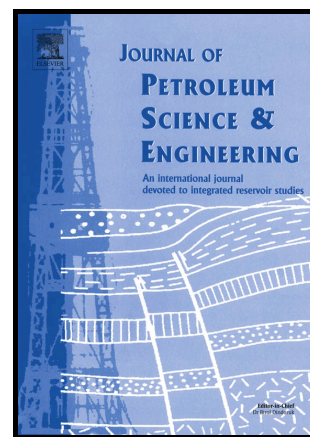


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Reducing Surfactant Adsorption on Rock by Silica

Nanoparticles for Enhanced Oil Recovery

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Abstract

This paper aims at making a thorough investigation on surfactant adsorption on rock under the influence of silica nanoparticles (SNP). The results showed that SNP can reduce surfactant adsorption effectively. With SNP concentration of 0.1, 0.2 and 0.3 wt%, static adsorption experiments showed that sodium dodecyl sulfate (SDS) adsorption can be significantly reduced to 2.57, 2.12, and 1.73 from 2.84 mg/g, and the dynamic adsorption of SDS decreased to 0.92, 0.77, and 0.66 from 1.16 mg/g, respectively. Our subsequent tests conformed a 4.68% growth of oil recovery by the injection of SNP - surfactant solution compared to the normal surfactant solution. The

mechanism of the enhanced oil recovery is assumed to be the inhibition of surfactant adsorption and the profile control capability of silica nanoparticles. This study proves the SNP - surfactant flooding is a cost-effective way for enhanced oil recovery.

Keywords: Silica nanoparticles; Surfactant; Adsorption; Enhanced oil recovery.

1. Introduction

Surfactant flooding has played a vital role in enhanced oil recovery, through lowering oil/water interfacial tensions (IFTs), emulsifying crude oil and altering the wettability of oil layer toward water-wet (Johannessen et al., 2013; Adams et al., 1987; Puerto et al., 2013; Wu et al., 2013). During surfactant flooding, the solution flows through the porous reservoir with huge surface areas, as a result, the inevitable loss of surfactant due to adsorption limits its extensive application in oil fields (Somasundaran et al., 1985). Reducing surfactant adsorption on rock in the reservoir is one of the most deciding factors for the success of a surfactant flooding (Ahmadall et al., 1993).

To reduce surfactant adsorption, some work have been reported by involving different additives in the last few years (Zhou et al., 2005; ShamsiJazeyi et al. 2013; Le et al., 2011; Ahmadi et al., 2012). Alkali as additives has been studied under low salinity (Al-hashim et al., 1996; Gupta et al., 2007), and the mechanism of which was considered as changing the charge density on the rock surfaces. Wang et al. have studied polymer for reducing surfactant adsorption in carbonate reservoirs. It was found that a polymer layer was formed on the rock surface, leading to a decrease of active adsorption sites (Wang et al.2013). In contrast, other works have conversely

proven additives as alkali and polymers inefficient due to the dissolution and instability in high-temperature and high-salinity reservoirs (Dai et al., 2010; Lorenz et al., 1989; French et al., 1990). Therefore, how to reduce surfactant adsorption is still a big challenge for a cost-effective surfactant flooding project.

Even though silica nanoparticles (SNP) have been commonly used as co-injectants with surfactants in chemical flooding (Mohajeri et al., 2015), the influences of the silica nanoparticles on surfactant adsorption remained unrevealed. In this research, the effect of silica nanoparticles on the surfactant adsorption was investigated in depth. Static adsorption and dynamic adsorption behaviors of SDS were investigated with and without SNP. Meanwhile, the inhibition mechanism of SNP on surfactant adsorption was proposed. Furthermore, the flooding efficiency of the SDS – SNP solution was also investigated.

2. Experiment section

2.1 Material

The sodium dodecyl sulfate (SDS, $\geq 86.0\%$) purchased from Aladdin Industrial Corporation was used as the surfactant. Hydrophilic silica nanoparticles composed of mainly SiO_2 with an average particle diameter of 15 nm were purchased from Aladdin Reagent Company. The size distribution curve of the silica nanoparticles is shown in Fig. 1. Silica nanoparticles were situated in weak alkaline solution with a pH of 8-10 to prevent precipitation.

