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REVIEW ARTICLE

Biosurfactants—a new frontier for social and environmental safety: a mini review

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Abstract Biosurfactants are amphiphilic compounds synthesized from plants and microorganisms. These compounds are well known to be promising alternative molecules for industrial and domestic applications due to their high biodegradability, low toxicity, multi-functionality, environmental capability, and availability of resources. In recent times, the chemical compounds of biosurfactants have gained much attention because they are considered as a suitable alternative and eco-friendly materials for remediation technology. The current society is facing several challenges of implementation, enforcing environmental protection and climate change for the next generations. Thus, studies on human and environmental safety to improve the efficiency of sustainable technologies on environmental remediation are being investigated. Biosurfactants exhibited an efficient and successful application in various industries such as cosmetic, pharmaceutical, food, petroleum, agricultural, textile, and wastewater treatment. In this regard, this review focused on the advantages of biosurfactants over the synthetic surfactants produced from petroleum-based products along with their potential application in different industries.

Introduction

Surfactants (surface-active materials) are part of the most versatile group of chemicals potentially used in various industries which include detergents, paints, paper products, pharmaceuticals, cosmetics, petroleum, food, and water treatment (Elazzazy, Abdelmoneim, & Almaghrabi, 2015; Guclu-Ustundag & Mazza, 2007; Gupta et al., 2013; Lu et al., 2017; Mahamallik & Pal, 2017; Varjani & Upasani, 2017). Currently, commercial surfactants are synthesized from petrochemicals, animal fats, plants, and microorganisms. Studies had shown that majority of the production markets relied on petrochemicals (De Almeida et al., 2016; Farn, 2007; Hayes, Kitamoto, Solaiman, & Ashby, 2009; Rufino, de Luna, de Campos Takaki, & Sarubbo, 2014). The development of new strategies for replacing petroleum, coal, and natural gas-based products with renewable, biodegradable, and sustainable green energies are the novel challenges

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for humans and environmental protection agencies (Ajala, Aberuagba, Odetoye, & Ajala, 2015; Fantechi, 2009; Shaban & Abd-Elaal, 2017). Generally, petroleum is considered a unique source of energy because thousands of daily consumed products are sourced from petroleum. Besides, it is claimed that an increase in the production of petroleum generates two phenomena: firstly, it increases the level of environmental pollution which may affect public health and secondly, decline in petroleum production within the next few decades, which may impact the economy level of oil-producing countries (Frumkin, Hess, & Vindigni, 2009). Based on these two phenomena, the demand for green alternative products may increase to canter for the potential needs of industrial and domestic applications. Thus, additional studies and developments are required to visualize the market requirements. In addition, natural surfactants can be employed to replace synthetic surface-active materials from petroleum feedstock, since they are cost-effective as compared to the synthetic origin compounds (Boruah & Gogoi, 2013; De, Malik, Ghosh, Saha, & Saha, 2015; Goel, 2010; Md, 2012; Piispanen, 2002; Torres, Moctezuma, Avendaño, Muñoz, & Gracida, 2011). On the other hand, the costs of biosurfactants are relative to the raw material availability, and many biosurfactants are expensive due to a shortage of potential feedstock (Chaprão et al., 2015; Rufino et al., 2014).

Currently, biosurfactants are becoming an attractive alternative in the market as the manufacturers are producing eco-friendly biosurfactants from different natural and sustainable sources (Marchant & Banat, 2012a). Usually, surfactants extracted from organic compounds contain both hydrophilic (water-loving) and hydrophobic (water-heating or oil-loving) compartments (Fracchia, Cavallo, & Giovanna, 2012). Natural surfactants (saponins) belong to the group of secondary metabolites which are abundantly found in various plants and some marine organisms (Boruah & Gogoi, 2013; Cheeke, 2010; Cheok, Salman, & Sulaiman, 2014). Generally, they can be found in different parts of plants, including seeds, leaves, roots, flowers, and fruits (Goel, 2010; Oleszek & Hamed, 2010). The word saponin is a Latin word which means foaming agents from the plants. Saponins are soluble in water with higher molecular weights in the ranges of 600–2000 Da (Goel, 2010; Piispanen, Persson, Claesson, & Norin, 2004). The aim of the present review was to provide information about biosurfactants and their potential application as environment-friendly products and alternative compounds to the synthetic origin surfactants.

