Comparative investigation of nanoparticles effect for enhanced oil recovery - experimental and mechanistic study

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Abstract. Nanofluid flooding has become one of the advantageous enhanced oil recovery (EOR) techniques due to the transcendental property of nanoparticle. Nanoparticles with various morphology presents different effects and mechanisms of EOR. To provide some guidance on the selection of nanomaterials for flooding, 4 kinds of nanomaterials, including silicon dioxide (SiO₂), magnesium oxide (MgO), graphene oxide (GO) and molybdenum disulfide (MoS₂), are chosen to serve as research objects in the study. In lab, the morphology of four nanomaterials were systematically characterized by scanning electron microscope (SEM) tests. Moreover, nanofluid flooding experiments were further conducted to explore the relationship between the morphology of nanomaterials and EOR. Results show that the SiO₂ was spherical structure, and the MgO was blocky structure, while the GO and MoS₂ were both sheet structure. All the four nanomaterials have similar spatial dimensions. Flooding experiments revealed that MoS₂ enable improves the oil recovery by approximately 11.53 %, and GO was followed with 10 %, twice as much as both SiO₂ and MgO. From the results, it can be inferred that spherical materials only realize “point-to-surface” contact at multiphase interfaces, while sheet materials can achieve “surface-to-surface” contact with a higher interfacial activity. This paper is the first to focus morphology of nanomaterials on flooding, which contributes to the optimization of nanomaterials for high-efficiency oil displacement.

1. Introduction
Most of the oilfields in the world have undergone primary and secondary oil recovery and the oil well production declines severely. Under adverse conditions such as high water injection and complex reservoir geology (e.g., ultra-low porosity and permeability, etc.), about 50% or more of the original oil in place (OOIP) unable be developed [1]. Therefore, it is particularly important to improve recovery by tertiary oil recovery technologies. Chemical flooding is a practical method to counter this challenge, which has achieved great success in China. However, as the development of unconventional reservoirs continues to expand, the main application target of chemical flooding has shifted to ultra-low porosity and permeability reservoirs, where smaller pore size and larger specific surface area result in the bottleneck of "no injection, no recovery" for conventional chemical flooding systems [2].
Nanotechnology has gradually become a research hotspot in oil and gas field development. It has been widely applied in some fields, such as drilling and completion, fracturing and stimulation, especially in oil and gas recovery enhancement, great progress has been made in recent years. The nanoparticles can pass through nanopores, and the excellent properties of high specific surface area, surface activity, and special chemical reaction make the nanoparticles have great potential for application in enhancing recovery [3-4]. Nano oil-displacing agents can effectively reduce the water injection initiation pressure gradient, and overcome the problem of inadequate water injection or high water injection pressure in tight oil reservoirs [5-6]. Nanoparticles applied to oilfield chemistry areas can be broadly classified into two categories: spherical and flake. The spherical nanomaterials usually include: SiO$_2$, TiO$_2$, MgO, etc. M Turkyilmazoglu [7] analyzed the flow and heat transfer of different nanofluid film streams on a moving tilted substrate. Wu et al [8] studied the performance characteristics of the nano oil displacing agent iNanoW1.0. The treatment agent enable reduces the interaction forces between water molecules and facilitates the initiation pressure reduction. Moreover, this nanomaterial can improve the anti-expansion effect of anti-expansion agents, which helps the development of water-sensitive reservoirs. Ren et al. [9] evaluated the basic performance of silane coupling agent modified nano-oil-displacing agent with nano-SiO$_2$ as the main component. They found that the novel agent has lower oil-water interfacial tension, good hydrophilicity and certain static adsorption capacity. The oil recovery can be significantly improved compared with water. Cheraghian [10] introduced nano TiO$_2$ into partially hydrolyzed HPAM and dodecyl sodium dodecyl sulfate for oil flooding experiments. The results showed that the TiO$_2$ nanomaterials obviously improved the oil recovery compared with using two oil-displacing agents alone. The flake nanomaterials usually include: MoS$_2$, graphene oxide, etc. Infant Raj et al [11] used synthetic amphiphilic MoS$_2$ nanosheets as surfactant at very low concentrations to modify the wettability of cores, and the results showed that 18.25% of residual oil was recovered from core samples saturated with crude oil. Luo et al [12] modified the amphiphilic nature of graphene oxide by alkylamine. The amphiphilic GO nanosheets were prepared by changing the amphiphilicity of graphene oxide through alkylamine. Results showed that the formed nanofluid of this nanosheet dispersed in brine could enhance the recovery of crude oil by 15.2 %, which is three times higher than conventional nanoparticles displacing agents.

