Removal of Oil from SZ36-1 Simulated Oil Sands Using Sophorolipid Biosurfactant

Junqi Wang¹,², Juan Wang³, Sihao Dong³, Guobin Li³, Xiangping Kong¹,³*¹
¹The Key Laboratory of Well Stability and Fluid & Rock Mechanics in Oil and Gas Reservoir of Shaanxi province, Xi’an 710065, China
²School of Petroleum Engineering of Xi’an Shiyou University, Xi’an 710065, China
³College of Chemistry and Pharmacy, Qingdao Agricultural University, Qingdao 266109, China
*Corresponding author’s e-mail: kxp2004@163.com

Abstract. The sophorolipid biosurfactant was used to remove the oil from the SZ36-1 simulated oil sands. The effects of the sophorolipid concentration, the mass ratio of sophorolipid solution to oil sands (liquid/solid ratio), and the extraction time on the oil extraction efficiency were investigated. Based on the single-factor tests, the optimum results were obtained under the conditions of sophorolipid solution concentration to be 100 mg·L⁻¹, the liquid/solid ratio to be 50:1 and the extraction time to be 2 h. The corresponding oil extraction rate from oil sands reached up to 42%, which was comparable to the result from 2.5 g·L⁻¹ chemical surfactant of sodium dodecyl sulfate (the value of 2.5 g·L⁻¹ was higher than its critical micelle concentration). The oil extraction rate of crude oil with sophorolipid solution was almost not affected by the existence of sodium chloride. The sophorolipid biosurfactant has high surface activity and good oil removing capacity, and is expected to replace the synthetic surfactants to be used in petroleum exploitation and crude oil pollution treatment.

1. Introduction
At present, oil sands mining, tertiary oil recovery and oil pollution treatment have attracted the attentions of researchers in the petroleum industry[1-5]. Surfactants have been widely used in these industrial processes due to their good physicochemical characteristics such as detergency, emulsification, dispersion and solubilization effects[3]. Compared with traditional chemical synthetic surfactants, biosurfactants have excellent characteristics of high surface/interface activity, low toxicity, easy biodegradation, good temperature/salt tolerance[6], and have great application potential in these fields.

Sophorolipid is complex glycolipids comprised of the disaccharide sophorose linked to a hydroxy fatty acyl group by a glycosidic bond, and can be divided into two predominant forms: the macrolactone and the free carboxylic acid[6-8]. As one kind of important biosurfactants, the sophorolipid has been frequently used in medicine, cosmetics, environmental protection as well as petroleum exploitation. In this work, the oil extraction efficiency of sophorolipid solution from oil sands was investigated, and the results were compared with those from the common chemical surfactant of sodium dodecyl sulfate.
2. Experimental

2.1. Materials
Crude oil SZ36-1[9] (high viscosity, low wax, heavy oil) was produced by China National Offshore Oil Corporation. Sophorolipid[6] and 120° solvent oil were supplied by the Key Laboratory of Marine Chemistry Theory and Technology of Ministry of Education and Shanxi Sunshine Chemical Co., Ltd., respectively. The sands were taken from the Aoshanwei Beach of Jimo District, Qingdao. All the other chemicals used in this work were of analytical grade and all solutions were prepared with deionized water.

2.2. Methods
The SZ36-1 simulated oil sands were prepared according to the following method. The crude oil was extracted with chloroform to remove impurities. The lower organic layer was collected, and was evaporated at 40 °C to remove chloroform to obtain the crude oil for analysis. The sands were washed with 0.2 M acetic acid solution and were sterilized subsequently. The obtained crude oil was dissolved in petroleum ether, and poured into the sterilized sands, and then stirred and mixed thoroughly. After the petroleum ether was completely volatilized, it was naturally air-dried for 5 days to obtain simulated oil sands with the oil content of about 70 mg·g−1.