Properties of biosurfactants

Biosurfactants are amphiphilic compounds containing both hydrophilic and hydrophobic portions referring to as head and tail, respectively. In aqueous media, the terms hydrophobic groups are used as lyophobic and hydrophilic groups as lyophilic (Fracchia et al., 2012). Surfactants are active compounds found in detergents and soaps, and they reduce the surface tension or interfacial tension at the air–water and water–oil interfaces (De Almeida et al., 2016; Rufino et al., 2014; Satpute et al., 2010). Biosurfactants can be obtained from different low-cost materials available

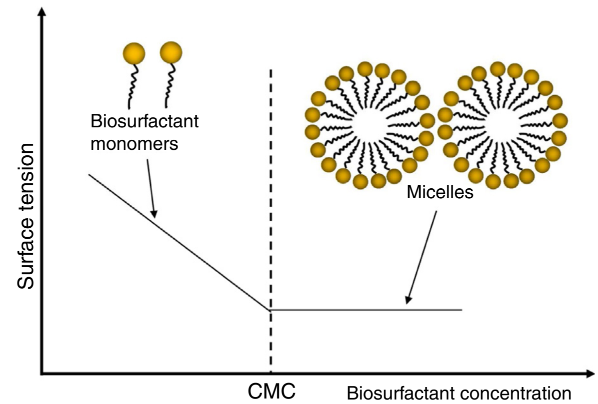

Figure 1 CMC and micelle formation of biosurfactant monomers.

in large quantities. They possess several advantages over synthetic chemical-derived surfactants which include low toxicity, bioavailability, biodegradability, high foaming, environment-friendly, low cost in terms of feedstock availability in nature, pH, and salinity. Thus, they are safe and better alternative to chemical surfactants, particularly in food, pharmaceutical, cosmetic, and edible oils (Bhadoriya, Madoriya, Shukla, & Parihar, 2013; Nitschke & Costa, 2007; Fracchia, Banat, Cavallo, Ceresa, & Banat, 2015). Basically, the growing environmental distress about chemically derived surfactants initiates a new concentration on natural biosurfactants due to their harmless characteristics. The desirable and efficient properties of biosurfactants as presented in Fig. 1 include reduction of surface tension, solubility enhancement, and low critical micelle concentrations (CMCs) (Jha, Joshi, & Geetha, 2016; Mulligan, 2009). An effective biosurfactant can reduce the surface tension of water from 72 to 35 mN/m and interfacial tension between a polar and non-polar liquid, for water against *n*-hexadecane from 40 to 1 mN/m (Mulligan, 2005; Soberon, 2011). Generally, the CMC is the maximum concentration of surfactant monomers in water which can be influenced by pH, ionic strength, and temperature of the solution (Mondal, Malik, Roy, Saha, & Saha, 2015; Pacheco, Ciapina, de Barros Gomes, & Pereira Junior, 2010; Shah et al., 2016).

Industrial applications of biosurfactants

Biosurfactants have a wide range of applications in different industries such as cosmetics, pharmaceutics, food, petroleum, wastewater, agriculture, textile, painting, and many other industries. Moreover, these compounds are well known as multifunctional agents, including stabilizing, wetting, antimicrobial, moisturizing, emulsifying, and anti-adhesive agents (Banat, Makkar, & Cameotra, 2000; Fracchia et al., 2014). Recently, biosurfactants achieved a potential interest for environmental applications in remediation of organic and inorganic contaminants, particularly in heavy metal removal from soil and water, cosmetic, pharmaceutical products, and enhanced oil recovery (Al-Wahaibi et al., 2014; Boruah & Gogoi, 2013; Vijayakuma & Saravanan,

Table 1 Application of biosurfactants in different industries.