The sand used in the experiments is quartz sand whose main mineral composition is SiO₂. The sand was screened by 80-100 mesh. The mineralogy of the "natural cores" used in the core flow tests consists of mainly quartz sand. The physical characteristics of the cores used in adsorption test is shown in table 1. The crude oil sample from Tahe oilfield with a density of 0.7593 g/cm³ and a viscosity of 1.728 mPa • s was used for the displacement experiments.

Cetyltrimethyl ammonium bromide (CTAB, cationic surfactant, Tianjin Guangfu Fine Chemical), dichloromethane (Sinopharm Chemical Reagent Co., Ltd.) and sodium sulfate anhydrous (Tianjin Hongyan Chemical Reagent Factory) were used for determining SDS concentration.

The deionized water was used for all experiments. The experimental temperature was 20 °C.

2.2 Determination of the surfactant concentration

To determine the concentration of SDS, the two-phase titration method using a mixed indicator of thymol blue-methylene blue was applied, following the procedure in the literature (Li, Z. 1984).

2.3 Static adsorption test

Static adsorption experiment, including the adsorption of SDS on SNP and on quartz sand, was conducted.

2.3.1 Adsorption of surfactant on SNP

The procedure is described as follows: in the first stage the SNP were added into deionized water; then the pH of the solution was adjusted to 9 to obtain a homogeneous dispersion of SNP. Subsequently, SDS was added into SNP solution. All samples were put in 100 mL conical flasks, then oscillated on a constant temperature shaker at 20 °C under atmospheric pressure. The upper liquid was centrifuged for 20 min at 10000 rpm to separate nanoparticles, the concentration of which was determined afterwards to study the static adsorption of surfactant on SNP.

2.3.2 Adsorption of surfactant on quartz sand

The quartz sand screened by 80-100 mesh was washed by deionized water for three times. Then, 6 g of quartz sand and 18 mL of surfactant solution with different SNP concentration were added to a 100 mL conical flask and oscillated on a constant temperature shaker at 20 °C under atmospheric pressure. The solution was centrifuged for 20 min at 2000 rpm to remove impurities. Subsequently, the upper liquid was centrifuged for 20 min at 10000 rpm to remove nanoparticles before investigating the influence of the SNP on surfactant adsorption. After centrifugation, the surfactant concentration in the supernatant was measured using the above-mentioned two-phase titration method. Static adsorption (q_e) was calculated using Eq. (1), as follows:

$$q_e = \frac{(C_0 - C)V}{M} \quad (1)$$

where q_e is the adsorption of the surfactant on SNP or quartz sand (mg/g); C_0 and C are the surfactant concentrations before and after the adsorption experiment, respectively (wt%); V is the volume of surfactant solution added to the conical flask

(mL); and M is the total mass of the clean particles (g, including SNP and quartz sand).

Static adsorption was obtained by comparing the initial surfactant concentration with the concentration of surfactant after reaching equilibrium adsorption.

2.4 Dynamic adsorption test

In order to determine the dynamic adsorption of SDS on sand under the influence of SNP, the experiments were conducted by flooding tests using natural cores. Firstly, the permeability and pore volume were determined. Then, the surfactant solution (formulas: 0.2 wt% SDS with silica nanoparticles of different concentrations ranging from 0 to 0.3 wt%) was injected into the core. The effluent was collected in certain volume continuously. The surfactant concentration was determined afterwards until it leveled at the initial injecting liquid concentration. Finally, deionized water was injected until the concentration of effluent was less than 10^{-5} mg/g. The injection rate was set at 1 mL/min in the core-flooding test. Dynamic adsorption was calculated using Eq. (2), as follows:

$$q_e = \frac{C_0 V - \sum_{i=1}^n C_i V_i}{m} \quad (2)$$

Where q_e is the adsorption of the surfactant on quartz sand (mg/g); C_0 is the initial concentration of surfactant (wt%); V is the total volume of injected surfactant solution (mL); C_i is the surfactant concentration in effluents collected from different time period (wt%); V_i is the volume of each effluent sample (mL); M is the total mass of

the natural core (g); and n is the total quantity of effluent samples until the surfactant concentration is less than 10^{-5} mg/g.

2.5 Enhanced oil recovery test

Oil displacement tests (Figure 2) were performed to simulate the processes of enhancing oil recovery by surfactant or SNP- surfactant flooding. The permeability of the cores ($\text{Ø}25 \times 100$ mm) were about $0.145 \mu\text{m}^2$. The cores were first saturated with oil, which was then displaced with water at a flow rate of 0.3 mL/min until water cut of the production fluid approached 100%. Then, surfactant or SNP- surfactant flooding was performed. The pore volume of the slug was 0.3 pore volume (PV). Afterwards, water flooding was continued until the water cut of the production fluid approached 100% again. The total recovery was the ratio of the volume of total produced oil and initial saturated oil in the cores.

