el medio poroso. El efecto simultáneo de las nanopartículas del núcleo y la mezcla de surfactantes fue evaluado en una prueba de desplazamiento en condiciones de yacimiento, obteniendo una recuperación final de aceite del 98%.

Palabras clave*: recuperación mejorada de petróleo; nanopartículas; surfactante*

1.Introducción

The surfactant flooding is a process applied to recover the residual and the remaining oil after the waterflooding (Qi, et al., 2017). This method involves the reduction in interfacial tension between oil and water with the purpose of enhancing oil recovery (Cheraghian et al., 2016). For a successful displacement process, the injected surfactant must achieve ultralow interfacial tension (IFT) to mobilize the residual oil and create a moving displacement front that allows the recovery of oil trapped by capillary forces. However, there was an important number of surfactant floods that were ineffective because to the IFT reduction was not low enough and the wettability alteration of the porous media did not drastically change to recover the trapped oil (Thomas, 2008). Hence, the use of nanoparticles has been studied by numerous researchers worldwide as an alternative method of chemical EOR. Most researchers focused their work on the use of silica gel nanoparticles for EOR applications. (Betancur, et al., 2018; Kazemzadeh, et al., 2018; Zargartalebi, et al., 2014, 2015).

Although silica gel represents a good alternative for chemical EOR, there are novel nanomaterials that involve two or more functionalities that give them unique properties as compared to their individual single-component materials. In this way, magnetic core-shell nanostructured materials have recently received great attention of researchers in the oil and gas area. The core-shell nanoparticles are composed of a core coated by a so-called shell. The core determines the magnetic or electrical characteristic, while the shell determines the binding affinity for a specific target. These properties allow the synthesis and design of nanoparticles with desired (custom-made) properties.

This study aims to synthesize, characterize and evaluate magnetic iron core-carbon shell nanoparticles like materials of easy recovered for its application in chemical EOR. The core with magnetic properties enables the nanoparticles manipulation via external magnetic field. Hence, the nanoparticles can be removed from the production fluids, which can allow its recovery and reutilization in additional EOR processes. The carbon material can be obtained from a wide variety of raw materials as a cost-effective alternative. In this work, the magnetic iron core-carbon shell nanoparticles were obtained following hydrothermal conditions by only one step. The effect of these nanomaterials on oil recovery was evaluated in a porous media based on core flooding test.

2. Materials and methods

2.1. Materials

Pyrocatechol (≥99% Merck, Germany), formaldehyde (mass fraction of 37%, Sigma Aldrich, United States), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, VWR, United States), urea (Merck, Germany), acetone (≥99.5%, VWR, United States) and distilled water were used for the synthesis of magnetic iron core-carbon shell nanoparticles. Two commercial surfactants: an hydrophilic and hydrophobic named S1 and S2, respectively, provided by Ecopetrol S.A. were used for the experiments. Sodium Chloride (NaCl, 99% Panreac, Spain), calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$, ≥99%, Sigma Aldrich, United States), magnesium chloride hexahydrate ($MgCl{\cdot}6H_2O$, ≥99%, Sigma Aldrich, United States) and potassium chloride (KCl, ≥99%, Sigma Aldrich, United States) were used to prepare the synthetic brine for all the experiments. An intermediate crude oil with 26.3°API was used for the wettability tests, the interfacial tension measurements and the core flooding tests. Silica sand (Minercol S.A., Colombia) was employed to prepare the sand packs for core flooding tests under reservoir conditions.

2.2. Methods

2.2.1. Synthesis of nanoparticles

The technique used for the synthesis of magnetic iron core-carbon shell nanoparticles was the hydrothermal process (Miladi, et al., 2016) using 0.075 moles of pyrocatechol, 0.090 moles of formaldehyde, 0.009 moles of $FeCl_3{\cdot}6H_2O$ and 0.15 moles of urea, which were dissolved in distilled water and the solution obtained was stirred for 10 minutes. After, the solution was transferred in a 100 mL teflon-lined autoclave, which was heated at 100 °C for 24 h. Then, the suspension was centrifuged and the product was washed. Subsequently, the wet product was dried at room temperature overnight and then in a microwave (Samsung electronics, Spain) under argon flow at 384 W for periods of 1 min until constant weight. Finally, the product was carbonized in a nitrogen flow (300 mL min^{-1}) at 900 °C.