Industry	Applications	References
Pharmaceutical/cosmetic	Body washes, hair products, lotions, eye shadow, acne treatment, lip colour, deodorants, anti-wrinkle products, skin smoothing, antimicrobial agent, antifungal agent, anti-adhesive agents, anti-cancer agent, antiviral agent, foaming agents	Boruah & Gogoi, 2013; Cheok et al., 2014; Vecino et al., 2017a
Food industry	Emulsifying agents, anti-adhesive agent, anti-microbial agent, food preservation	Boruah & Gogoi, 2013; Mnif & Ghribi, 2016; Nitschke & Costa, 2007
Petroleum	Emulsifier, demulsifier, oil recovery enhancer, transportation assistant	Boruah & Gogoi, 2013; El-sheshtawy, Aiad, Osman, Abo-elnasr, & Kobisy, 2016
Wastewater treatment	Biocomposite agent, heavy metal removal agent, bio-adsorbent	Fu & Wang, 2011; Vecino, Cruz, & Moldes, 2015; Zouboulis, Matis, Lazaridis, & Golyshin, 2003
Textile	Lubricant, scouring agent, leveling agent, bleaching assistant	Boruah & Gogoi, 2013
Agriculture	Soil remediation agent, fungicides, bactericides, pesticide, heavy metal removal, plant disease removal agent, root colonization	Boruah & Gogoi, 2013; Mnif & Ghribi, 2016; Zouboulis et al., 2003

2015). The applications of biosurfactants in some industrial process are summarized in Table 1.

Applications of biosurfactants in contaminated soils

Recently, most of the studies are focusing on the environmental applications of biosurfactants due to their diverse structure, better physicochemical properties, environment-friendly characteristics, suitability for many purposes which include remediation of hydrophobic organic compounds (HOCs) from soil, and removal of heavy metals from contaminated soil. Heavy metals are becoming part of the serious environmental problems. Basically, the most common heavy metals found in contaminated soils are lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), zinc (Zn), copper (Cu), and nickel (Ni) which can create many health issues categorized under inorganic chemical hazards for humans, animals, and plants (Adamu, Nganje, & Edet, 2015; Ali & Al-Qahtani, 2012; Hu et al., 2017; Khan, Cao, Zheng, Huang, & Zhu, 2008; Li & Qian, 2017; Liu, Wang, Li, & Li, 2015; Liu et al., 2017; Luo et al., 2012; Parizanganeh, Hajisoltani, & Zamani, 2010; Tang et al., 2015). In the past, chemical surfactants had been used to treat heavy metal-contaminated soils and solubilize HOCs. However, the chemical surfactants themselves are known to expose toxic substances and may cause other environmental issues due to its their degradability in the soil (Albuquerque et al., 2012; Liu et al., 2017; Santos, Rufino, Luna, Santos, & Sarubbo, 2016).

In comparison with chemical surfactants, biosurfactants derived from plants and microorganisms have shown better performance considered suitable in removing heavy metal from contaminated soil (Chibuike, Obiora, Chibuike, & Obiora, 2014; Luna, Rufino, & Sarubbo, 2016; Tang, He, Liu, & Xin, 2017; Vijayakuma & Saravanan, 2015). The mechanism of heavy metal removal from contaminated soil using ionic biosurfactants is shown in Fig. 3. Essentially, there are three main steps involved in the removal of heavy metals from the soil through washing with biosurfactant solution. The heavy metals adsorbed on the surface of soil particles separate through the sorption of biosurfactant molecules at the interfaces between sludge (wet soil) and metal in aqueous solution. Then, the metal will be absorbed by biosurfactants and trapped within the micelle through electrostatic interactions. Finally, the biosurfactant can be recovered through the method of membrane separation

