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Fluid-to-Fluid and Fluid-to-Rock Interaction on Sophorolipids Biosurfactant for Enhanced Oil Recovery: A Literature Review

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ABSTRACT - The promising glycolipids produced by non-pathogenic yeast as biosurfactants are called sophorolipids. Their advantages over chemical surfactants are that they give smaller environmental impact, have lower level of toxicity and are biodegradable. They can reduce interfacial tension (IFT), form microemulsions and alter wettability in enhanced oil recovery applications. In reservoir conditions, sophorolipids become potential as biosurfactants due to the resistance to both high salinity and high temperature. Laboratory experiments to enhance oil recovery (EOR) applications require to test fluid-to-fluid and fluid-to-rock interactions in the complex crude oil–rock–brine (CORB) system. This review discusses the sophorolipid mechanisms of fluid-to-fluid and fluid-to-rock interactions. The potency of sophorolipids in EOR processes can be determined by core flooding experiments, in which some research reported the incremental oil recovery obtained up to 20%. The review and discussion in this article are intended to have a broad impact on science and petroleum industries, particularly in EOR applications.

Keywords: sophorolipids, biosurfactant, fluid-to-fluid, fluid-to-rock.

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INTRODUCTION

A sophorolipid is a biosurfactant comprising sophorose sugar molecules and fatty acids. It acquires two dominant components namely a hydrophilic head and a hydrophobic tail. A sophorolipid hydrophilic head is made up of two sophorose molecules joined by a glycosidic link, which makes it polar and watersoluble (Desai & Banat 1997). The hydrophobic tail, on the other hand, comprises one or two fatty acid chains, such as oleic acid or palmitic acid rendering it insoluble in water but soluble in oil or hydrocarbons (Van Bogaert et al. 2007). The sophorolipid is classified as a nonionic surfactant since it lacks an electric charge or ionizable functional groups. Its uncharged hydrophilic head exhibits little attraction for ions, yet, its hydrophobic tail can interact with oil or hydrocarbons making it efficient as a surface tension–reducing agent and aiding in oil production efficiency in applications of enhanced oil recovery (EOR) as mentioned by (Sharma et al. 2018), Rocha et al. (2021) and Pal et al. (2023).

In laboratory tests for EOR applications, the fluid-to-fluid and fluid-to-rock interactions in the complex crude oil–rock–brine (CORB) system need to be considered (Buckley 1996); (Udoh & Vinogradov 2019). The fluid-to-fluid interactions in biosurfactant injection mechanisms include the effects of carbon chain degradation, microemulsion viscosity, and interfacial tension (IFT) reduction (Pandey, Krishnamurthy, Singh, et al. 2022). On the contrary, in fluid-to-rock interactions, wettability alteration and rock adsorption levels can be observed. Furthermore, pH conditions, salinity, and the addition of certain ions can affect the performance of biosurfactants on carbonate rocks (Shaik et al. 2020); (Bassir & Shadizadeh 2020).

The two major constraints of surfactant injection are (i) high salinity and high reservoir temperature and (ii) excessive surfactant adsorption on the rock surface impeding the recovery of trapped oil from the pores inside the rock. The identified reasons of surfactant adsorption are ion exchange, ion association, hydrophobic bonding, dispersion forces, electrostatic attraction, van der Waals forces, and electron polarization (Kamal et al. 2019; Paria & Khilar 2004; SARI et al. 2017; Zhang & Somasundaran 2006).

This review article details the sophorolipid mechanism in EOR and explains the dominant mechanism in sophorolipid injection.

Currently, to the authors' knowledge, there is no available literature comprehensively reviewing the carbon chain degradation, IFT values, microemulsion viscosity, wettability alteration, and adsorption in regards to sophorolipid injection on incremental oil recovery through coreflooding.

METHODOLOGY

Sophorolipids

Candida bombicola, C. petrophilum, and C. apicola are the primary producers of sophorolipids constituted by a dimer of the carbohydrate sophorose

connected to a long chain hydroxy fatty acid (Figure 1). This biosurfactant is a blend of six to nine distinct hydrophobic sophoroside molecules (Oliveira et al. 2018).

