

Review Article

Use of Surfactants and Biosurfactants in Oil Recovery Processing and Cellulose Hydrolysis

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Introduction

Surfactants are a group of surface active molecules. Generally, these molecules reduce the surface tension and interfacial tension in both aqueous solutions and hydrocarbon mixtures. These properties create micro-emulsions in which micelle formation occurs, where hydrocarbons or other hydrophobic substrates can solubilise in water, or water in hydrocarbons. Biosurfactants are a group of surfactants produced by microorganisms. The properties of the various biosurfactants have been extensively reviewed [1-5]. Generally, the structure of biosurfactants includes a hydrophilic moiety composed of amino acids or peptides, anions or cations, or mono-, di-, or polysaccharides. The hydrophobic portion is often made up of saturated, unsaturated or hydroxylated fatty acids [5], or composed of amphiphilic or hydrophobic peptides. World-wide interest in biosurfactants has increased due to their ability to meet most synthetic surfactants' requirements [6]. Biosurfactant(s) spontaneous release and function are often related to hydrocarbon uptake; therefore, they are predominantly synthesized by hydrocarbon degrading or tolerating microorganisms. However, some biosurfactants have been reported to be produced on water-soluble compounds, including carbohydrates and alcohols such as glucose, sucrose, glycerol or ethanol [7]. Chemical surfactants have been utilized in the oil industry to aid the clean-up of oil spills and Enhance Oil Recovery from oil reservoirs (EOR). These compounds are not biodegradable and can be toxic to the environment. Biosurfactants have been shown in many cases to have equivalent emulsification properties and are biodegradable. Thus, there is an increasing interest in the possible use of biosurfactants in mobilizing or removing heavy crude oil, transporting petroleum through pipelines, managing oil spills, controlling oil pollution, cleaning oil sludge from oil storage facilities,

Abstract

Surfactants are amphiphilic compounds which can reduce surface and interfacial tensions by accumulating at the interface of immiscible fluids, increasing the solubility, motility, bioavailability and subsequent biodegradation of hydrophobic or insoluble organic compounds. Biosurfactants are surfactants that are produced extracellularly or as a part of the cell membrane by bacteria, yeasts and fungi. Their applications in the environmental industries are promising due to their biodegradability, low toxicity and effectiveness in enhancing the biodegradation and solubilisation of hydrophobic compounds. Examples include rhamnolipids produced by *Pseudomonas aeruginosa*, sophorolipids produced by *Candida bombicola* and *Bacillus subtilis* which produces a lipopeptide called surfactin and other biosurfactant producing microorganisms. The beneficial environmental applications of surfactants and biosurfactants in oil recovery processing is discussed in this review. The recent utilization of these molecules in cellulose hydrolysis is also evaluated.

Keywords: Surfactants; Biosurfactants; Oil Recovery Processing; Cellulose Hydrolysis

soil/sand bioremediation and Microbial Enhanced Oil Recovery (MEOR). MEOR offers major advantages over conventional EOR in that lower capital and chemical/energy costs are required and safety towards environment [8]. On the other hand, biosurfactant has been one of the most common additives in the bioconversion of lignocellulose to enhance the hydrolytic performance of cellulase enzymes [9]. In this review, a variety of environmental surfactants and biosurfactants applications are discussed. Specific uses of these molecules in oil recovery processing are described. In addition, the application of surfactants and biosurfactants in the hydrolysis of cellulose is also discussed.

Surfactants and Biosurfactants

Surfactants

Surfactants are amphiphilic compounds that reduce the free energy of the system by replacing the bulk molecules of higher energy at an interface. Surfactants have been used industrially as adhesives, flocculating, wetting and foaming agents, de-emulsifiers and penetrants [10]. The petroleum industry has traditionally been the major user, as in enhanced oil removal applications. In this application, surfactants increase the solubility of petroleum components [11]. The typical desirable properties are solubility enhancement, surface tension reduction, and low critical micelle concentrations. The effectiveness of a surfactant is determined by its ability to lower the surface tension, which is a measure of the surface free energy per unit area required to bring a molecule from the bulk phase to the surface [12]. The surface tension correlates with the concentration of the surface-active compound until the Critical Micelle Concentration (CMC) is reached. Efficient surfactants have a low critical micelle concentration (i.e. less surfactant is necessary to

Table 1: Industrial environmental applications of chemical surfactants and biosurfactants.

