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A mini-review on biosurfactants from natural-based resources: Sources, production, and application in oil industries

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ABSTRACT

Increasing energy demand and depletion of producing wells around the globe necessitate oil industries to seek alternative mechanisms to increase oil production. Among various chemical enhanced oil recovery (CEOR) unveiled today, surfactants have become indispensable chemical agents in oil industries because of their wide applications in both onshore and offshore operational activities. Unfortunately, considerable numbers of these surfactants are synthetic causing treatment and disposal of effluents uneconomical to oil industries. This arises due to strong legislation laws enforced by governing bodies to ensure cleaner and safer environments. Consequently, the search for biodegradable surfactants from natural-based resources has revolved around the oil industries aimed at reducing the impacts of synthetic products both environmentally and economically. Plants are widely recognised as natural resources to obtain biosurfactants from their naturally producing saponins. In addition, other chemical compounds derived directly from plant parts are converted to biosurfactants commonly referred to as green biosurfactants. However, researchers have expressed reservations about sustainable biosurfactant production from plants due to limited access to plant resources. The present review discusses the types, properties, sources, synthesis, and applications of biosurfactants in EOR. Furthermore, the paper presents prospects of biosurfactants in EOR and proposes a sustainable production mechanism.

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1. INTRODUCTION

In recent years, there has been an increasing focus on sustainable practices within various industries, driven by the urgency to mitigate environmental impacts and address the challenges posed by conventional methods (Raihan et al., 2023; Østergaard et al., 2023). One such area of interest lies within the oil industry, where the extraction, processing, and utilisation of petroleum resources have historically been associated with significant environmental degradation. Amidst these concerns, the exploration of alternative, eco-friendly solutions have gained prominence, and biosurfactants derived from natural-based resources have emerged as a promising avenue for sustainable development (Bachari et al., 2019). Biosurfactants, amphiphilic molecules synthesised by microorganisms, plants, or animals, possess unique surface-active properties that make them invaluable in various industrial applications, particularly in the oil sector (Bachari et al., 2019; Natalya, et al., 2019). Unlike their chemical counterparts, biosurfactants are biodegradable, non-toxic, and often exhibit superior performance, making them an attractive alternative for use in diverse processes, ranging from oil recovery to environmental remediation. Therefore, fossil fuels (crude oil & gas) have been anticipated to continuously dominate the future energy sectors to about 77% in 2040 according to the United States Energy Information Administration (Jezard,2017). Moreover, fossil fuels have been the dominant energy source and contributed to stabilizing the world's economy for more than a century (Adam et al., 2020; Hassan et al., 2021; Hassan et al., 2022a; Hassan et al., 2022b; Hassan et al., 2023; Hassan et al., 2022c). This is because fossil fuels provide different types of energy resources and useful chemicals ranging from the famous petrol/gasoline (car fuel) to other fractions such as LPG (cooking gas), diesel (truck fuel), kerosene (jet fuel), naphtha (solvents), bitumen (road construction), lubricating oils, wax (candles & polish), ship fuel, and other hydrocarbon gases (Hamza et al., 2017). Additionally, considering the exponential increase in human population, the world has become excessively reliant on energy supplies for domestic and industrial use. As a result, worldwide energy consumption is predicted to increase by 50% by the year 2050 (Adam et al., 2020).

Crude oil extraction typically begins with primary methods, leveraging reservoir pressure to naturally lift oil to the surface (Hassan et al., 2021). However, as reservoir pressure diminishes over time, primary production becomes less efficient, ultimately leading to declining production rates until cessation. This initial extraction method typically recovers only 15–30% of the available oil reserves (Bachari et al., 2019). To augment oil recovery rates, secondary methods are employed, involving the injection of water into the reservoir to maintain or reestablish pressure, thereby sustaining oil production. This technique has been successful in increasing oil extraction by an additional 10–15% (Hamza et al., 2018a). However, despite its effectiveness, secondary recovery methods encounter several challenges (Hamza et al., 2017). One significant limitation is the phenomenon of viscous fingering, where injected water forms preferential flow paths, or "fingers," within the reservoir (Hamza et al., 2018b; Hassan et al., 2022d). This leads to inefficient displacement of oil, resulting in diminished production yields (Ahmed et al. 2018; Kargozarfard et al., 2019). Viscous fingering occurs primarily due to differences in viscosity between the injected water and the oil within the reservoir. Efficient oil displacement relies on ensuring that the viscosity of the injected water surpasses that of the oil, thus mitigating the risk of viscous fingering. Failure to achieve this viscosity contrast exacerbates the formation of undesirable finger channels, hampering the effectiveness of secondary recovery methods (Beteta, 2022).