3. Results and discussion

3.1 Static adsorption behavior of the surfactant on the quartz sand surface

3.1.1 Adsorption parameters optimization

To ensure static adsorption reaching equilibrium, it is necessary to investigate the effect of the adsorption time and liquid-solid (quartz sand) ratio on static adsorption.

The adsorption of SDS was first studied at different adsorption time in the range from 2 h to 35 h with SDS concentration of 0.2 wt% and liquid-solid ratio of 30:1. The adsorption result is shown in Fig. 3. In the early stage (adsorption time less than 20 h),

the SDS adsorption increased gradually. After 20 h, the adsorption of SDS reached equilibrium and kept at a constant value. Herein the aging time was set at 30 h to ensure surfactant adsorption reaching equilibrium in the following experiments.

Subsequently, surfactant adsorption was determined at different liquid-solid ratios ranging from 1:1 to 35:1 with 0.2 wt% surfactant solution. As shown in Fig. 4, the static adsorption increased rapidly when the liquid-solid ratio was less than 5:1, then changed slightly and reached stable when the liquid-solid ratio was higher than 25:1, indicating the static adsorption has reached saturation. Consequently, the liquid-solid ratio was set at 25:1.

In addition, experiment was conducted to investigate surfactant adsorption on SNP surface. The zeta potential of SNP in solutions of pH 8 ~ 10 was of -17.81 to -57.62 mV. Results showed that trace amounts of surfactant molecules adsorb on silica nanoparticles surface. Therefore, the adsorption on SNP was neglected in following investigations.

3.1.3 Effect of SNP concentration

The effect of SNP concentration on surfactant static adsorption behavior on quartz sand surface was investigated. The results are shown in Fig. 5. At the same SDS concentration, the addition of silica nanoparticles can greatly restrain the adsorption of SDS on sand. The saturated adsorption of SDS solution without SNP is 2.84 mg/g, which clearly decreased with the increase of SNP concentration. When the concentration of SNP was 0.1 wt%, the adsorption of SDS was 2.57 mg/g, and the

value of which further decreased to 1.61 mg/g when the concentration of SNP increased to 0.5 wt%. It is assumed that the retained silica nanoparticles in the core can shield the sand wall. Some surfactant molecules will collide on silica nanoparticles surface instead of on sand wall, therefore, will decrease the surfactant adsorption.

It is also important to point out that silica nanoparticles tend to aggregate at high concentration. Thus the reduction of the surfactants adsorption is not that obvious when the silica nanoparticles concentration increased to 0.4 wt%. Taking economic cost into consideration, the optimal silica nanoparticles concentration were considered to be 0.2 ~ 0.3 wt%.

3.2 Dynamic adsorption

The dynamic adsorption of SDS on the natural cores was investigated at 20 °C by the core-flooding tests with different SNP concentrations from 0 to 0.3wt%. The pore volume (PV) and permeability of the natural cores are about 8.53 cm³ and 0.682 μm², respectively. The dynamic adsorption results are shown in Fig. 6.

It is found that there was a complete dynamic adsorption and desorption process for SDS on the natural core. When the volume of the injected SDS slug exceeded 2 PV, the dynamic adsorption reached saturation. In the following water flooding stage, the adsorption decreased dramatically in the beginning. When the injection volume increased to 5 PV, dynamic retention reached equilibrium. It is clear from the Fig. 6 that the surfactant with SNPs reached a lower saturated adsorption and a lower

dynamic retention in all cases investigated. Meanwhile, both values decrease with the increase of SNP concentration. The saturated adsorption and dynamic retention of single SDS solution are 1.16 mg/g and 0.30 mg/g. At SNP concentration of 0.1 wt%, the saturated adsorption decreased to 0.92 mg/g and the dynamic retention was reduced to 0.17 mg/g, while the values of which further decreased to 0.66 and 0.06 mg/g when the concentration of SNP increased to 0.3 wt%. The ratio of the reduced adsorption is calculated as 26.9%, 33.7% and 43.6% respectively, suggesting a superior capability of inhibiting adsorption of silica nanoparticles.