In the extraction experiments, effects of the sophorolipid concentration, the ratio of extraction agent to oil sands, and the extraction time were investigated with single-factor experiments. All the experiments were repeated three times, and the mean values were used as results for calculation and analysis. The oil extraction rate (R) from oil sands was calculated according to equation (1):

\[ R = \frac{C_0 - C}{C_0} \times 100\% \]  

where \( R \) is the oil extraction rate, %; \( C_0 \) and \( C \) are the oil contents in the original oil sands and the treated oil sands by surfactant solution, respectively, mg·g−1. \( C_0 \) and \( C \) were determined with the solvent oil extraction method[10]. The oil extraction rate was close to 100% under the conditions of mass ratio of 120° solvent oil to oil sands to be 10:1, repeated times of 3, extraction time of 40 min and extraction temperature of 75 °C by the magnetic stirring. The oil content of 120° solvent oil solution was measured with UV-2600 UV-Vis spectrophotometer (Shimadzu Scientific Instruments Inc., Japan).

The crude oil for analysis was dissolved in 120° solvent oil to obtain about 50 mg·L−1 oil solution. Taking 120° solvent oil as a control, a full scan with a wavelength of 200-600 nm was performed to get the UV-visible absorption curve of the oil solution using the UV-2600 UV-Vis spectrophotometer. The UV-visible absorption curve of 120° solvent oil was similarly obtained using deionized water as a control.

3. Results and discussion

3.1. The UV-visible absorption curve

![Figure 1. The UV-visible absorption curves of 120° solvent oil and crude oil solution](image1)

![Figure 2. Effect of the sophorolipid solution concentration on extraction rate of crude oil](image2)
As shown in Figure 1, both 120° solvent oil and crude oil have no absorption peak in the visible region, suggesting that the visible light region is not suitable for measuring crude oil content in 120° solvent oil solution. Taking 120° solvent oil as a control, the maximum absorption wavelength of crude oil is 228 nm. However, the absorption of 120° solvent oil is strong and the absorption intensity changes greatly near the wavelength of 228 nm, which can lead to large measurement errors. The wavelength of 228 nm is not suitable for determining the crude oil content in 120° solvent oil solution. At a wavelength of 260 nm, the crude oil has an absorption peak and the absorption intensity is almost unchanged near this wavelength. The absorption intensity of 120° solvent oil is weak, and there is almost no change around the wavelength of 260 nm. Thus, the background interference caused by 120° solvent oil is small, and the measurement results of crude oil content in 120° solvent oil solution has high accuracy. Therefore, the wavelength of 260 nm is found to be preferable for determining the crude oil content in 120° solvent oil solution.

3.2. The extraction experiments
The crude oil was dissolved in 120° solvent oil to obtain crude oil standard solutions at different concentrations of 10.00, 20.00, 30.00, 40.00 and 50.00 mg·L⁻¹, respectively. The absorbances of these standard solutions were measured at 260 nm using UV-2600 UV-Vis spectrophotometer. A standard curve was drawn based on the absorbances of the standard solutions and the corresponding mass concentrations, and the linear regression equation was A=0.0183ρ−0.0074 with R² of 0.9990. The crude oil from oil sands and treated oil sands with sophorolipid solution was extracted with 120° solvent oil, respectively. Then the absorbance was measured, and the crude oil content in 120° solvent oil solution was obtained according to the standard curve. Thus, the oil extraction rate could be calculated.