The latest technology developed today that substitutes the secondary method is known as enhanced oil recovery (EOR) which can overcome the challenges of viscous fingering faced during the secondary extraction process (Ahmed et al., 2018). EOR has recorded unprecedented successes in achieving higher oil recovery factors and has since been commercialised for nearly 50 years, impacting economic gain for global oil and gas industries (Tang et al., 2022). EOR differs from the primary and secondary methods in such a way that different types of chemicals that can change or alter the reservoir properties, both physically and chemically are injected (Bachari et al., 2019; Bello, 2022; Hassan et al., 2022e; Hassan et al., 2022f).

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In a general term, Fig.1 describes the different types of EOR operations based on the flooding chemical agents and each of the chemicals has distinct target properties. For example, polymer is primarily used to increase water viscosity so that problems like viscous fingering can be addressed (Arab et al., 2022). Furthermore, some reservoirs are associated with law permeability causing difficulties for viscous fluids to penetrate through tiny pores to mobilise oil in the stranded zones. To mitigate this problem, gas has been studied and recommended as an ideal fluid because of its high diffusion rate through tiny pores in reservoir formation (Gbadamosi et al., 2022). Nevertheless, observations have established that gas diffuses faster and bypasses oil without achieving the ultimate objective. This phenomenon is known as 'early gas breakthrough' which has remained a topic of discussion in gas flooding EOR.

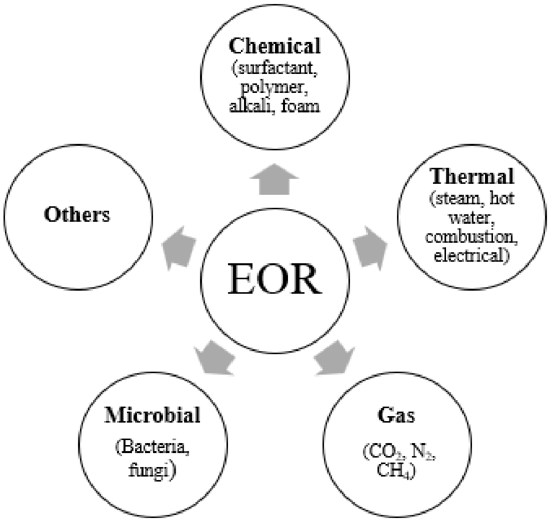

Fig. 1. Different types of EOR operations involving chemical agents

Source: Author's Illustration

To overcome this challenge, a method called water-alternating-gas (WAG) was developed with the idea that if water and gas are injected in an alternative manner, the early gas breakthrough could be reduced or totally eliminated, and at the same time mobilizing oil in low permeable zones (Ahmadi et al., 2015). A method to further reduce gas mobility has led to the emergence of foam-assisted-water-alternating-gas (FAWAG) (Aarra et al., 2002). The only difference between the WAG and FAWAG is that, instead of using water as in the case of WAG, a slug of surfactant formulation is replaced. During alternate gas injection into the surfactant solution, it resulted in the generation of a gas bubble described as a 'foam' which is behind the name FAWAG. In FAWAG there has been efficient control of early gas breakthroughs because it imprisoned the gas in bubble cells (Muhammad & Hamza, 2022).