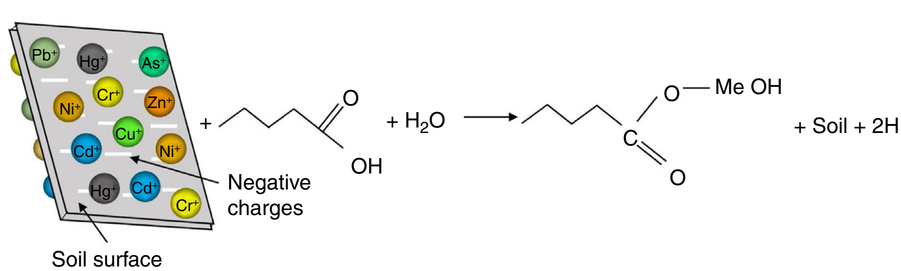

Figure 2 Chemical reaction between heavy metal contaminated soil, water, and biosurfactant.

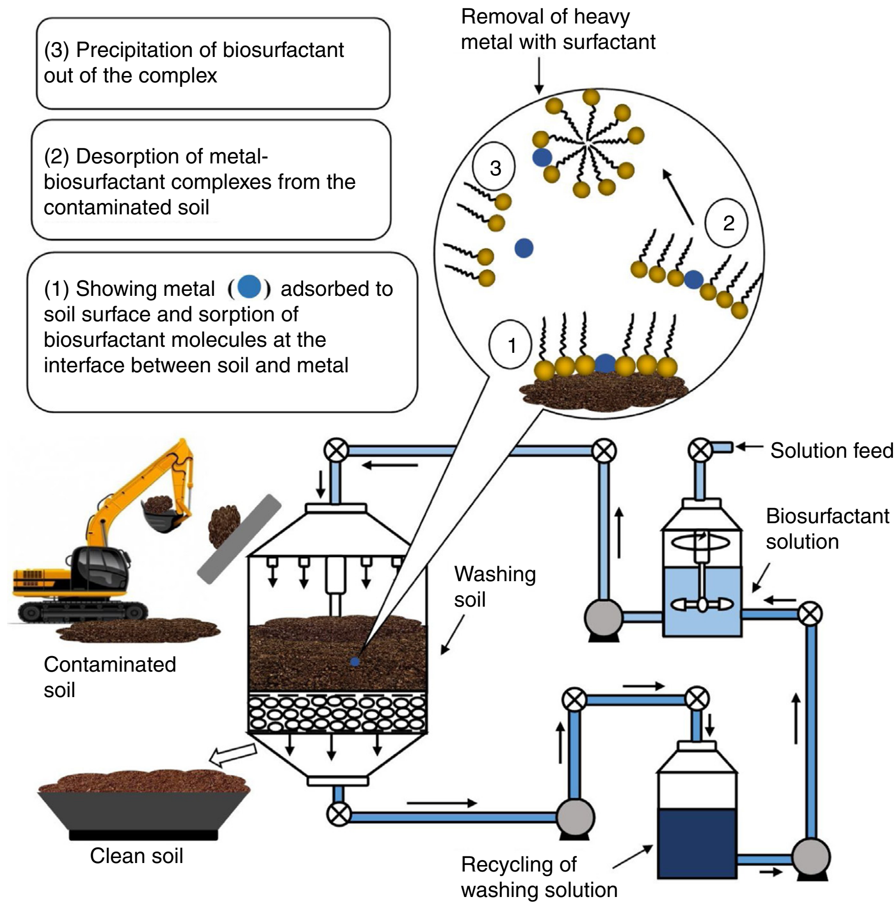

Figure 3 Mechanism of heavy metal removal from contaminated soil using biosurfactants.