To date, the research progress on the effect of nanoparticle morphology on crude oil recovery is relatively rare. In this paper, we focus on the influence of different morphologies of nanoparticles on oil flooding efficiency. Numerous experiments were conducted in lab to analyze the morphology of four nanomaterials, and nanofluid flooding experiments were further carried out to explore the relationship between the morphology of nanomaterials and EOR. Materials and Methods.

1.1. Materials
MoS$_2$ were made in the laboratory, and MgO, SiO$_2$ and graphene oxide (abbreviated as GO) were purchased from Merck. The specific parameters of the nanoparticles are shown in Table 1. All nanoparticles were not surface modified. Aviation kerosene was purchased from Beijing Aviation Kerosene Co. The stratigraphic crude oil was taken from Jimsaer region, Xinjiang, China. The oil used in this work was a simulated oil prepared by diluting the formation crude oil with kerosene at a volume ratio of 1:1.5, with a viscosity of 20 cP and the density is 0.838 g/cm$^3$. Core samples were obtained from the Jimsaer region of Xinjiang, China.

| No. | Type of Nanoparticle | Particle Size (nm) | Purity(%) | Geometry |
|-----|----------------------|-------------------|-----------|----------|
| 1   | MoS$_2$              | 20-40             | 99        | sheet    |
| 2   | MgO                  | 20-50             | 98        | blocky   |
| 3   | SiO$_2$              | 20-40             | 99.5      | spherical|
| 4   | GO                   | 50                | 98        | sheet    |
1.2. Preparation of nanofluid
The simulated formation water was a KCl solution with the concentration of 2 %, a viscosity of 1 mP·s, and the density is 1 g/cm$^3$. Nanoparticles with a concentration of 50 mg/L were ultrasonically dispersed in brine to prepare nanofluids. Before each experiment, the nanofluids were sonicated for 15 min and then gently stirred for 1 h. This step allows for homogeneous stabilization of the nanofluid. The stirring time is the optimal time screened in the laboratory.

1.3. Nanoparticle morphology
The morphology of the nanomaterials was investigated by scanning electron microscope (SEM: FEI Quanta 200F, Thermo Fisher Scientific U.S.A.)

1.4. Contact angle measurement
Contact angle measurements were performed to quantify the degree of change in wettability of the nanomaterials on the reservoir cores. Prior to this test, the cores were aged in simulated oil for one week to restore their condition under reservoir conditions. The treated cores were then immersed in nanofluid for 4 hours.

For contact angle measurements, the core is supported by a stainless steel holder and placed in a glass cuvette, as shown in Figure 1. When the bottom surface of the core is immersed in nanofluid, a drop of simulated oil is gently placed on the bottom surface of the core using a syringe with a needle. The JY-PHb type contact angle tester was used to capture the change of contact angle of oil drops on core surface with time. The purpose of this study is to explore the wettability alteration ability of the nanofluids.

1.5. Interfacial surface tension (IFT) measurement
The IFT of nanomaterials with different mass concentrations was tested by the “hanging ring” method, and each concentration was tested five times, and then the arithmetic mean was taken.

1.6. Zeta potential
Zetasizer nano ZS (Malvern Instruments, U.K.) was used to test the zeta potential of nanoparticles.

1.7. Core flooding test
Step-1: A dry core was placed in a closed container, vacuumed and filled with simulated formation water and pressurized to 20 MPa. Constant pressure saturation for one day.

Step-2: Load the core into a core holder as shown in Figure 2. the experimental temperature is 70 °C and the confining pressure is 15 MPa. The simulated oil was injected into the core holder at a rate of 0.2 ml/min until the brine is completely driven out. This step is designed to simulate the condition of formation reservoirs.