To date, the cumulative recovery factor in conjunction with the EOR operations nearly reached up to 60%, leaving behind about 40% stranded oil in the reservoir (Hassan et al., 2022c). Properties such as capillary force, interfacial tension (IFT), and wettability are critical and responsible for holding oil in the reservoir formation (Hassan et al., 2021). Several research investigations on surfactants have opened a door for intensive research mainly to overcome the IFT, wettability, and capillary force challenges (Tackie-Otoo et al., 2020; Liang et al., 2021). Moreover, some studies focus on the adsorption behaviour of surfactants onto the rock surface, which provides insights into efficient oil extraction (Mushtaq et al., 2014; Azam, et al., 2013). However, most surfactants used in EOR today are synthetic and pose serious environmental

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concerns due to their non-biodegradable nature. This has increased high expenditure for produced water remediation in the oil and gas industries. However, it is noted that some synthetic surfactants have shown reasonable improvement in reducing the interfacial tension between crude oil and other fluids which in turn enhanced oil recovery (Hassan et al., 2023; Hassan et al., 2022g). However, in certain circumstances, some synthetic surfactants have low recovery factors and were found to be extremely detrimental to the reservoir rocks causing blockage of pores particularly if the selection of the surfactant was not properly adhered (Hassan et al., 2021).

Consequently, for the benefit of a green environment, biodegradable surfactants (biosurfactants) are necessary and important in the fields of EOR. These biosurfactants are known as eco-friendly and biodegradable which makes them competitive to chemical surfactants (Bhardwaj et al., 2013). In general, the surfactants market is expanding globally with increasing demand reaching up to USD39.86 billion in the year 2021 (Gaur et al., 2022), with a 4.3% growth rate. It is estimated that the global market for biosurfactants alone stood at USD2.6 billion in 2023 (Panjiar et al., 2020) and could reach up to USD7.5 billion by the end of 2031. The common sources of these biosurfactants are produced directly from living matter (plants & animals) (Xi et al., 2021). Other alternative sources are the essential oils extracted from plants and treated with caustic soda to produce biosurfactants. Biosurfactants have been investigated to possess IFT and capillary effects, similar to their synthetic counterparts, thus recommended for use in EOR operations (Mujumdar et al., 2019). Hence a need to further explore more biosurfactants to replace their synthetic counterparts (Naughton et al., 2019). The only concern about biosurfactant utilisation is the issue of sustainable production, reports on the sustainable availability of plant resources for use in EOR have been limitedly discussed, and various approaches for sustainable production have also not been adequately presented.

This review aims to provide a comprehensive overview of biosurfactants sourced from natural-based resources, focusing on their sources, production methods, and applications within the oil industry. By examining the latest advancements and trends in biosurfactant research and technology, this review seeks to underscore the potential of these biocompatible compounds as sustainable solutions for addressing the challenges faced by the oil sector. In summary, this review endeavours to underscore the significance of biosurfactants derived from natural-based resources as sustainable alternatives within the oil industry. By synthesizing current knowledge and exploring future directions, it seeks to inspire further research, innovation, and adoption of these eco-friendly solutions, ultimately paving the way toward a more environmentally conscious and resilient oil sector.

2. SURFACTANT: TYPES & PROPERTIES

Surfactants are chemical substances distinguished with unique characteristics and features of hydrophilic head and hydrophobic tail groups in their structures as shown in Fig. 2. To demonstrate these two physical properties, a surfactant must have a chemical structure with two different functional groups having different affinities within the same molecule. They have the abilities of self-assembly, orientation and interfacial properties whenever they are in contact with two or more aqueous media. A cluster of self-assembled molecules of surfactant is called a micelle as described in Fig. 2 (Nakama, 2017).