Similar water-soluble sophorolipid combinations from other fungi have also been described (Ron & Rosenberg 2001). For instance, Candida bogoriensis creates a glycolipid in which sophorose is connected to docosanoic acid, as demonstrated by Cutler and Light (Gautam & Tyagi 2006). Figure 1 shows the general structure of sophorolipids.



Structure of sophorolipids (Maeng et al. 2018)

These microorganisms produce surface-active compounds that have amphipathic properties, meaning they have both hydrophilic and hydrophobic regions. In water environments, these biosurfactants are able to spontaneously self-assemble into molecular clusters called micelles. Biosurfactants are used in a range of industrial products, including petrochemicals, foods, pharmaceuticals, cosmetics, agrochemicals, and pesticides. They provide benefits over chemically synthesized surfactants, such as being more sustainable, environmentally friendly, and biodegradable. Biosurfactants have properties to reduce surface tension, ease emulsification, modify wetting, and form foaming which make them useful in various applications. Its characteristics can be utilized in oil industries as enhanced oil recovery (EOR) (Pal et al. 2023).

Fluid-to-Fluid and Fluid-to-Rock Interaction on Sophorolipids Biosurfactant for Enhanced Oil Recovery: A Literature Review (Taufan Marhaendrajana et al.)

N	Author	Year	Sample				
No			Core	Oil	Brine	Biosurfactant	RF %
1.	Adelzadeh et al.	2010	Iran Oil Well	Iran Oil Field	synthetic brine	Bacteria (Pseudomonas aeroginosa MR01)	20
2.	Al- Sulaimani et al.	2011	Omani Core plug	Omani Oil Field	Omani Water Formation	Bakteri (Bacillus subtilis)	23 (10 + 13)
3.	Ghojavand et al.	2012	Iranian Oil Field	n- hexadeca ne	synthetic brine	Bacteria (Bacillus mojavensis)	15 - 23
4.	Al-Wahaibi et al	2014	Oman Oil Fields	Berea Sandstone	Oman Formation Water	Bacteria (Bacillus subtilis B30)	17-26 and 31
5.	Elshafie et al	2015	Berea sandstone	Omani Oil Field	synthetic brine	Sophorolipids by Candida bombicola	27.27
6.	Hadia et al.	2019	Berea sandstone	Oil from Field (27.3 and 41.6° IPA	synthetic brine	Bacteria (Bacillus subtilis)	1.3-5
7.	Astuti et al.	2019	South Sumatra Heavy and light oil	Sand Pack	South Sumatra Brine	Bacteria (Pseudoxanthomo nas sp. G3)	20
8.	Sulistyarso et al.	2020	Synthetic Core plug sandstone	Kawenga n Oil Field	Kawengan Water Formation	U-Champ	37.5
9.	Imanivarnos faderani et al.	2021	Calcite core	n-decane	Low saline brine	Rhamnolipid dan SDBS	14.98
10.	Aboelkhair et al.	2022	Egyptian field	Egyptian oil field	Egyptian oil field	Bacteria (various reservoir)	25 - 39

Table 1 Presents the oil recovery factor from coreflooding tests of various biosurfactants.

Crude Oil-Rock-Brine (CORB)

Buckley (1996) described CORB system as a system which is complicated involving interactions that are fluid-to-fluid and fluid-to-rock. The interaction belongs to a sophisticated phenomenon that affects the mechanism of oil movement within the pores of reservoir rocks.

The main categories of CORB interactions identified so far include the following (Figure 2): Crude oil comprises numerous chemical components, including organic acids, organic bases and other polar substances that can engage the rock surface. Polar chemicals, like asphaltene and resins, are able to adsorb onto the rock surface altering the rock wetting qualities; The ion concentration in brine (including Na⁺, Cl⁻, Mg²⁺, Ca²⁺) influences the interaction between oil and rock. Brine can facilitate the development of adsorption layers on the rock surface influencing the distribution of oil-water phases within the rock pores; Reservoir rocks may exhibit hydrophobic (oil-wet), hydrophilic (waterwet), or mixed-wet properties, contingent upon the historical interactions of oil, rock and water. The chemical and physical interactions of oil, brine, and rock dictate wettability, a crucial element in the efficiency of EOR techniques; Wettability is strongly influenced by the balance between the adsorption of polar compounds in the crude oil and the interaction of ions from the brine with the rock surface. Buckley emphasizes that changes in wettability can occur due to modifications in brine composition or the addition of surfactants and other chemicals.