(Guan et al., 2017; Ibrahim, Hassan, & Azab, 2016). Eq. (1) and Fig. 2 describe the chemical reaction between heavy metal ions and the functional group of biosurfactants. Since soil particles and other organic matters have negative charges on their surfaces, thus, cationic materials can easily be adsorbed to negative charges of the soil surface:

$$\text{Soil} - \text{Me}^{n+} + \text{R} - (\text{COOH})_m + \text{H}_2\text{O} \rightarrow \text{Soil} + \text{R} - \text{O} - \text{Me}^{n+} - (\text{COOH})_m + 2\text{H} \quad (1)$$

where Me^{n+} represents metal ions and R– $(\text{COOH})_m$ is the surfactant molecules. As it can be seen in Eq. (1), surfactants enhanced the extraction of heavy metals from the soil because of the existing carboxylic functional group in biosurfactants which act as organic ligands (Tang et al., 2017).

The traditional methods of removing heavy metals from contaminated soil such as washing with water, organic and inorganic acids, metal-chelating agents, soil replacement, thermal desorption, and chemical surfactants had been used. However, these methods showed the improper removal of heavy metals from the soil (Shah et al., 2016). Previous studies had reported that the remediation technique using biosurfactants is the best method to eliminate heavy metals from the soil with about 100% efficiency. Guan et al. (2017) and Hong, Tokunaga, and Kajiuchi (2002) studied the efficiency of biosurfactants for removing heavy metals from sludge and soil and achieved the removal rates of 90–100% for Cu, Zn, Cr, and Cd. In addition, natural surfactants are found to be effective in treating contaminated soils with crude oil and diesel (Da Rosa, Freire, & Ferraz, 2015).

Applications of biosurfactants in cosmetic and pharmaceutical industries

Biosurfactants have attracted the interest of cosmetic and pharmaceutical industries because of their potential use as detergents, wetting, emulsifying, foaming, solubilizing, and many other useful properties (Marchant & Banat, 2012b). The use of biosurfactants in these two industries are very wide since they are one of the main essential components in producing products such as shampoo, hair conditioners, soap, shower gel, toothpastes, creams, moisturizers, cleansers, and many other skin care and healthcare products (Boruah & Gogoi, 2013; Chakraborty et al., 2015; Satpute et al., 2010). Several studies had reported that the use of chemically based surfactants in cosmetic formulations is one of the most challenging problems due to their potential risk of skin allergy and irritation (Bujak, Wasilewski, & Nizioł-Łukaszewska, 2015; Nitschke & Costa, 2007; Sil, Dandapat, & Das, 2017; Vecino, Cruz, Moldes, & Rodrigues, 2017a). However, the excellent characteristics of bio-based surfactants make them an excellent component as a green product