This can be attributed to several reasons. Firstly, the sand surface is shield by the remained SNP (Alonso et al., 2009), promoting surfactant molecules remain on silica nanoparticles surface instead of on sand. The retention ratio of nanoparticle can reach 60 %. As shown in the work of Dai (Dai et al., 2017), large amount of nanoparticles were found to adsorb on the surface of core. Besides, the fierce collision and friction effect between silica nanoparticles and sand wall may lead to easily dropping down of adsorbed surfactant molecules from rock when transporting in porous media. Herein, the surfactant adsorption on rock was reduced.

3.3 Enhanced oil recovery test

Core-flooding test was conducted to investigate the capacity of enhanced oil recovery of single 0.2 wt% SDS solution and 0.2 wt% SDS + 0.2 wt% silica nanoparticles solution. The experiments include three stages: initial water flooding, injecting surfactant solution, following with water flooding with the injection rate of

0.3 mL/min. The physical model parameters and oil recovery capacity of the two systems are shown in table 2. The oil recovery and water cut curves of two systems are shown in Fig. 7 and Fig. 8, respectively. During the flooding process, 0.3 PV of surfactant/surfactant adding silica nanoparticles solution was injected.

It can be found that the ultimate enhanced oil recoveries of the two systems are 4.43% and 9.11%. As shown, the SNP - surfactant flooding improves the efficiency of 4.68% higher than the normal surfactant flooding. This is because silica nanoparticles reduces the adsorption of surfactant which is vital to enhance the performance of the chemical flooding. The moderate surfactant adsorption by silica nanoparticles guarantees its field application during the flooding process and is an important trial for enhanced oil recovery with probable benefit effect.

4. Conclusions

In this work, static adsorption and dynamic adsorption of SDS with and without SNP were investigated. The result showed adding SNP reduces the surfactant adsorption on rock. This can be attributed to the decrease of the adsorption area due to the occupation of silica nanoparticles on sand wall. As a result, the contact probability between surfactants and sand wall and the friction between the nanoparticles and sand wall were reduced. Meanwhile, the collision and friction effect between silica nanoparticles and sand wall lead to easily dropping down of adsorbed surfactant molecules from sand wall. Enhanced oil recovery test showed SNP - surfactant flooding can improve the efficiency. The study indicates the application of silica

nanoparticles to surfactant flooding can be a cost-effective way for enhancing oil recovery.

Acknowledgments

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Fig. 1. Distribution curve of the silica nanoparticles.

Fig. 2 Experimental set-up for enhanced oil recovery experiment. 1 – Pump; 2 – Six-way valve; 3 – Surfactant solution container; 4 – Valve; 5 – Deionized water

container; 6 – Core; 7 - Cuvette

Fig. 3. The effect of adsorption time on static adsorption.

Fig. 4. The effect of liquid-solid ratio on static adsorption.

Fig. 5. The effect of SNP on static adsorption.

Fig. 6. The effect of SNP on dynamic adsorption.

Fig. 7. Enhanced oil recovery test of normal surfactant flooding (The permeability of the cores ($\text{\O}25\times98.96$ mm) is $0.149 \mu\text{m}^2$. Injection rate is 0.3 mL/min. The pore volume of the injected surfactant solution were 0.3 PV.)

Fig. 8. Enhanced oil recovery test of SNP – surfactant flooding. (The permeability of the cores ($\text{\O}25\times10.24$ mm) is $0.142 \mu\text{m}^2$. Injection rate is 0.3 mL/min. The pore volume of the injected surfactant –SNP solution were 0.3 PV.)

Table 1. Physical characteristics of nature cores used in adsorption test.

silica nanoparticles concentration/ (wt%)	Permeability/ (μm^2)	Pore volume/ (mL)	Length/ (cm)
0	0.684	8.34	5.23
0.1	0.673	8.57	5.38
0.2	0.692	8.46	5.42
0.3	0.678	8.72	5.46

Table 2. Physical model parameters and oil recovery capacity of two systems.