CORB Interactions flow chart

RESULT AND DISCUSSION

Fluid-to-fluid interactions

Carbon chain degradation

Pandey et al. (2022) conducted a specific study related to the potential degradation of the bacteria in conditions whether there is the assistance of biosurfactants. The GC fingerprints of the bacterial culture demonstrated that incorporating biosurfactants significantly influenced both the n-hexadecane and diesel degradation. In the period of incubation, the bacteria themselves degraded 26.68% of n-hexadecane and 48.36% of diesel. Abiotic losses were determined to be 1.64% for n-hexadecane and 9.20% for diesel. An increased degradation rate was also noted in the context of biosurfactant-assisted degradation. The isolate demonstrated improved degradation of 77.33% for diesel and 55.98% for n-hexadecane using crude biosurfactant throughout a 7-day incubation period. N-hexadecane and diesel degradation by bacteria was facilitated by glycolipopeptide biosurfactants. Biosurfactants are not the sole determinants of petroleum hydrocarbon degradation. Other bacterium genes and their protein products possess a potency to contribute hydrocarbon solubilization which differ by some factors in different environments (Pandey, Krishnamurthy, Pal, et al. 2022; Sari & Kussuryani 2013).

The hydrophobicity data studied by (Saborimanesh & Mulligan (2015) indicated that the bacteria metabolized hydrocarbons primarily alter the structures of cell surface during natural biodegradation and enhance the hydrocarbon micellar dispersion in the biodegradation treatment requiring sophorolipid.

The investigation validated a substantial role of indigenous bacteria in the biodegradation of weathered diesel, biodiesel and light crude oil. It also confirmed the sophorolipid benefits on this process (Kadarwati & Herlina 2022; Saborimanesh & Mulligan 2015).

Abidin et al. (2023) confirmed the existence of functional groups and the chemical structure of biosurfactants, consistent with most prior research. The micellization of biosurfactants occurred spontaneously and released heat. Higher temperatures reduced the water content of the hydrophilic rhamnose groups, facilitating micelles formation at lower concentrations within 24 to 72 hours. The suggested minimum biosurfactant concentration to be included in the oil degreaser formulation is 0.1% w/v, which is considered very low. This study elucidated the variables that impact the effectiveness of oil degreasing, such as temperature and concentration (Abidin et al. 2023).

The sophorolipid was examined for its ability to improve bioavailability and biodegradation of crude oil. It exhibited superior soil flushing efficiency compared to all other evaluated nonionic surfactants. Moreover, it was the most effective agent for increasing biodegradation of manufactured pollutants, including n-hexadecane, 2-methylnaphthalene, and pristine. Sophorolipid is also applicable and acceptable for the soil bioremediation of non-polar refined oils, including diesel, gasoline, and kerosene. The results suggest that sophorolipid may facilitate the bioremediation of hydrocarbon-contaminated locations which requires low water solubility and that sophorolipid may enhance the microbial consortia bioavailability for biodegradation (Kang et al. 2010). Sophorolipid surfactants are commonly employed in sludge research due to their excellent emulsification properties and the notable reduction of water surface tension supporting the separation of oil and sediment (Liu et al. 2019).

Microemulsion viscosity

Biosurfactants can be utilized to produce enduring emulsions with a prolonged shelf life (Gudiñaand & Rodrigues 2019). They can also stabilize emulsions. Biosurfactants which require high molecular weight are typically more efficient to be emulsifiers. T. Bombicola sophorolipids were discovered the lower surface and interfacial tension, although (Manga et al. 2021) reported that they exhibit limited emulsifying properties.