Step-3: After step-2, the core saturated with crude oil was obtained. The simulated formation water (2-3 PV) is injected at a rate of 0.2 mL/min until no oil produced at the outlet. This step is simulating the secondary recovery process.
Step-4: After the end of step-3, 3-6 PV of nanofluids is injected into the core at a rate of 0.2 mL/min until no oil recovered at the outlet.

Figure 2. Multi-functional core displacement device.

2. Results and Discussion

2.1. Stability analysis of silica nanofluids
To understand the stability of the nanofluid, we performed zeta potential measurements, as shown in Figure 3. The zeta potential of SiO$_2$ is about -20.6 mV under experimental conditions at pH 7. The zeta potential of MoS$_2$ is about -25 mV; the zeta potential of GO is about -22.6. Overall, the highly negative zeta potentials (above ±20 mV) indicates all the three nanofluids are stable under ambient conditions, which is consistent with the basic principle of DLVO (Derjaguin, Landau, Vervey, and Overbeek) theory, which describes the stability of particles dispersed in a fluid by considering the electrostatic repulsion and van der Waals gravity between the particles [13]. However, the zeta potential of MgO is 0.62 mv, which indicates the poor stability of this fluid.

Figure 3. Measurement results of zeta potential of different nanofluids.

2.2. Nanoparticle morphology

Figure 4. SEM images of different nanoparticles (A is nano-SiO2, B is GO, C is MoS2, D is nano-MgO).
As shown in Figure 4, SiO$_2$ is a spherical material with a size of 20-40 nm, GO is a sheet material with a size of 50 nm, MgO is a bulk material with a size of 20-50 nm, and MoS$_2$ is also a sheet material with a size of 20-40 nm.

2.3. Wettability alteration

Wettability alteration is a common method to enhance recovery from oil-wetting formations and mixed-wetting formations. The formation rock surface has been in contact and reaction with the subsurface crude oil for millions of years prior to the development of the oil recovery process, so the reservoir usually behaves as oil-wetting or mixed-wetting environment. By changing the formation wettability, the capillary forces can be reduced and the mobility of the oil phase can be improved.

Therefore, the wettability alteration ability of different nanomaterials will be discussed in this section. Contact angle tests were performed after placing oil droplets on the bottom surface of a core submerged by nanofluids. Figure 5 summarizes the measured contact angles between oil and cores immersed in different nanoparticle solutions. The contact angle of oil droplets in simulated formation water is 75°, which is a distinct oil-wetting state. After treatment with different nanoparticle solutions, the contact angle gradually becomes larger. SiO$_2$ nanofluid has a contact angle of 122.1°, which is the lowest among the four nanomaterials. The contact angle in MgO nanofluid is 142°. MoS$_2$ and GO have similar contact angles of 136.6° and 135.6°, respectively. Overall, both the spherical nanoparticles and flaky nanoparticles can change the core from an oil-wetting state to a strong water-wetting state. Both of them have the potential to enhance the recovery of crude oil.

![Figure 5. Contact angle of different nanofluids.](image)

2.4. Investigation of the effect of nanoparticles on interfacial tension

To better understand the effect of nanoparticles on the nanofluid/oil sample IFT, IFT measurements were carried out at different concentrations of nanoparticles from 0.05-0.5 wt%. The results are provided in Figure 6 shown. The interfacial tension between the simulated formation water and oil samples was 27 mN/m, which is the same as the reference value [12]. When 0.005 wt% of nanoparticles were added to the water, the IFT of the four nanoparticles decreased to below approximately 4 mN/m, indicating that nanoparticles can effectively reduce the interfacial tension. Further increase nanoparticle concentration (0.5%wt) resulted in a slight decrease in IFT, reaching 3.69 mN/m, 3.31 mN/m, 1.89 mN/m, and 2.04 mN/m for SiO$_2$, MgO, MoS$_2$, and GO, respectively, at 0.5%. several factors were reported to contribute to the decrease in IFT in the presence of nanoparticles; however, the high stability of the nanofluid and at the water interaction with the oil interface are the main reasons for this process. It is evident from the experimental results that the interfacial tension of the flaky nanoparticles is less than that of the spherical nanoparticles. The spherical nanoparticles are in "point-surface" contact with the oil-water interface, while the flake nanoparticles are in "surface-surface" contact with the oil-water interface, which has a larger specific
surface area and more interfacial active sites. The specific surface area is larger and the interfacial active sites are more, which has a better interfacial effect.