Injecting formula	Permeability / ($\mu\text{ m}^2$)	Oil saturation / (%)	Oil recovery/ (%)	Enhanced oil recovery / (%)
0.2wt% SDS	0.047	82.37	55.65	4.43
0.2wt% silica nanoparticles+0.2wt % SDS	0.051	81.75	57.64	9.11

Highlights

- Silica nanoparticles were found to reduce surfactant adsorption effectively
- EOR test proved a 4.68% growth of oil recovery by the injection of SNP - surfactant solution
- The mechanism of the inhibition using SNP was proposed

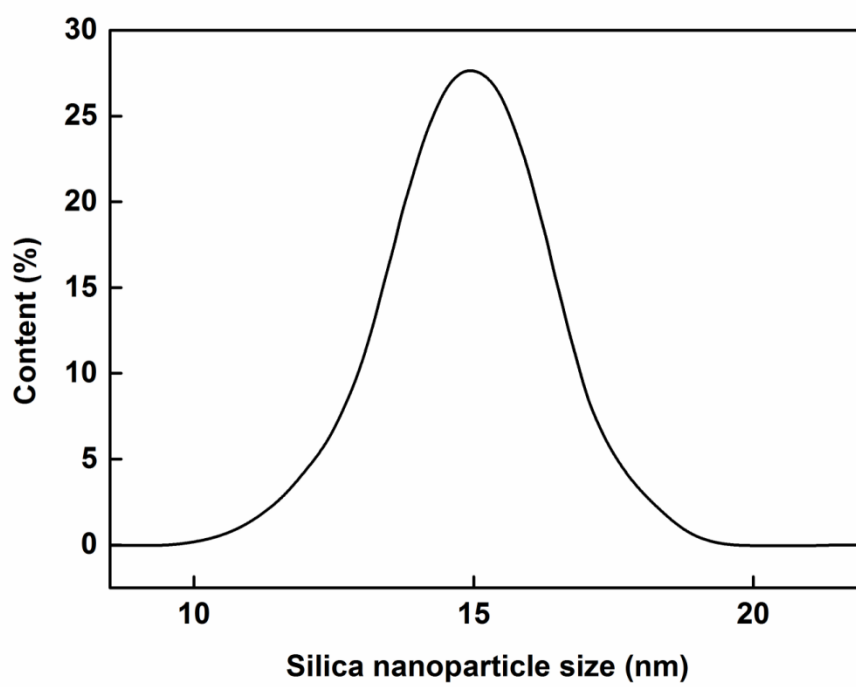
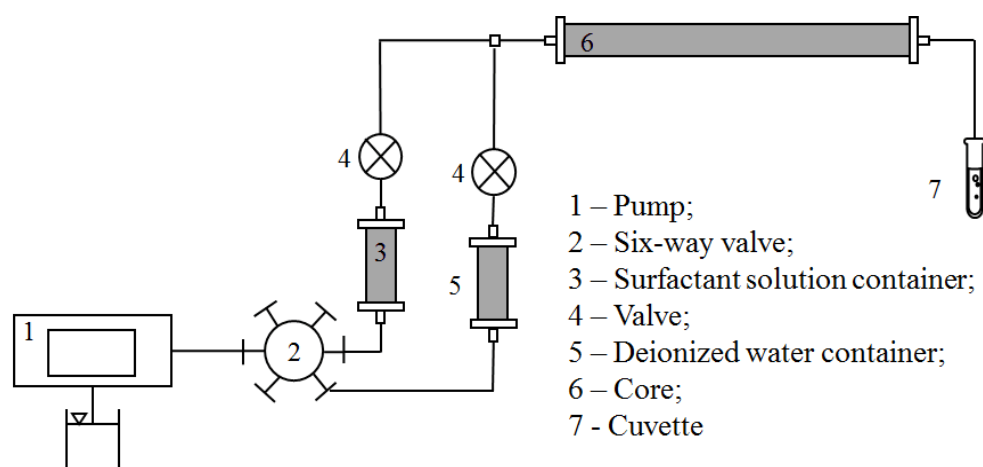