3.2.1. Effect of sophorolipid solution concentration on oil extraction rate. At room temperature, the effect of sophorolipid solution concentration on oil extraction rate was tested with sophorolipid solution to oil sands of 50:1 (m:m) and extraction time of 6 h under the electromagnetic stirring conditions. As shown in Figure 2, the oil extraction rate increased rapidly within the sophorolipid solution concentrations of 0 to 50 mg·L⁻¹, and then increased steadily within the concentrations of 50 to 100 mg·L⁻¹ until it remained almost unchanged. It may be explained by the critical micelle concentration (CMC) of sophorolipid solution. When the sophorolipid solution concentration is lower than the CMC, the surface activity of sophorolipid solution increases rapidly as the concentration of the sophorolipid solution increases. Correspondingly, the oil extraction rate will increase rapidly with the increasing sophorolipid solution concentration. The CMC of sophorolipid solution is about 36.5 mg·L⁻¹[6], so the oil extraction rate increases rapidly as the concentration of the sophorolipid solution increases at concentration of lower than 50 mg·L⁻¹. When the concentration of the sophorolipid solution is within 50 to 100 mg·L⁻¹ (slightly higher than CMC), the surface activity of sophorolipid solution and the oil extraction rate increase steadily with the increasing sophorolipid concentration. When the concentration of the sophorolipid solution is larger than 100 mg·L⁻¹ (far higher than the value of CMC), the surface activity of sophorolipid solution and the oil extraction rate almost do not change with the increasing sophorolipid concentration. Therefore, considering the extraction efficiency and economic factors, the concentration of the sophorolipid solution was selected to be 100 mg·L⁻¹.

3.2.2. Effect of sophorolipid solution to oil sands ratio on oil extraction rate. The effect of mass ratio of sophorolipid solution to oil sands (liquid/solid ratio) on oil extraction rate was investigated with sophorolipid solution concentration of 100 mg·L⁻¹ and extraction time of 6 h. As can be seen from Figure 3, the oil extraction rate of crude oil first increased and then decreased slightly with the increased ratios of liquid/solid. When the ratios were less than 50:1, increasing the values of ratio resulted in the increased contact between the oil sands and the solvent, thereby increased the oil extraction rate. When the liquid/solid ratio was higher than 50:1, the oil sands and the solvent could
not be mixed completely under the electromagnetic stirring condition, which lead to the slightly decrease of oil extraction rate. As shown in Figure 3, the maximum oil extraction rate of slightly higher than 42% was obtained when the liquid/solid ratio was 50:1. Thus, 50:1 was chosen as the optimum ratio of sophorolipid solution to oil sands.

3.2.3. Effect of extraction time on oil extraction rate. The effect of extraction time on oil extraction rate was tested with liquid/solid ratio of 50:1 and sophorolipid solution concentration of 100 mg·L⁻¹ under the electromagnetic stirring conditions. As shown in Figure 4, the oil extraction rate increased in the first 2 hours, and then remained almost constant with the increase of extraction time. The dissolution of crude oil in the sophorolipid solution needs a certain amount of time. After the sophorolipid solution and oil sands interacted for 2 hours, the crude oil was in a dissolved equilibrium state in the sophorolipid solution, and the maximum oil extraction rate of about 42% was obtained. Therefore, the extraction time was selected to be 2 hours.

![Figure 3. Effect of the mass ratio of sophorolipid solution to oil sands on extraction rate of crude oil](image)

![Figure 4. Effect of the extraction time on extraction rate of crude oil](image)

3.3. Effect of NaCl concentration
The effect of NaCl concentration on oil extraction rate was investigated with liquid/solid ratio of 50:1, the sophorolipid solution concentration of 100 mg·L⁻¹ and extraction time of 2 h. When the concentrations of sodium chloride were 10, 30, 50, 80 and 100 g·L⁻¹, respectively, the oil extraction rates of crude oil were all slightly higher than 42%, which was consistent with no existence of sodium chloride. The results showed that the oil extraction rate of crude oil with sophorolipid solution was almost unaffected by concentrations of NaCl, which could be explained by the fact that the surface activity of sophorolipid solution was almost not affected by existence of inorganic salts[8].