Usually, the molecules of the surfactants have an alkyl chain with 8-22 carbons. Accordingly, the head group can be identified with different charges and classified as anionic (negative charge), cationic (positive charge), amphoteric/zwitterionic (positive & negative charge) and non-ionic (zero charge) (Cortés et al., 2021). All the classes of surfactants have the same features of self-assembly but demonstrate different behaviours at aqueous interfaces because of the nature of their charge groups (Gonçalves et al., 2023). In actual sense, the hydrophilic head has a strong affinity to the polar group, while the hydrophobic head has a strong affinity to the non-polar group. Common characteristic structural features of surfactants are shown

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in Fig.2. When surfactant molecules orient at the oil/formation water interface, the polar head interacts with water molecules while the tail group gets attached to the oil phase. This mechanism resulted to the formation of adsorbed film which lowers or weakens the force uniting oil and water, and subsequently, reduces the capillary forces preventing oil extraction, thus more oil flows at ease from the reservoir pore throats (Gbadamosi et al., 2019).

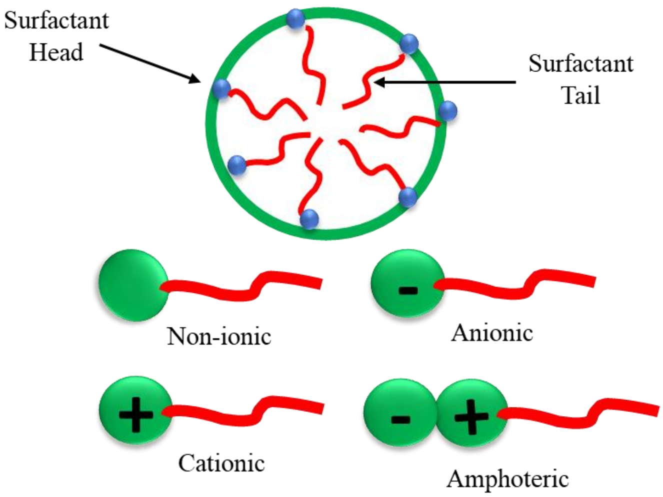

Fig. 2. A structure of surfactant illustrating its feature, self-assembly and classes

Source: Author's Illustration

3. SOURCES/PRODUCTION OF BIOSURFACTANTS

3.1 Fermentation

Various biosurfactants are produced by the fermentation process using several microorganisms such as bacteria, yeasts, and filamentous fungi (Campos et al., 2013) through growth-associated metabolic characterisation (Sarubbo et al., 2022). However, the composition and yield of biosurfactants are governed by several conditions like the reactor, reaction process, nutrients, pH, temperature, and oxygen (Costa et al., 2018). Generally, batch, fed batch, and continuous are three types of fermentation processes, and each of these processes has better advantages over one another (Abacha et al., 2016). In a batch process, the feedstock nutrients are supplied at once at the start of the fermentation process and the product is then harvested after the reaction. In the fed-batch, which is like a batch, few nutrients are supplied at the starting point and others are added when the process progresses. In a continuous process, the nutrients are added continuously, and the product is collected simultaneously at the same flow rate (Abacha et al., 2016). The advantage of the fermentation process involves the use of a lower amount of water, energy, and simple equipment. Additionally, it requires low-cost substrates (Costa et al., 2018; Akpinar & Urek, 2012). This process has been applied widely in the production of biosurfactants. For instance, (Samak et al., 2020) produced a biosurfactant using a fed-batch fermentation process with the aid of isolated *Pseudomonas aeruginosa* and *Starmerellabombicola*. The biosurfactant was evaluated for various EOR parameters. Their findings revealed that the IFT was reduced from ~11.83 to ~0.13 mN/m, wettability alteration to excellent water-wet condition, and oil recovery up to 66%. Similarly, Choi, et al. (1996) has produced emulsan through a fed-batch process and reported to have biosurfactant properties and application in microbial EOR.

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3.2 Agro-industrial wastes

Agro-industrial wastes are commonly regarded as low-cost materials to produce biosurfactants because of their availability and large amounts of carbon sources (Gaur et al., 2022). The wastes usually come from several industrial and local processing activities of food and non-food materials such as cassava, plantain, rice, cereals, pulse, molasses, skin, bones, dairy, oil, etc. They are regarded as substrates through which other essential materials for biosurfactant productions are extracted (Saharan et al., 2011). For example, corn steep liquor and soybean frying oil treated with a Saccharomyces cerevisiae yeast have been reported to produce biosurfactants that exhibited good interfacial tension properties (Galdiano Ribeiro et al., 2022). This is in line with the optimisation production of biosurfactants by (Ebadipour et al., 2016) from the same corn steep liquor as a low-cost agricultural waste using a response surface approach. Moreover, in the study of (Panjiar et al., 2020), the authors observed that tonnes of agricultural residue, particularly rice & wheat straws are disposed of by open field burning causing environmental threats. This has prompted the authors to produce thermally stable and emulsifying active biosurfactants from rice straw as part of management strategies.