![Figure 6. IFT changes with the concentrations of nanoparticles.](image)

2.5. Core flooding test

The reservoir cores were used for oil-displacing experiments to acquire the recovery data of nanofluids formulated with different morphologies of nanoparticles. Table 2 shows the summary results of the cores used in this work. Figure 6 shows the oil recovery dynamics curves of crude oil with different nanofluids.

| Sample Name | Rock Description | Diameter (cm) | Length (cm) | Permeability (mD) | Injecting nanofluid |
|-------------|------------------|---------------|-------------|------------------|---------------------|
| JM-1        | Reservoir Rock   | 2.525         | 5.002       | 0.86             | SiO2                |
| JM-2        | Reservoir Rock   | 2.525         | 5.003       | 0.79             | MgO                 |
| JM-3        | Reservoir Rock   | 2.525         | 5.018       | 0.82             | MoS2                |
| JM-4        | Reservoir Rock   | 2.525         | 4.9684      | 0.87             | GO                  |

As shown in Figure 7 and Figure 8, after injecting 2.5 PV of simulated formation water, the nanofluid was injected instead. The experiment results indicating that the water drive could only recover 40% of the original oil in-place (OOIP), and the residual oil trapped in place unable be recovered by water injection. Nanofluid treatment increased oil recovery by 1.44-11.53%. Among the tested four nanofluids, the recovery rates of both nano-SiO2 and nano-MgO were less than 7%, which is similar to what has been reported in the literature [14]. In contrast, the GO and MoS2 have better recovery enhancement abilities, with the recovery rate of MoS2 reaching nearly 11.53%.

Combined with the previous experiments, it can be found that the interfacial tension and zeta potential of nano-SiO2 and GO are almost the same, and both have excellent wetting inversion ability. However, the crude oil recovery of both go increased by 5% compared with nano-SiO2. The results indicating that the crude oil recovery of sheet nanoparticles is better than that of spherical nanoparticles. MoS2 interfacial tension is lower than that of GO, so the crude oil recovery of MoS2 is slightly higher than that of GO. Nano-MgO's zeta potential is positively charged and will be heavily adsorbed on the core surface, so the crude oil recovery is the lowest and the least effective.

From the structural analysis of nanoparticles, spherical nanoparticles with regular shape and smaller size are highly hydrophilic and difficult to adsorb from the aqueous phase to the oil-water interface, so the interfacial tension and oil-displacing efficiency are relatively low. However, there is an evident difference in hydrophilicity between the base and edge of the sheet nanomaterials. The base surface is generally hydrophobic and the edges are hydrophilic due to the presence of carboxyl groups.
and phenolic hydroxyl groups, etc., which makes it behave similar to surfactants in aqueous media. The experimental results also confirm this conclusion.

![Figure 7. Dynamic curve of crude oil recovery with different nanofluids.](image)

![Figure 8. Crude oil recovery with different nanofluids.](image)

3. Conclusion
This paper investigates the recovery of crude oil from four types of nanoparticles. Based on the experimental results, the main findings are as follows:

1. From the results of Zeta potential test, the absolute values of surface charge of SiO$_2$, MoS$_2$ and GO are greater than 20 mV, and the stability is better. While the surface charge of MgO is only 0.62 mV, which is less stable and easy to settle.

2. Nanoparticles can effectively reduce the interfacial tension. At the same concentration of 0.5 %, the interfacial tension of flaky nanoparticles is smaller than that of the spherical nanoparticles with higher interfacial activity, because the flaky nanoparticles have similar structure with surfactant.

3. All four kinds of nanomaterials can convert oil-wetting cores into strong water-wetting state, and the wettability alteration effect was obvious, which is one of the factors to improve oil recovery.

4. All four kinds of nanomaterials can obviously improve oil recovery. The recovery rate of flaky nanoparticles is generally above 10 %, much higher than that of spherical nanoparticles, indicating the flaky nanoparticles is a kind of potential high-efficiency oil-displacing material.

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