Fig. 1

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**Fig. 2**

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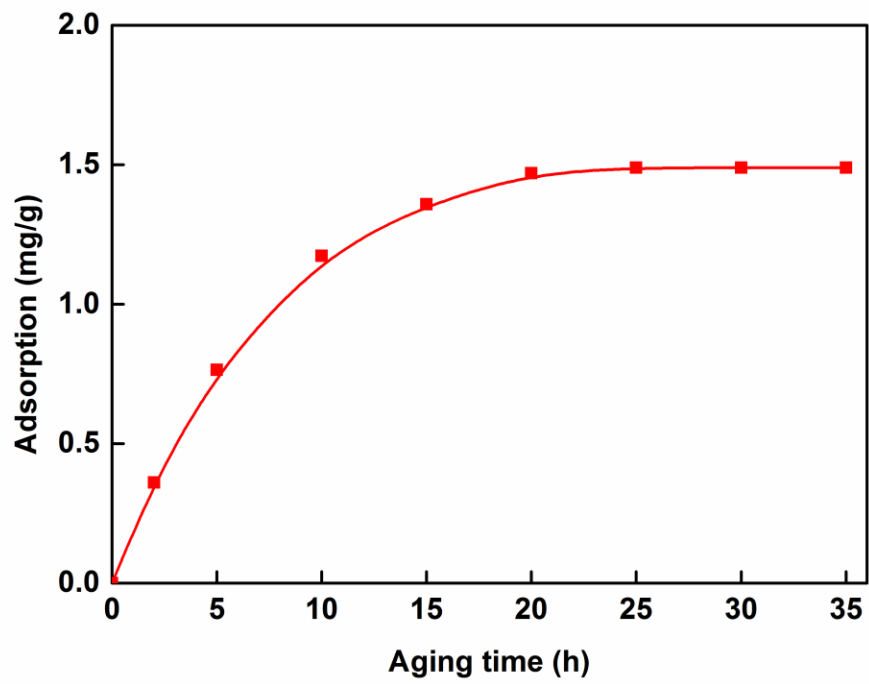


Fig. 3

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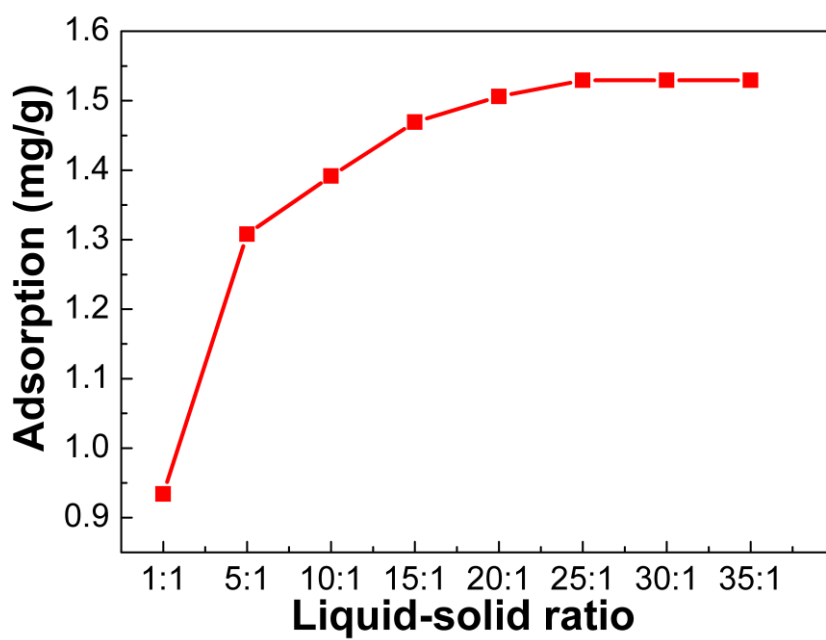
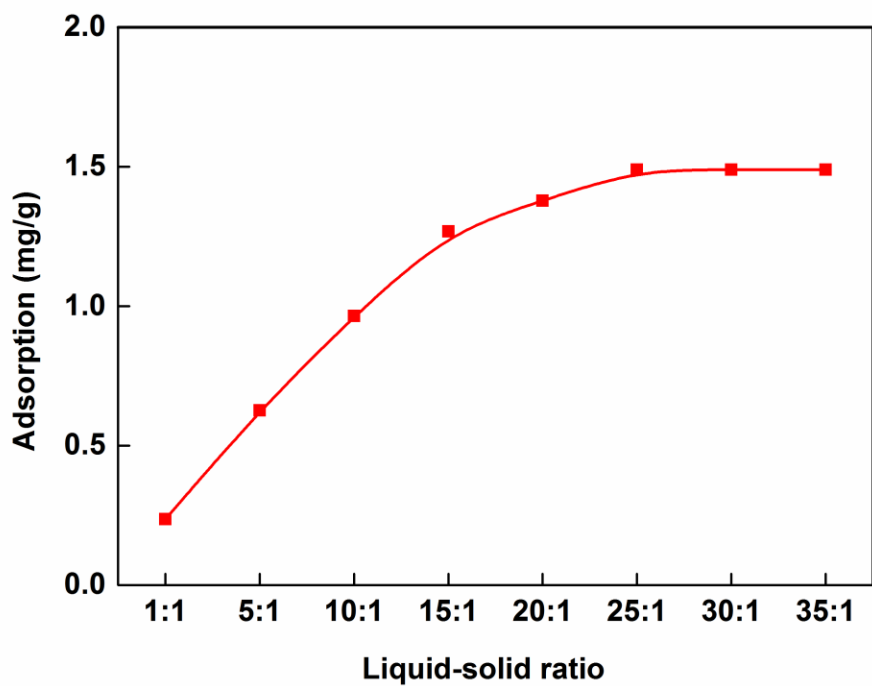