Industry	Application	Role of surfactants and biosurfactants
Petroleum	Enhanced oil Recovery	Improving oil drainage into well bore; stimulating release of oil entrapped by capillaries; wetting of solid surfaces; reduction of oil viscosity and oil pour point; lowering of interfacial tension; dissolving of oil
	De-emulsification	De-emulsification of oil emulsions; oil solubilization; viscosity reduction, wetting agent
Environmental	Bioremediation	Emulsification of hydrocarbons; lowering of interfacial tension; metal sequestration
	Soil remediation and flushing	Emulsification through adherence to hydrocarbons; dispersion; foaming agent; detergent; soil flushing

decrease the surface tension). The CMC is defined as the minimum concentration necessary to initiate micelle formation [13]. In practice, the CMC is also the maximum concentration of surfactant monomers in water phase and it is influenced by pH, temperature and ionic strength. The choice of surfactant is primarily based on product cost [14]. In general, surfactants are used to save energy and consequently energy costs. Charge-type, physicochemical behaviour, solubility and adsorption mode are some of the most important selection criteria for surfactants. New markets are currently being developed for use in the bioremediation of contaminated lands [15]. Surfactants, in addition to organic solvents, chelating agents, acids and bases, have been used to enhance heavy metal removal [16].

Biosurfactants

Some surfactants, known as biosurfactants, are biologically produced by yeast or bacteria from various substrates including sugars, oils, alkanes and wastes [17]. Biosurfactants are grouped as glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids, polymeric and particulate compounds [18]. The CMCs of the biosurfactants generally range from 1 to 200 mg/L and their molecular mass is from 300 to 1500 Da [19]. For example the CMC of *Staphylococcus* sp. 1E biosurfactant is 750 mg/l [8]. They can be potentially effective with some distinct advantages over the highly used synthetic surfactants including high specificity, biodegradability and biocompatibility and safety to human health and environment [1]. For example, glycolipids from *Rhodococcus species* 413A were 50% less toxic than Tween 80 in naphthalene solubilization tests [20]. A group of biosurfactants that has been studied extensively is the rhamnolipids from improved concentrations of sophorolipid of 150 g/L have been obtained using canola oil and lactose as the substrate [21]. *Bacillus subtilis* produces a lipopeptide called surfactin (Figure 1) containing seven amino acids bonded to the carboxyl and hydroxyl groups of a 14-carbon acid [22]. Surfactin concentrations as low as 0.005% reduce the surface tension to 27 mN/m, making surfactin one of the most powerful biosurfactants. The primary structure of surfactin was determined many years ago [22]. It is a heptapeptide with a β -hydroxy fatty acid within a lactone ring structure. More recently, the three dimensional structure was determined by 1H NMR techniques [23]. Surfactin folds into a β -sheet structure, which resembles a horse saddle in both aqueous solutions and at the air/water interface [24].

Industrial and Environmental Applications

Chemical and biological surfactants play an important role in oil recovery and pollutant bioremediation. Various surfactants environmental applications are shown in Table 1.

Oil recovery and processing

Chemical surfactants and biosurfactants can increase the pseudo-

solubility of petroleum components in water [25]. Surfactants are effective in reducing the interfacial tensions of oil and water *in situ* and can also reduce the viscosity of oil and remove water from oil prior to processing [26]. Biosurfactants can be as effective as the synthetic chemical surfactants and for certain applications they have many advantages such as high specificity. Most of the biosurfactants and many chemical surfactants employed for bioremediation purposes are biodegradable.

Microbial enhanced oil recovery: Poor oil recovery in oil-producing wells may be due to either the low permeability of some reservoirs or high viscosity of the crude oil, resulting in poor mobility. The concept of Microbial Enhanced Oil Recovery (MEOR) was first proposed nearly 80 years ago but received only limited attention until the early 1980's [27]. MEOR technology has advanced from laboratory-based studies in the early 1980's to field applications in the 1990's. The ability of indigenous or injected microorganisms to synthesize useful fermentation products to improve oil recovery from the oil reservoirs is exploited in MEOR processes. MEOR-participating microorganisms produce a variety of products such as biosurfactants, polysaccharides, carbon dioxide, methane and hydrogen [27]. Enhanced oil recovery of the residual oil in reservoirs can also be achieved by the plugging of highly permeable watered out regions of oil reservoirs with bacterial cells and biopolymers [27]. MEOR processes may be implemented by direct injection of nutrients with microbes that are capable of producing desired products *in situ* for the mobilization of oil or alternatively the process may involve the injection of the microbial products. These biological interventions are followed by reservoir re-pressurization, interfacial tension/ oil viscosity reduction and selective plugging of the most permeable zones to move the additional oil to the producing wells. The application of biosurfactants which aid oil emulsification and oil films detachment from rocks have considerable potential in MEOR processes [28]. Microorganisms are capable of synthesizing biosurfactants from crude oil, pure hydrocarbons and a variety of non-hydrocarbon substrates such as simple carbohydrates (exp: glucose), acids and alcohols (exp: glycerol). Any biological method requires consideration of the environmental conditions of the reservoir in terms of salinity, pH, temperature and pressure [29]. Among microorganisms, only bacteria are considered promising candidates for MEOR. Molds, yeasts, algae and protozoa are not suitable either due to their morphological characteristics and/or to the growth conditions present in reservoirs [29].