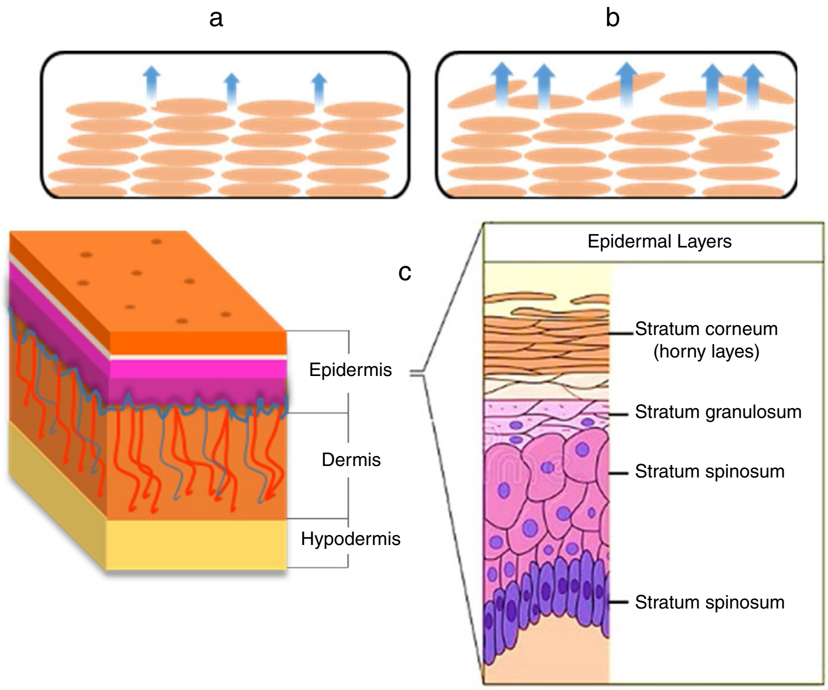

Figure 4 Describing normal and healthy stratum corneum layer of skin with naturally balanced water loss (a) and (b) showing ceramide-deficient skin and damaged stratum corneum layer in dry skin with excess moisture loss. (c) Representing the four layers of epidermis.

for cosmetics (Ferreira et al., 2017; Lee, Lee, Yu, & Lim, 2017). In recent years, it has been found that biosurfactants are very useful for skin moisturizing similar to ceramides (Kitagawa et al., 2011). Ceramides are epidermal lipids important for skin barrier and dryness. The depletion of ceramides in *stratum corneum* (horny layer) layer of the skin can cause chronic skin diseases such as psoriasis, atopic dermatitis, and aged skin due to water loss and barrier dysfunction in the epidermis (Meckfessel & Brandt, 2014; Mizutani, Mitsutake, Tsuji, Kihara, & Igarashi, 2009; Tessema, Gebre-Mariam, Lange, Dobner, & Neubert, 2017). The epidermis consisted of four layers, namely *stratum corneum*, *stratum granulosum*, *stratum spinosum*, and the innermost stratum basale. *Stratum corneum* is the outermost surface layer of the skin that forms a barrier between the external environment and the internal body (Thakur, Batheja, Kaushik, & Michniak, 2009; Van Smeden, Janssens, Gooris, & Bouwstra, 2014). This layer is responsible for maintaining skin barrier function and preventing excess water loss from the skin. Fig. 4 describes the healthy and damaged *stratum corneum* layers of the skin with four layers of the epidermis. It has been found that ceramides are effective to treat damaged skin, prevent skin roughness, and dryness. Ceramide is sphingolipids (glycosylceramides) that represent about 50% of intercellular lipids in the *stratum corneum*. Kitagawa et al. (2011) discovered that microorganism-based surfactants besides having a good ability as an emulsifier could be applied as ceramides to enhance skin roughness and get rid

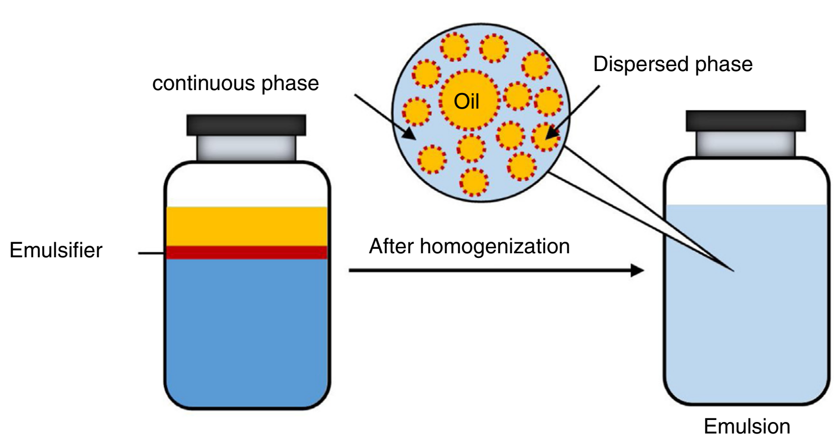

Figure 5 Emulsification of the emulsions using biosurfactants.

of ceramide deficiency in the skin. It is also claimed that the combination of biosurfactants in cosmetics such as skin care lotions and moisturizing creams can improve the quality of the product and helps in roughness improvement (Kitagawa et al., 2011; Vecino et al., 2017b).