2.2.2. Characterization of nanoparticles

The nanoparticles were characterized using scanning electron microscopy (SEM) using a HITACHI S-510 microscope (Hitachi High-Technologies, Japan) and dynamic light scattering (DLS) using a nanoplus-3 (Micromeritics, United States) for particle size determination. The surface chemical composition was determined from X-ray photoelectron spectroscopy (XPS) with an X-ray photoelectron spectrometer Kratos Axis Ultra DLD (Kratos Analytical, United Kingdom). N_2 adsorption isotherms were obtained with an Autosorb-1 (Quantachrome Instruments, United States) for surface area (S_{BET}) determination (Brunauer, et al., 1938). The magnetization of the nanoparticles was measured with a Quantum Design MPMS XL magnetometer (Quantum Design, Inc., United States). Powder X-ray diffraction (XRD) measurements were performed with a BRUKER D8 DISCOVER diffractometer (Bruker, United States).

2.2.3 Adsorption isotherms

In this work, two different surfactants (S1 and S2) conventionally used in the oil industry were selected for all the experiments based on the tuning with the crude oil employed in this study. The ratio used for the two surfactants S1 and S2 was 80:20 based on the recommendation of the provider. The mass fraction of surfactant of 0.2% was selected for further evaluations. A synthetic brine was prepared to carry out all the experiments of this work. For the adsorption isotherms, the solutions with surfactants and magnetic iron core-carbon shell nanoparticles were prepared based on previous studies (Betancur et al., 2018). The solutions were stirred for 2 h and left to stand for 24 h. Then, nanoparticles were added to the surfactant solutions at concentrations between 100 mg L^{-1} and 1000 mg L^{-1}. The adsorption experiments were performed through thermogravimetric analyses with a TGA analyzer (Q50, TA Instruments, Inc., New Castle, DE).

2.2.4. Interfacial tension experiments

The interfacial tension (IFT) experiments were performed at 52 °C using a spinning drop tensiometer SDT (Krüss GmbH, Germany) by adding a drop of oil to the surfactant solutions with magnetic iron core-carbon shell nanoparticles at concentrations between 10 mg L^{-1} and 1000 mg L^{-1}. Each measurement was performed in triplicate.

2.2.5. Dynamic adsorption isotherms

The dynamic adsorption tests allow quantifying the adsorption of the surfactant during the injection. Two sand packs were employed for these tests and were prepared from clean silica sand (US sieves 70-80 and 40-50 mesh, Minercol S.A., Colombia). The sand pack 1 was used to evaluate the adsorption of the surfactant mixture (in the absence of nanoparticles) and the sand pack 2 to evaluate the effect of the nanoparticles in the adsorption of the surfactant mixture. The nanofluid was prepared with the synthetic brine as described in the materials section, 2000 mg L^{-1} of the surfactant mixture and 100 mg L^{-1} of the magnetic iron core-carbon shell nanoparticles. All tests were carried out at a constant temperature of 52 °C.

2.2.6. Core flooding tests

The core floods were carried out to evaluate the performance of magnetic iron core-carbon shell nanoparticles for enhancing oil recovery at reservoir conditions. Two sand packs were used for these tests. A synthetic brine was employed for the preparation of the nanofluid. The concentration of surfactant mixture was 2000 mg L^{-1} and the nanoparticles were added to the solution at a concentration of 100 mg L^{-1}. All tests were carried out at a constant temperature (52 °C) and pressure (1500 psi). The overburden pressure (1500 psi) was controlled by pumping an incompressible fluid into the core holder. The first core flooding test considered the following stages: waterflooding, surfactant flooding, water drive, and surfactant flooding at the last stage. The second core flood was similar to test 1 except for the stage of the injection of the nanoparticles surfactant system (nanofluid).