They have the ability to emulsify several types of hydrophobic substances (Figure 3), such as vegetable oils, hydrocarbons like n-hexadecane (25.19%), crude oil (100%), diesel (25%), machine oil (60.7%), kerosene (56.7%), and more (Sen et al., 2017); (E. F. Ahuekwe et al. 2016).

The biosurfactant addition to the crude oil sample is able to change the microemulsion viscosity (Singh & Cameotra 2004). According to (Budiharjo 2020), it can reduce the microemulsion viscosity of the mix sample (Geetha et al. 2018). This study shows that as the concentration of biosurfactant increases, the microemulsion viscosity decreases.

Additionally, as temperature increases, microemulsion viscosity decreases and it stabilizes at high temperatures (Budiharjo S. et al. 2020).



Figure 3 Emulsify Ability of Sophorolipids

Interfacial tension (IFT)

The lower the IFT value, the more easily the task of biosurfactants to facilitate oil flow within the rock pores. Biosurfactants reduce IFT by adsorbing at the interface between two types of fluid, utilizing the groups of polar and non-polar presented in the biosurfactant (Joice & Parthasarathi 2014). The use

of biosurfactants enhances capillary forces within the porous media, leading to the improved oil recovery (Negin et al. 2017).

Biosurfactants can disperse oil within the water system, creating low IFT (Zhao et al. 2015). This dispersion begins at the outer part of the oil droplets. Before adding biosurfactants, the oil appears as spherical droplets. After the addition, the oil elongates and thins. As a result, the droplets can exit the rock pores out (Viades-Trejo & Gracia-Fadrique, 2007); (Prasad et al. 2021).

Elshafie et al. (2015) has stated that the production of sophorolipid biosurfactant using Candida bombicola ATCC 22214 demonstrates a decrease in surface tension from 28.56 to 0.42 mN/m and IFT from 2.13 to 0.09 mN/m within 72 hours. Santos et al. (2016) has reported that efficiency and effectiveness belong to the critical characteristics of a qualified surfactant. The critical micelle concentration (CMC) has been used to measure the efficiency, whereas interfacial tension has been used to measure effectiveness (Zeng et al. 2018). Biosurfactant CMCs range from 1 to 2000 mg/L with appropriately interfacial (oil-water) and surface tensions of around 1 and 30 mN/m.

An efficient biosurfactant can reduce water surface tension from 72 to 35 mN/m and n-hexadecane IFT from 40 to 1 mN/m (Dong et al. 2019). The CMC value of roughly 10-2 mN/m, as seen in Figure 4, is considered modest compared to chemical surfactants. Hence, the biosurfactant process plays a minor role in decreasing interfacial tension when it comes to enhance oil recovery.

Fluid-to-Rock Interactions

Wettability Alteration

The addition of biosurfactants has a strong impact on the wettability alteration (Ghojavand et al. 2008), influencing reservoir characteristics, such as relative permeability fluid distribution in rock pores and fluid flow behaviour during recovery processes (Austad & Standnes 2003). Sandstone, for example, has homogeneous wettability because of its consistent mineralogy and lower organic content than that occurs in shale (Wang et al. 2011); (Boneau & Clampitt 1977).

The wettability of rocks can be determined by measuring the contact angle, which is based on the IFT balance at the water–oil–rock system surface using Young's equation. The wettability of rock surfaces is categorized as water-wet from 0° to 75° , intermediate-wet from 75° to 105° , and oil-wet from 105° to 180 (Standnes 2001).

Any changes occurring on surface wettability qualities of reservoir rocks leads the adjustments in

surface wettability postulated as one of the major mechanisms for the microbial enhanced oil recovery (MEOR) (Elazzazy et al. 2015). Biosurfactants metabolized by Bacillus subtilis B30 reduced the hydrophobic surface contact angle from 58.7 0.85° to 28.4 1.03° and 27.2 0.72° , according to (Al-Wahaibi et al. 2014; Al-Sulaimani et al. 2011, 2012), previously discovered that biosurfactants metabolized by Bacillus subtilis W19 reduced the water contact angle from 70.6 0.3° to 25.32 0.06° at 0.25% (w/v).