3.3 Plant-derived surfactants

Several plants possess plenty of biosurfactants in the form of saponins in their body tissues as secondary metabolites (Nowrouzi et al., 2020). Their presence serves as a defence mechanism against diseases and other microbial-related infections (Crouzet et al., 2020). Literature report reveals that plenty of plants bearing saponins could be employed as good sources of natural biosurfactants. (Nowrouzi et al., 2020) reported the successful extraction of saponin from the Iranian *Anabasis Setifera* plant using a maceration method. The biosurfactant was then investigated for various EOR parameters such as IFT, wettability, foamability, and EOR. Furthermore, the author in a separate study modified the structure of the extracted surfactant by esterification method into a Double-Chain Single-Head molecule and observed improved properties (Nowrouzi et al., 2020).

3.4 Animal-derived surfactants

Similar to plant sources, surfactants can also be derived from animal parts and products. Sohail & Jamil (2019) reported the extraction of biosurfactants from various sources, including animal fat. The authors observed that the highest biosurfactant production was obtained from animal fat oil with production up to 30%.

3.5 Pyrolysis

Pyrolysis is a process of heating or decomposition of organic matter in the absence of oxygen at any temperature above 500 ℃. Since the heating does not require oxygen, combustion does not occur, but simply the organic matter is converted into combustible gases which can be liquified. Pyrolysis has been one of the technologies commonly available for the conversion of organic matter to intermediate liquid products. These products can further be refined to pure hydrocarbon biofuels, oxygenated fuel additives, and petrochemical replacements. Research has employed the pyrolysis method to develop chemical EOR by utilizing palm oil shells. The pyrolysis resulted in a high yield of phenolic compounds of about 56.042%. The surfactant upon investigation for EOR has accounted for incremental oil recovery.

3.6 Synthesis from natural matter

Synthetic biosurfactants including lignin and essential oils are generally obtained from laboratory chemical reactions (Amanat et al., 2022) which are widely used for commercial and industrial applications (Hamza et al., 2017). They are synthesised directly from natural components of living matter. Lignin is a complex organic polymer found in plant tissues that can be a source of material for biosurfactant production.

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It has become the second known available natural rubber after cellulose and is readily converted into value-added products (Alwadani & Fatehi, 2018). Ganie et al.(2019) experimentally developed lignin biosurfactant by treating lignin with sodium sulphite to form lignosulfonate and subsequent treatment with amines. The surfactant was evaluated for IFT and EOR. Comprehensive information on lignin for biosurfactants has been extensively reported by Alwadani & Fatehi (2018).

Essential oils are long-chain saturated and unsaturated hydrocarbons found in a plant's body such as seeds, leaves, bark, and root (Tongnuanchan, 2014). They have received increasing attention as common sources of materials to synthesise biosurfactants. Muhammad & Hamza (2022) have extracted essential oil from Fenugreek seeds and converted them to a biosurfactant for application in foam-assisted-water-alternative EOR. Similarly, (Hamza et al., 2018c) synthesised C18-conjugated zwitterionic biosurfactant using linoleic acid essential oil. The biosurfactant has been evaluated and screened for various EOR parameters.

4. APPLICATIONS OF BIOSURFACTANTS IN THE OIL INDUSTRY

Biosurfactants have various applications and are widely used in the cosmetic, food, and pharmaceutical industries. However, in oil and gas industries their applications are unprecedented because they are employed in different operational activities in petroleum production. Some of these activities include cement slurries, drilling, demulsification, fracturing, corrosion inhibition, acidization, transportation, water flooding, chemical, foam, and steam flooding, cleaning, and environment protection (Bhardwaj & Hartland, 1993). Table 1 provides details and different types of biosurfactants investigated on different parameters related to petroleum production.