3. Results

3.1. Nanoparticles characterization

The particle size distribution of the magnetic iron core-carbon shell nanoparticles was determined through SEM and DLS measurements The mean particle size obtained by DLS was 60 nm. In addition, the measured surface area (S_{BET}) of the nanoparticles was 123 m^2 g^{-1}. The crystallographic structure of nanoparticles was verified using X-ray diffraction (XRD). The peaks in the XRD pattern matched with the standard cubic Fe (0) structure data (Joint Committee for Powder Diffraction Studies, JCPDS, Card No. 98-005-2258) (Mahto et al., 2018). On the other hand, according to the results of the XPS spectrum, the percentage of Fe on the surface of the nanoparticles is around 0.2%. This result indicates that the Fe is effectively in the core of the nanoparticles. The magnetization of the nanoparticles was measured at the reservoir temperature of interest (52 °C). This temperature is within the range of most of the surfactant floods implemented at the field scale. The obtained values of magnetization are in agreement with the saturated magnetization reported in the literature for Fe (0) (Huber, 2005). Additional details about the characterization of nanoparticles can be found in this work by Betancur et al. (2019).

3.2. Adsorption isotherms

Figure 2 shows the adsorption isotherm for surfactant mixture onto magnetic iron core-carbon shell nanoparticles at 25 and 52 °C. Type III isotherm is observed according to the International Union of Pure and Applied Chemistry (IUPAC) classification scheme. (Thommes et al., 2015). This behavior is due to the reduction of available active sites of nanoparticles for adsorption by mass unit, produced by the increase in nanoparticles concentration. The increase of nanoparticles concentration favors the nanoparticle-nanoparticle interaction and thus, the available actives sites of nanoparticles surface for the adsorption of surfactants. In all cases of this work, the surfactant solutions were prepared with a surfactant mixture of 2000 mg L^{-1}, which is above CMC (≈1800 mg L^{-1}). This suggests that the multilayer formation can be due to the presence of micelles of surfactants. In addition, as observed in Figure 2, the adsorption of surfactants onto nanoparticles surface decreases when the temperature increases. This behavior indicates that for this system, the adsorption is an exothermic process.

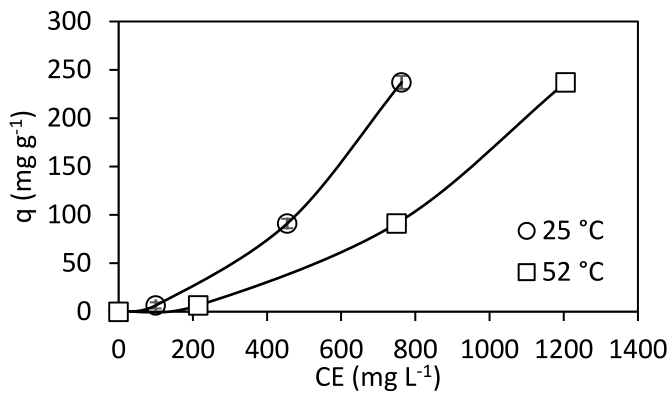

Figure 1. Adsorption isotherm for surfactant mixture of S1 and S2 in an 80:20 ratio onto magnetic iron core-carbon shell nanoparticles at 25 and 52 °C.

3.3. Interfacial tension experiments

In a successful displacement process, the IFT must be less of 1×10^{-2} mN m^{-1} for mobilizing residual oil through the injection of surfactant solutions (Rosen, et al., 2005). Figure 3 shows the interfacial tension values obtained for different nanoparticles concentration between 0 and 1000 mg L^{-1} at 52 °C. The aqueous phase was the synthetic brine used for the adsorption experiments and contains the surfactant mixture at a fixed concentration of 2000 mg L^{-1}. The dotted line represents the IFT of the surfactant mixture corresponding to 2.2×10^{-4} mN m^{-1} (Figure 3). However, only the nanoparticles-surfactant solution with a nanoparticles concentration of 100 mg L^{-1} achieves to reduce the IFT to 1×10^{-4} mN m^{-1}, which is a slightly lower IFT value than the obtained with the tuned surfactant mixture solution. The reduction in IFT values can be due to the synergy between the free surfactant present in the bulk and the nanoparticles with adsorbed surfactant onto their surface.