The efficiency of biosurfactants as an emulsifier is well known and widely used in the emulsification process. An emulsion is a heterogeneous system consisting of two immiscible phases, whereby one phase is dispersed in another (continuous phase) in the form of droplets. The applications of biosurfactants in different industries particularly in pharmaceutical and cosmetic formulations were found to have a satisfactory result due to their low toxicity and higher biodegradability. Generally, biosurfactants with higher molecular mass are considered effective emulsifiers to stabilize the emulsions for a long period of time (Nitschke & Costa, 2007). In terms of preparing nano-emulsions, higher homogenizing speed would be effective to disperse the phase in nano-sizes (Bhadoriya et al., 2013; Piorkowski & McClements, 2013). There are two types of emulsions: oil-in-water (O/W) and water-in-oil (W/O). In an O/W type, the continuous phase is water referring to as water-based emulsions. However, the oil-based emulsion is a W/O type, whereby the oil acts as the continuous phase. An example of an O/W emulsion is shown in Fig. 5. The main function of an emulsifier surfactant is to accumulate between phases and lower the surface and interfacial tension of the emulsion which finally results in the formation of an emulsion. Moreover, the cosmetic and pharmaceutical formulations deal with both emulsion types (Masmoudi, Le, Piccerelle, & Kister, 2005). In cosmetics, plant-based essential oils are considered as an important component for moisturizing and anti-aging purposes (Ferreira et al., 2017). In order to stabilize these types of emulsions, the presence of surfactants is necessary as an emulsifier. Particularly, bio-based surfactants are safe as they can cure in a natural way (Vijayakuma & Saravanan, 2015).

Applications of biosurfactants in oil recovery

Currently, several enhanced oil recovery (EOR) processes are employed in petroleum industries which include thermal, physical, and chemical methods. Injection of air/gas or water has been traditionally applied in the oil reservoirs. Moreover, chemical-based surfactants are extensively used in petroleum industries for different purposes, mainly in the EOR. However, these methods are known as potentially expensive, harmful to the environment, and resulted in lower yield as well (Al-Wahaibi et al., 2014). The low rate of oil recovery in EOR is also attributed to some factors such as trapped hydrocarbons in the porous matrix, the high viscosity of oil, and high interfacial tension between the injected water and oil (Fernandes et al., 2016; Zhao et al., 2017a; Zou et al., 2013). Besides, injection of chemical surfactants into the oil reservoir can result in crucial problems such as pollution of underground water and contamination of soil which can finally lead to the serious health risks to humans, plants, and animal species (Jha et al., 2016). Different studies had reported that the utilization of microorganisms that can produce biosurfactants are efficiently considered a suitable method for EOR. This method is referred to as microbial-enhanced oil recovery (MEOR) (Banat et al., 2000; Banat, 1995a; Banat, 1995b). In MEOR technique, several microbial species had been applied to generate biosurfactants for oil recovery enhancement such as *Bacillus megaterium*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Bacillus amyloliquefaciens* (Al-Wahaibi et al.,