Other oil-processing operations: Since chemical surfactants have the properties of solubility enhancement and surface tension reduction of crude oil, they also have a potential application for oil recovery from petroleum tank bottom sludges and facilitating heavy crude transport through pipelines [30]. Emulsan, an excellent bioemulsifier produced by *A. calcoaceticus* RAG-1, formerly *Arthrobacter* RAG-1,

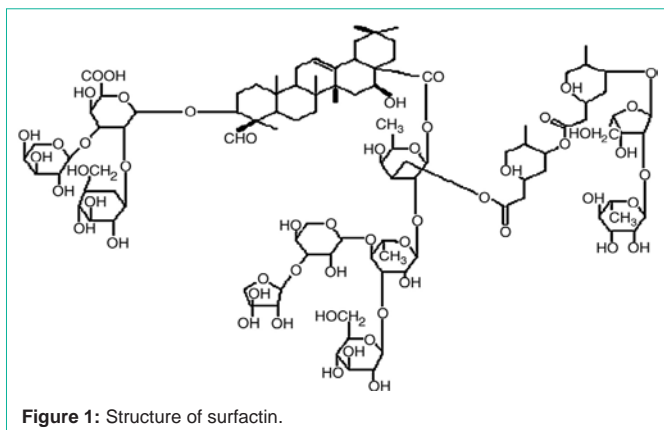


Figure 1: Structure of surfactin.

is a polyanionic heteropolysaccharide bioemulsifier which consists of N-acetyl-D galactosamine, N-acetylgalactosamine uronic acid and an amino sugar linked covalently with fatty acid side chains of α - and β - hydroxydodecanoic acid [30]. The application of Emulsan has been found to reduce the viscosity of Boscon heavy crude oil from 200,000 to 100 cP, thus facilitating the pumping of heavy oil 26,000 miles in a commercial pipeline [30]. Kuwait Oil Company has used biosurfactants for crude oil storage tank clean-up with up to 90% oil recovery [31]. Rhamnolipids biosurfactant can be used to remove the soaked oil from the used oil sorbents [31]. Although >95% of oil removal was achieved, with rhamnolipids JBR215 (Jeneil Biosurfactant Company, USA), concentration had little effect when tested at two concentrations 10 and 20 cm³/dm³ and the main factors affecting oil removal were the sorbent pore size and washing time [31].

Effects of surfactants and biosurfactants on cellulose hydrolysis

Lignocellulose is the most abundant renewable resource on earth [32]. The hydrolysis of lignocellulosic biomass into simple sugars and subsequent fermentation to biofuels has a great meaning to energy and environmental benefits, thus attracting extensive attention of researchers [33]. Surfactant has been one of the most common additives in the bioconversion of lignocellulose to enhance the hydrolytic performance of cellulase enzymes [33]. Chemical surfactants like PEG 6000, Tween 80 and glyceryl alcohol have been demonstrated to increase lignocelluloses hydrolysis in many cases [34]. The mechanisms of enhancing the enzymatic hydrolysis of biomass by surfactants have been interpreted as increasing the stability of enzyme and reducing the nonproductive adsorption caused by lignin [35]. Sophorolipid from saccharomycetes increased the saccharification of oat spelt xylan and wheat bran by 20% [36]. As an important category of biosurfactants, lipopeptide may also have beneficial effect on lignocellulose hydrolysis. The mechanism of improving biomass hydrolysis by lipopeptide was also studied. Liu et al, [37] found that the lipopeptide from *Bacillus* sp. W112, could enhance the enzymatic hydrolysis by fungal and bacterial enzymes. Lipopeptide was shown to be more effective in promoting saccharification than chemical surfactants at low dosages, with a best stimulatory degree of 20.8% at 2% loading of the substrates (w/w). Lipopeptide increased the thermostability in commercial cellulase cocktails. Moreover, the dual effects of lipopeptide on the adsorption

behaviors of cellulases were found. It specifically lowered the non-productive binding of cellulases to lignin and increased the binding of cellulases to cellulose.

Conclusion

The application of chemical surfactants in the desorption of hydrophobic contaminants from soil and subsequent biodegradation have been widely studied. The use of biosurfactants in the remediation of contaminated sites also has many advantages. They seem to enhance biodegradation by influencing the bioavailability of the contaminant. Due to their biodegradability and low toxicity, they are very promising for use in remediation technologies. However, more information is needed on their structure, their interaction with soil and contaminants and scale up and cost for production. Compared to chemical surfactants, biosurfactants have a broader prospect for industrial applications because they are more environmentally friendly and more effective in some researches. Surfactants have attracted increasing interest for their capability to improve the enzymatic hydrolysis of lignocellulosic biomass.

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