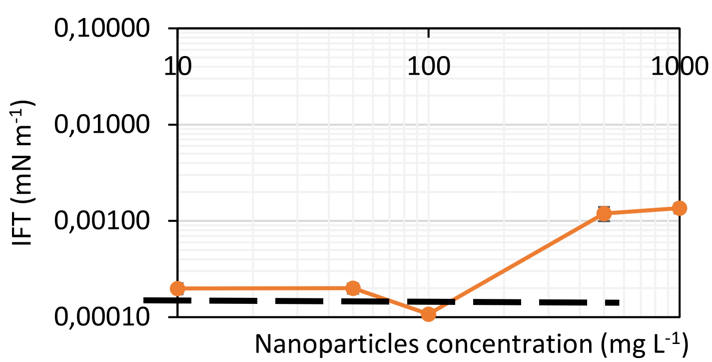

Figure 2. Interfacial tension of crude oil/synthetic brine with surfactant mixture of S1 and S2 at 2000 mg L^{-1} (dashed line) and in presence of the magnetic iron core-carbon shell nanoparticles at concentrations between 10 mg L^{-1} and 1000 mg L^{-1} and at a constant temperature of 52 °C.

3.4. Dynamic adsorption

Figure 4 shows the concentration curves in the effluent for the tracer (base and nanofluid), the surfactant mixture solution, and the nanofluid based on magnetic iron core-carbon shell nanoparticles and the surfactant mixture. The amount of mass adsorbed in the porous media is calculated based on the area between the influx curves of the tracer and the surfactant. The adsorption of surfactant in the porous media was estimated in 0.4 mg of surfactant per gram of rock. While the adsorption of the nanofluid (nanoparticle-surfactant system) was 0.27 mg of surfactant per gram of rock. This represents a 33% reduction of the surfactant adsorption. This behavior may be because the surfactant is being adsorbed on the surface of the nanoparticles (Betancur et al., 2018). If this is the case, there will be less surfactant available to get adsorbed onto the rock surface.

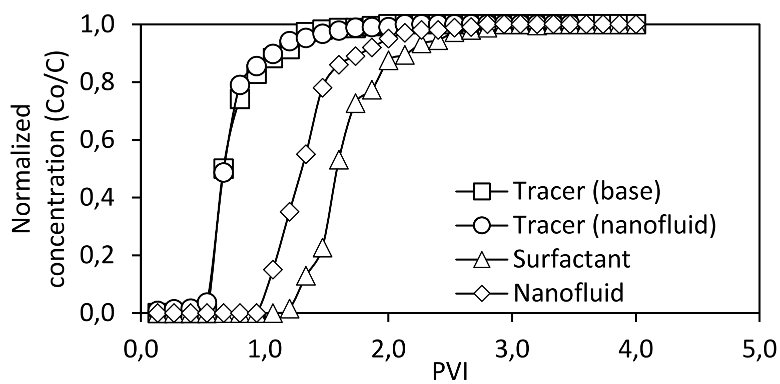

Figure 3. Dynamic adsorption in porous media for the surfactant mixture solution of S1 and S2 and the nanofluid based on magnetic iron core-carbon shell nanoparticles at 52 °C.

3.5. Core flooding at reservoir conditions

Core flooding tests were carried out to evaluate the effect of magnetic iron core-carbon shell nanoparticles on the oil recovery at reservoir conditions. The nanofluid based on nanoparticles-surfactant was prepared with the synthetic brine described in the materials section, using a total surfactant (S1+S2) and nanoparticles concentration of 2000 mg L^{-1} and 100 mg L^{-1}, respectively.

Oil recovery curves for surfactant flooding and nanoparticles-surfactant flooding are shown in Figure 5. The displacement tests were carried out at a constant temperature (52 °C) and pressure (1500 psi). As observed, in both cases, the oil recovered with waterflooding was approximately 66%. In the region between 5 and 5.3 PVI, the oil recovered for the surfactant flooding is almost constant.