Fig. 4

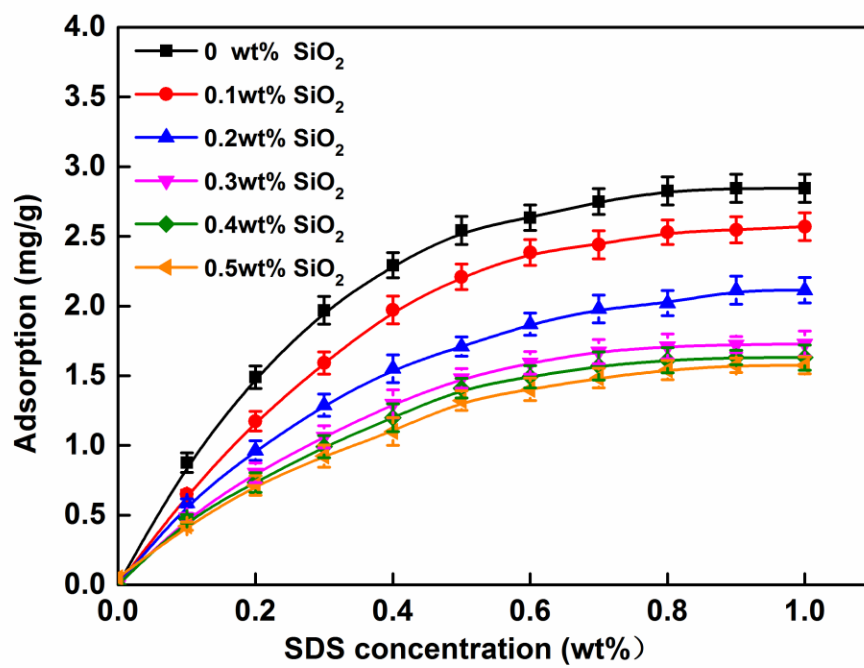


Fig. 5

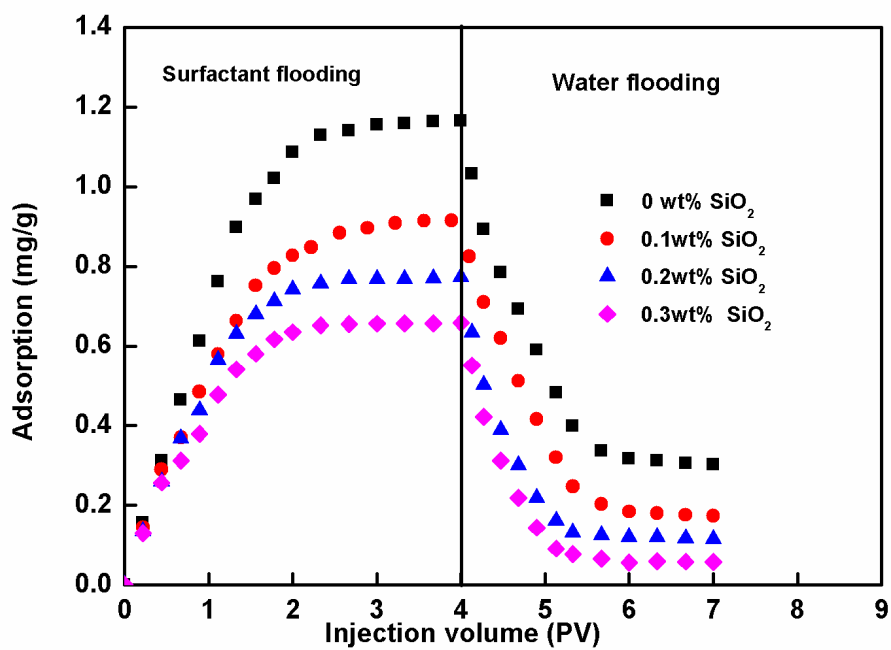


Fig. 6

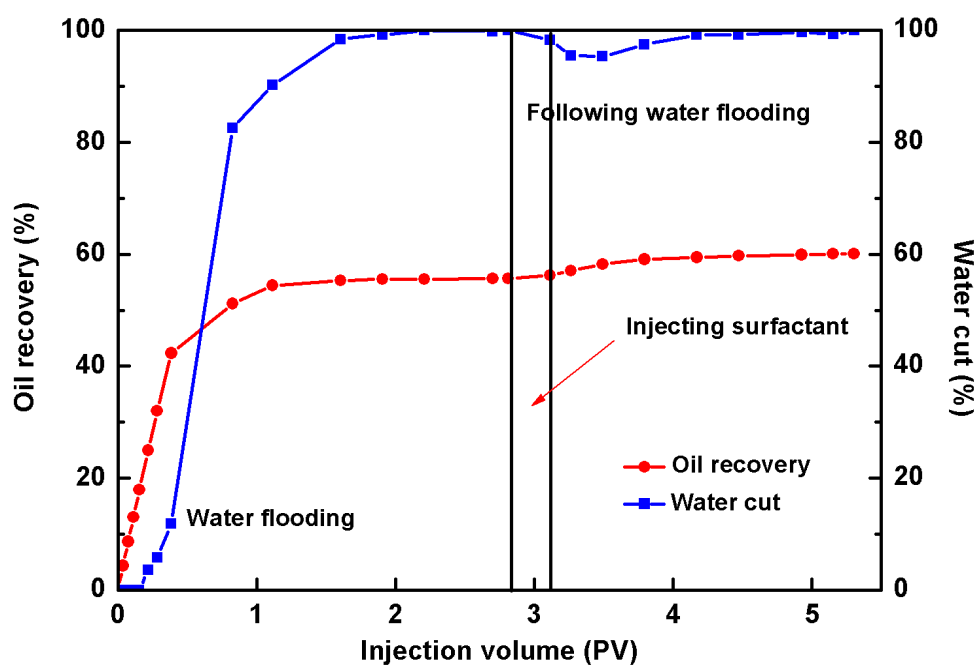