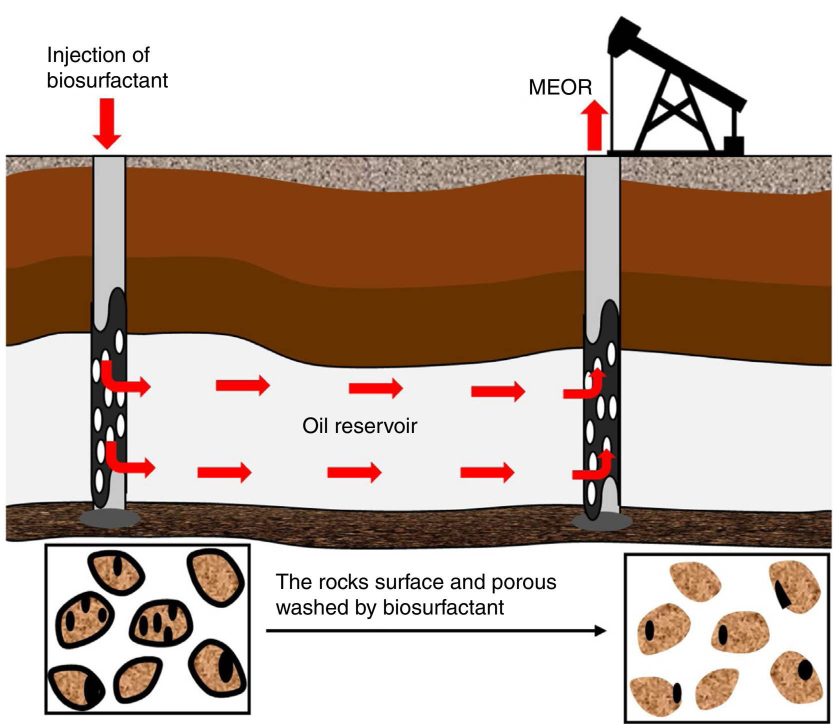

Figure 6 MEOR of crude oil.

2014; Dhanarajan et al., 2017; Fernandes et al., 2016; Zhao et al., 2017b; Zhao, Li, Guo, Shi, & Zhang, 2018). The principle behind this technique is that the injection of microbes causes the reduction of oil viscosity and interfacial tension between oil hydrocarbons and surface of rock matrix, which can facilitate the mobilization of oil and further increment of oil recovery (Al-Wahaibi et al., 2014; Hosseininoosheri, Lashgari, & Sepehrnoori, 2016) as shown in Fig. 6. Generally, biosurfactants with high molecular weight are known for their emulsifying properties, therefore they can enhance the heavy oil mobility and oil recovery. However, low-molecular-weight biosurfactants are suitable for reducing surface tension and interfacial tension between oil and water and thus enhancing oil recovery (Banat et al., 2010).

Basically, there are two ways that microbes can contribute to the generation of biosurfactants for MEOR. They are known as ex-situ and in-situ applications (Geetha, Banat, & Joshi, 2018). In ex-situ applications, the generation of biosurfactants occurs inside a bioreactor through the aerobic fermentation of microbes, and then they can be injected into the oil reservoirs to enhance oil recovery. However, in-situ biosurfactant production is a process where the bacteria and their nutrients inject into the oil reservoir, and the production of biosurfactants happens inside the reservoir which can eventually enhance the oil recovery (Geetha et al., 2018). Comparing to ex-situ applications, in-situ biosurfactant production is considered more advantageous for MEOR application due to the low production cost (Cui, Sun, Luo, Yu, & Zhang, 2017; Youssef et al., 2007). To perform a better in-situ application in MEOR, it is necessary to study the properties of microbes suitable for in-situ application under the conditions of oil reservoir such as pressure, temperature, pH, oxygen level, and salinity (Liang et al., 2017; Zhao et al., 2017a).

Conclusions

Biosurfactants are widely known as multi-functional compounds due to their non-harmful properties as compared to the synthetic surfactants. Therefore, industries such as cosmetic, pharmaceutical, food, petroleum, wastewater treatment, textile, and agricultural sections employed biosurfactants for different purposes. However, some challenges are facing the production of biosurfactants and possible biological sources. In this regard, various studies revealed that these problems can be tackled by further investigating of different microorganisms and plant as alternative sources. This review significantly outlined the latest studies related to the application and properties of natural surfactants and their influence on the environment and human health. Expectedly, it was found that bio-based surfactants could be applied for a better treatment of contaminated soil and water with heavy metals, treatment of skin diseases, oil recovery enhancement, food preservation, and removal of diseases from plants.

Conflicts of interest

The authors declare no conflicts of interest.

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