Long-term crude oil immersion was used by Liu et al. (2021a 2021b) to treat hydrophobic core samples with varying permeabilities. They discovered that biosurfactants changed the hydrophobic wettability of the core sample surfaces by the increased water wetting found in cores with varied permeabilities (Batista et al. 2006). The contact angle of core samples with a permeability of 0.1 mD dropped from 103.2° to 68.6° after three days of biosurfactant immersion and to 30.9° after 28 days of immersion. The contact angle of core samples with permeabilities of 1 mD dropped from 108.5° to 65.4° after three days of biosurfactant immersion and to 34.6° after 28 days of immersion. Finally, for core samples with a permeability of 100 mD, the contact angle decreased from 91.7° to 61.7° after three days of biosurfactant immersion and to 30.9° after 28 days of immersion (Bordoloi & Konwar 2008).

Zezzi do Valle Gomes & Nitschke (2012) applied contact angle measurements to assess the rhamnolipid and surfactin effectiveness to reduce bacterial adhesion on surfaces. The contact angle is the angle between the liquid and the surface in contact. A smaller contact angle allows the liquid to spread on the surface more easily and tends to exhibit more hydrophilic (water-friendly) surface properties (Fardami et al. 2022).

On the other hand, a more extensive contact angle limits the spread of liquid on the surface and tends to exhibit more hydrophobic (water-repellent) surface properties.

In a recent study, the contact angle results for rhamnolipids at concentrations of 0.25%, 0.5%, and 1% were 72.47°, 64.19°, and 11.45°, respectively (Gayathiri et al. 2022).

Most reservoir formations consist of a mixture of silica, clays, limestone, and dolomite. Based on the

wettability tendency of the silica matrix component, most oil reservoirs are assumed to have a water-wet nature (Adelzadeh et al. 2010). However, many oil-wet reservoirs have been discovered through laboratory analysis by measuring the contact angle between fluids and reservoir rocks from various regions worldwide (Tobergte & Curtis 2013). I.K. Shaik et al. (2019); Shaik et al. (2020) examined the impact of wettability alteration in biosurfactant injection on carbonate rock using various types of brine. The addition of different ions to the brine affected the wettability properties of the rock, as determined through contact angle (Figure 5).



Wettability of biosurfactant (Shaik et al. 2020)

Adsorption

The majority of chemical EOR applications take place in sandstone reservoirs, with only a few stimulation initiatives in carbonate reservoirs (Sheng 2013). One of the reasons for the limited usage of surfactants in carbonate reservoirs is the strong adsorption of anionic surfactants in carbonates. Another reason for high alkalinity is the presence of anhydrite in carbonates, which causes precipitation. Bassir and Shadizadeh (2020) conducted static adsorption tests (Figure 6) of biosurfactants with cationic and nonionic properties on carbonate minerals.

The study revealed that higher adsorption occurred with biosurfactants exhibiting cationic properties compared to those with nonionic properties (Nikolova & Gutierrez 2021).



Adsoption test of biosurfactants (Bassir & Shadizadeh 2020)

Core flooding

Elshafie et al. (2015) conducted core flooding studies which showed that using sophorolipids could recover 27.27% of trapped residual oil (Sor) within the pores of Berea sandstone cores (Elshafie et al. 2015). This result indicates that sophorolipids can be utilized effectively as biosurfactants in MEOR applications to enhance oil production from oil reservoirs (Shekhar et al. 2015).

Ahuekwe et al. (2016) discussed the production of sophorolipids from oil waste and rice bran and the application of sophorolipids in the oil and gas industry (E. Ahuekwe et al. 2016). Their research findings indicate that Candida species can produce more sophorolipids compared to Pleurotus. Similarly, crude palm oil waste and rice bran were found to be highly effective carbon sources in the production of sophorolipids (Varjani & Upasani 2016).

Furthermore, this analysis of the literature shows that sophorolipids have a large potency in the oil and gas business, notably in EOR procedures, where a 12.3% crude oil recovery was achieved after injecting the culture supernatant (Ghojavand et al. 2012).