Fig. 7

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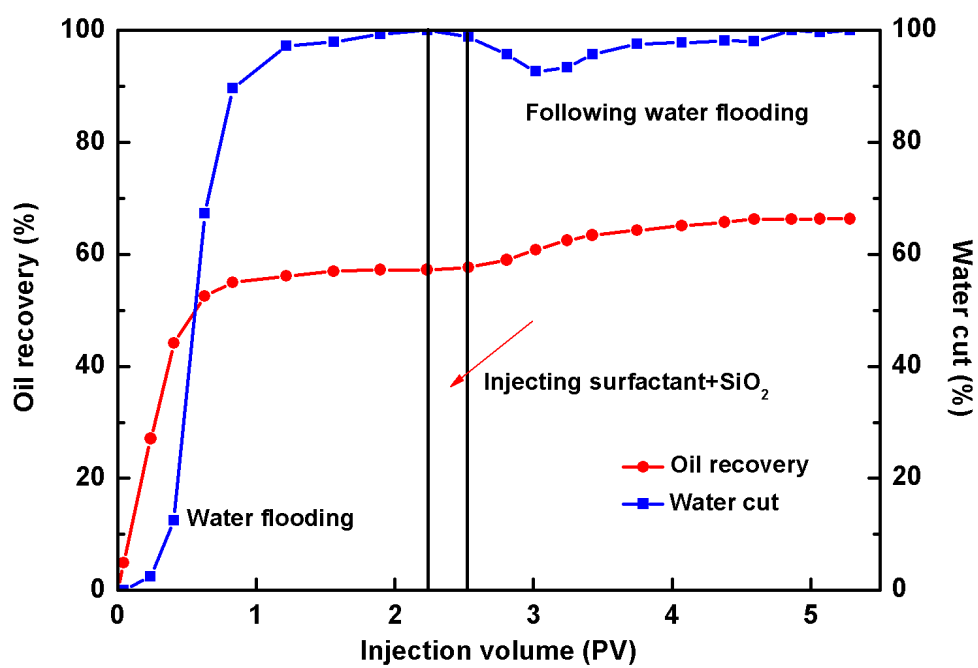


Fig. 8