This behavior suggests that the surfactant mixture has been adsorbed in porous media. However, for nanoparticles-surfactant flooding, the slope of the oil recovery curve is higher, which suggests that the adsorption of the material in porous media is reduced. Additionally, water drive performance for the nanoparticles-surfactant flooding is also higher than the water drive for the surfactant flooding with oil recoveries of 72 and 69%, respectively. The final recovery obtained with the nanoparticles-surfactant system was approximately 98%. This increase in the oil recovery represents about 30% more than obtained with waterflooding and 7% more than achieved with conventional surfactant flooding. In addition, the reduction of initial residual oil saturation (Sor) was 85% and 74% for nanoparticles-surfactant flooding and surfactant flooding, respectively, which corroborates the increase in oil recovery due to the reduction of surfactant adsorption onto the rock by the presence of nanoparticles.

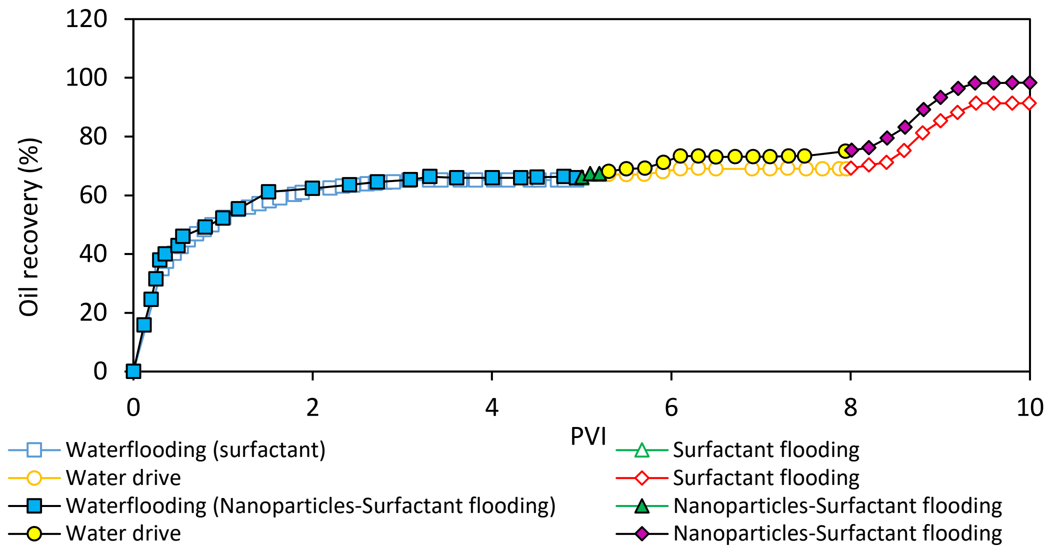

Figure 4. Oil recovery for the surfactant flooding and the nanoparticles-surfactant flooding.

4. Conclusions

Magnetic iron core-carbon shell nanoparticles were synthesized by a novel one-pot hydrothermal procedure. XPS spectrum confirmed the presence of Fe in metallic state of the core and was adequately coating with carbon shell. On the other hand, the surfactant mixture showed Type III isotherms according to the IUPAC scheme, which indicated the multilayer formation onto the nanoparticles surface due to the adsorption of surfactant micelles. The nanoparticles-surfactant solution with 100 mg L^{-1} of nanoparticles concentration decreased the IFT to 1×10^{-4} mN m^{-1}, which is a slightly lower IFT value than obtained with the surfactant mixture solution (2.2×10^{-4} mN m^{-1}). This behavior can be related to the synergy between the free surfactant and the nanoparticles with adsorbed surfactant onto their surface. The adsorption of surfactant onto nanoparticles was confirmed by adsorption isotherms. In addition, the dynamic adsorption tests prove that the nanoparticles decrease the adsorption of the surfactant in the porous media. This behavior can be due to the surfactant adsorption onto nanoparticles surface that reduces the amount of surfactant available to get adsorbed onto the rock. The nanoparticles-surfactant flooding achieved an oil recovery up to 98%.

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