After injecting a concentration of a sophorolipid solution, an extra recovery of 15.7% of residual oil was reported (Sari et al. 2019). Another study (Table 1) found that utilizing biosurfactant-based microorganisms can boost RF by 5-20% (Hadia et al., 2019); (Astuti et al., 2019); (Imanivarnosfaderani et al. 2022); (Aboelkhair et al. 2022).

Budiharjo et al. (2020) conducted core flooding tests on biosurfactants using sandstone synthetic cores.

This experiment shows an increase in the oil recovery factor (RF) of up to 37.5% with the addition of soaking-time biosurfactant. Summary of the coreflooding recovery can be seen in Table 1.

Sophorolipids mechanism

Sophorolipids biosurfactants have a key mechanism that differs from common chemical surfactants in enhanced oil recovery (EOR). The optimal function of biosurfactants relies not alone on the lowering of interfacial tension (IFT), but more comprehensively, on their influence in altering the physicochemical parameters of the reservoir environment. The primary processes of biosurfactants that contribute to their efficacy are as follows:

Wettability alteration

Biosurfactants can alter the wetting characteristics of reservoir rocks from oil-wet or mixed-wet to water-wet. This alteration in wettability facilitates the extraction of oil confined inside the minute pores of the rock, thus enhancing oil recovery efficiency. This occurs when biosurfactants adsorpt onto the rock surface and compete with the previous adsorbed oil molecules.

Oil dispersion (Oil mobilization)

Biosurfactants can create stable oil-water emulsions or microemulsions, facilitating the mobilization of crude oil from rock pores. This capability is more substantial than IFT reduction alone, particularly for oil confined in low porosity regions.

Reduction in interfacial tension

While biosurfactants may not consistently attain ultra-low interfacial tension levels comparable to commercial surfactants, they facilitate a reduction in interfacial tension to enhance oil mobility within rock pores.

Ion interaction in brine

More stability is frequently shown by biosurfactants in harsh reservoir conditions, such as salinity and temperature elevation. Biosurfactants can engage the ions in brine to inhibit or diminish scale development and decrease fouling potential.

Biocompatibility and degradation of viscous oils

Biosurfactants can facilitate the biodegradation of complex hydrocarbon components, such as asphaltene and resins in heavy oils. Hence, oil mobilization is enhanced.

Biosurfactants offer several advantages over chemical surfactants, including environmental friendliness (they degrade naturally and exhibit lower toxicity), effectiveness in extreme conditions (they remain stable at elevated temperatures, high salinity, and extreme pH levels), and compatibility with reservoirs (they reduce the risk of formation damage due to more selective adsorption). The principal mechanism of optimal biosurfactant involves a combination of wettability alteration, oil mobilization via emulsification (Figure 7) and a synergistic effect on reservoir physicochemical conditions. Although the decrease in interfacial tension (IFT) may be less pronounced than that of chemical surfactants, this process offers a benefit in more demanding reservoir conditions.





Figure 7 Sophorolipids mechanism

CONCLUSIONS

Sophorolipid biosurfactants outperform chemically manufactured surfactants in terms of biodegradability, environmental impact, foamability, specific activity at severe temperatures, pH levels, and salinities. Sophorolipids have the ability to degrade the carbon chains and lower the IFT, although this is not the primary mechanism. They have the ability to create microemulsions that enhance fluid mobility when passing through porous media.

The dominant mechanism of sophorolipids is wettability alteration and formed microemulsion, representing a substantial prospect to improve oil recovery.

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Symbol	Definition	Unit	
EOR	Enhanced Oil Recovery		
CORB	Crude Oil-Rock-Brine		
IFT	Interfacial Tension	mN/m	
CMC	Critical Michelle	mN/m	
CIVIC	Concentration		
CA	Contact Angle	0	
Co	Concentration	%	
qe	Adsorbat teradsorpsi	mg/g-rock	
RF	Recovery Factor	%	

GLOSSARY OF TERMS

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