Table 1. Various applications of biosurfactants in EOR

Types of surfactants		Parameters investigated	Findings	References
1.	Biosurfactant	IFT	FT was reduced from 11.83 to 0.13 mN/m.	(Mujumdar, 2019).
2.	Corn steep biosurfactant	IFT	The corn steep biosurfactant produced good IFT biosurfactant.	(Galdino Ribeiro et al., 2022)
3.	Fenugreek surfactant	Foam foamability & stability	Fenugreek surfactant demonstrated excellent foam stability.	(Muhammad & Hamza, 2022)
4.	Linolyel dimethyl amidopropyl betaine	Foam foamability & stability	Biosurfactant was reported with significant formability in the absence and presence of crude oil.	(Hamza et al., 2018c)
5.	Rhamnolipid Biosurfactant	Zeta potential	Highly negative zeta potential was recorded to be ≤ -39.3	(Onaizi et al., 2021)
6.	Rhamnolipid Biosurfactant	Emulsion stability	The biosurfactant created a highly stable O/W nano emulsion.	(Onaizi et al., 2021)
7.	Biosurfactant	Wettability	Wettability alteration has reduced to an excellent water-wet condition.	(Samak et al., 2020)
8.	Biosurfactant	EOR	The oil recovery has increased up to 66 %	(Samak et al., 2020)

Source: Author's illustration

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5. CHALLENGES & PROPOSED SUSTAINABLE PRODUCTION

Over a period, there have been debates on sustainable mechanisms of biosurfactant production due to various reasons. Among which scientists had opined the high cost of production makes commercialisation very challenging. However, it is reported that if advanced methods are developed there could be further progress in terms of production (Perfumo et al., 2010). This paper has identified that apart from other sources of biosurfactants production approaches such as agro-industry-based resources and microorganisms, plant biotechnology would also be an ideal technology to overcome the challenges of production. Plant biotechnology is a scientific tool that involves various techniques for the manipulation of plant genetics to develop sterile and mass populations of useful plants and their products (Kalia, 2018). It is viewed as an alternative avenue for the development of new plant varieties that can be populated to achieve certain objectives. Previously, plant varieties were dominantly obtained through the seed propagation method. However, the advent of micropropagation which is a segment in plant biotechnology has offered practical alternative sources of many plant species (Bhatia & Sharma, 2015). In this technique, any parts of plants such as leaves, roots, shoots, buds, etc can be manipulated into a full-grown mass population within a short period. Consequently, prospective plants that are useful directly or indirectly in biosurfactant manufacture can be exposed to plant biotechnology techniques to produce a large and sustainable population (Hamza et al., 2016). This can also be integrated into a farm-based industry or greenhouse exclusively for harvesting biosurfactants and/or substrates.

6. CONCLUSION

Biosurfactants are important chemicals that find various applications in oil & gas industries such as reducing the IFT, changing the rock wettability, increasing mobility ratio, sweep efficiency, and enhancing recovery factor. They have advantages over synthetic counterparts for being biodegradable, non-toxic, and environmentally friendly. They are known as cost-effective materials during production. Biosurfactants have continued to dominate surfactant industries as the global market for biosurfactants alone is forecast to reach up to USD 7.5 billion by the end of 2031. This could be efficiently achieved if the plant biotechnology approach is deployed as a suitable sustainable production mechanism.

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CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare the absence of conflicting interests with the funders.

AUTHORS' CONTRIBUTIONS

Mohammed Falalu Hamza: Conceptualisation, and writing-original draft; **Lukman Ismail**: Conceptualisation, and draft preparation; **Yarima Mudassir Hassan**: Writing- review and editing; **Surajudeen Sikiru**: Writing- review and editing; **Hassan Soleimani**: Writing- review and editing; **Saifullahi Shehu Imam**: Writing- review and editing.

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