3.4. Comparison with sodium dodecyl sulfate solution
Sodium dodecyl sulfate (SDS) is one of the widely used chemical surfactants in petroleum exploitation and crude oil pollution treatment. Therefore, the ability of the sophorolipid biosurfactant to extract crude oil from the oil sands can be estimated by comparing the crude oil extraction rates of the sophorolipid solution to those from the SDS solution. The crude oil extraction rates using 100 mg·L⁻¹ sophorolipid solution and 2.5 g·L⁻¹ SDS (the CMC is about 2.3 g·L⁻¹) were investigated with agent to oil sands ratio of 50:1 and extraction time of 2 h, respectively. The oil extraction rates from oil sands using the sophorolipid solution and SDS were 42.8% and 43.4%, respectively. It suggested that sophorolipid biosurfactant with much lower concentration could achieve comparable oil extraction efficiency to chemical surfactant SDS of higher concentration.

4. Conclusions
The optimum conditions for the oil removal from SZ36-1 simulated oil sands using sophorolipid biosurfactant were obtained with sophorolipid solution concentration of 100 mg·L⁻¹, the liquid/solid
ratio of 50:1 and extraction time of 2 h. Under these conditions, the oil extraction rate from oil sands could reach up to 42%, which was comparable to the result from 2.5 g·L\(^{-1}\) chemical surfactant of SDS. The oil extraction rate of crude oil with sophorolipid solution was almost not changed with the increasing concentration of sodium chloride. The sophorolipid biosurfactant is expected to replace the synthetic surfactants to be used in the petroleum exploitation and crude oil pollution treatment.

**Acknowledgments**

This work was subsidized by the Key Research & Development Plan Project of Shaanxi Province of China (2018KW-037), the Open Project of the Key Laboratory of Well Stability and Fluid & Rock Mechanics in Oil and Gas Reservoir of Shaanxi Province of China (WSFRM20180303003) and the Students’ Innovation Education Project Funds of Qingdao Agricultural University.

**References**

[1] Kim, S.-J., Choi, D.H., Sim, D.S., Oh, Y.-S. (2005) Evaluation of bioremediation effectiveness on crude oil-contaminated sand. Chemosphere, 59: 845-852.

[2] Saxena, N., Kumar, S., Mandal, A. (2018) Adsorption characteristics and kinetics of synthesized anionic surfactant and polymeric surfactant on sand surface for application in enhanced oil recovery. Asia-Pac. J. Chem. Eng., 13(4): 1-14.

[3] Bera, A., Kumar, T., Ojha, K., Mandal, A. (2013) Adsorption of surfactants on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies. Appl. Surf. Sci., 284: 87-99.

[4] Fu, L.P., Zhang, G.C., Ge, J.J., Liao, K.L., He, Y.F., Wang, X., Li H.T. (2017) Study on dual-frequency ultrasounds assisted surfactant extraction of oil sands. Fuel Process. Technol., 167: 146-152.

[5] Zou, C.J., Zhao, P.W., Ge, T.T., Li, D., Ye, H., Huang, G. (2016) Bitumen recovery from Buton oil sands using a surfactant under the effect of ultrasonic waves. Energ. Source. Part A, 38(2): 270-276.

[6] Song, D.D., Liang, S.K., Wang, J.T. (2011) Structure characterization and physi-chemical properties of sophorolipid biosurfactants. Environ. Chem., 30(8): 1474-1479 (in Chinese).

[7] Sembayeva, A., Berhane, B., Carr, J.A. (2017) Lipase-mediated regioselective modifications of macrolactonic sophorolipids. Tetrahedron, 73(14): 1873-1880.

[8] Wang, J., Kong, X.P. (2015) Interaction of sophorolipids with polyacrylamide. Appl. Chem. Ind., 44(9): 1655-1658 (in Chinese).

[9] Zhang, R.H., Qu, T., Dai, C.Y. (2002) Make the best use of crude oil SZ36-1 to produce premium bitumen. Petrol. Asphalt, 16(3): 46-49 (in Chinese).

[10] Han, D. Y., Cao, Z. B., Xu, X. Q. (2013) Study on solvent extraction of Mongolia outcrop oil sands. Energ. Source. Part A, 35(14): 1368-1374.