A Study of Surface Biosurfactants Applications on Oil Degradation

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Abstract:
Biological decomposition techniques and isolation of environmental pollutions using biosurfactant bacteria are one of the effective methods of environmental protection. Biosurfactants are amphiphilic compounds produced from several species of bacteria. They are environmentally friendly, biodegradable, less toxic and non-hazardous. This paper is designed to investigate experimentally removal of oil from oily sludge by biosurfactants. For this purpose, Preparation of biosurfactant was done in glass flasks and laboratory conditions. The surface tension of culture was measured by tensiometer. Finally, a study for the feasibility of removing oil from sludge by biosurfactant sixteen of experiments were designed.

Key words: Biosurfactants; Bacteria; Decomposition; Biodegradation.

1. Introduction
The release of contaminants, such as petroleum and petroleum derived products, into the environment is one of the main causes of global pollution. A large number of contaminants are toxic and carcinogenic, placing both human and animal health at risk. Through capillarity, hydrocarbons adsorb to surfaces and are trapped in a water immiscible phase, making these compounds difficult to remove from contaminated environments [1, 2].

Storage and management of oily sludge is a crucial issue for petroleum companies because of the hazardous nature of the sludge which typically consists of 10–12% solids, 30–50% water and 30–50% oil by weight. It has been suggested that the recovery of oil from oil sludge is economically feasible if the sludge contains at least 10% oil [3].

There are various methods for remediation of this type sludge, these common methods are presented have some restrictions and the efficiency of common remediation techniques such as bio remediation using hydrocarbon degrading bacteria or plants are significantly hindered from the presence of high pollutant concentrations in sludge[3]. Conventional landfarming approaches to bioremediation of refinery and other petroleum sludges are not acceptable environmentally and are banned in most North American jurisdictions. Incineration and thermal desorption are regarded to be among the most expensive treatment methods and the high temperatures involved requires high energy input and results in significant greenhouse gas emissions [5]. Surfactants are molecules that contain both a hydrophobic and a hydrophilic moiety and that partition at interfaces between liquids with different polarity and hydrogen bonding. Therefore, surfactants are capable of
lowering the surface and interfacial tension affecting the way other molecules behave at interfaces and in solution. These properties make surfactants extremely useful in many industries for a vast number of applications involving emulsification, detergency, wetting, foaming, dispersing or solubilization. Biosurfactants are natural surfactants produced by certain microorganisms primarily when living on water-immiscible substrates. Because of their unique properties, natural surfactants, also known as biosurfactants, have received extensive attention in the past years as promising replacements of synthetic surfactants. Biosurfactants are not only biodegradable and nontoxic but they also have all the advantages of chemically produced surfactants. In addition, some biosurfactants have shown more effective and specific surface-active properties than many conventional synthetic surfactants, providing new possibilities for industrial applications. Biosurfactants have a tremendous potential in environmental protection, pharmaceutical and cosmetic production processes as well as in petroleum, biocides, agriculture, and food industries. As a result, every year millions of tons of surfactants (equivalent to billions of dollars) are commercialized in the world. The major consumers of this market are North America with 35%, followed by Asia-Pacific with 29%; and Western Europe with 23%. Looking for more environmentally friendly processes in contrast to traditionally produced surfactants based on petroleum feedstock, extensive research has been done on biosurfactants in the last few decades. Biosurfactants are generally microbial metabolites that are excreted to the extracellular media or incorporated in the cell wall mainly to facilitate the diffusion of a hydrocarbon substrate into the cell [6].

Remediation techniques for hydrocarbon contamination have been researched extensively; one practical alternative is the elimination of oil pollutions from oil sludge by using biosurfactant. In recent years, oil removal from sludge and contaminated soils by washing processes is achievable, and the inclusion of biosurfactant in the washing process is a promising strategy. Washing in general does not produce additional harmful products, and bio-surfactants are biodegradable and have low toxicity. Biosurfactants show better environmental compatibility and high activity at extreme temperatures, pH and salinity than synthetic surfactants and can be blended with other (bio and/or synthetic) surfactants and solvents to offer desired performance characteristic [3]. Removal efficiency is directly related to the chemical structure of the compounds, their bioavailability (concentration, toxicity, mobility and access) and the physicochemical conditions of the environment [2]. These characteristics make biosurfactants attractive for environmentally friendly processes especially in the food, Pharmaceutical, and oil industries.

2. Classification and Properties of Biosurfactants

Unlike chemically synthesized surfactants, which are classified according to their dissociation pattern in water, biosurfactants are categorized by their chemical composition, molecular weight, physico-chemical properties and mode of action and microbial origin. Based on molecular weight they are divided into low-molecular-mass biosurfactants including glycolipids, phospholipids and lipopeptides and into high-molecular-mass biosurfactants/bioemulsifiers containing amphipathic polysaccharides, proteins, lipopolysaccharides, lipoproteins or complex mixtures of these biopolymers. Low-molecular-mass biosurfactants are efficient in lowering surface and interfacial tensions, whereas high-molecular-mass biosurfactants are more effective at stabilizing oil-in-water emulsions [7].

Among the best studied biosurfactants are rhamnolipid that belong to the glycolipid class. Rhamnolipid have been identified predominant from Pseudomonas aeruginosa [8]. Biosurfactant activities depend on the concentration of the surface-active compounds until the critical micelle concentration (CMC) is obtained [7]. The concentration at which micelles began to form was represented as the CMC [9]. At concentrations above the CMC, biosurfactant molecules associate to form micelles, bilayers and vesicles (Figure 2). Micelle formation enables biosurfactants to reduce the surface and interfacial tension and increase
the solubility and bioavailability of hydrophobic organic compounds. The CMC is commonly used to measure the efficiency of surfactant. Efficient biosurfactants have a low CMC, which means that less biosurfactant is required to decrease the surface tension. Micelle formation has a significant role in microemulsion formation. Microemulsions are clear and stable liquid mixtures of water and oil domains separated by monolayer or aggregates of biosurfactants. Microemulsions are formed when one liquid phase is dispersed as droplets in another liquid phase, for example oil dispersed in water (direct microemulsion) or water dispersed in oil (reversed microemulsion) [7].

Figure 2. Chemical structures of Rhamnolipid biosurfactants [10].

3. Role of Biosurfactants in Biodegradation Processes

A promising method that can improve bioremediation effectiveness of hydrocarbon contaminated environments is the use of biosurfactants. They can enhance hydrocarbon bioremediation by two mechanisms. The first includes the increase of substrate bioavailability for microorganisms, while the other involves interaction with the cell surface which increases the hydrophobicity of the surface allowing hydrophobic substrates to associate more easily with bacterial cells. By reducing surface and interfacial tensions, biosurfactants increase the surface areas of insoluble compounds leading to increased mobility and bioavailability of hydrocarbons. In consequence, biosurfactants enhance biodegradation and removal of hydrocarbons. Addition of biosurfactants can be expected to enhance hydrocarbon biodegradation by mobilization, solubilization or emulsification (Figure 3) [7].
Figure 3. Mechanisms of hydrocarbon removal by biosurfactants depending on their molecular mass and concentration [7].

The mobilization mechanism occurs at concentrations below the biosurfactant CMC. At such concentrations, biosurfactants reduce the surface and interfacial tension between air/water and soil/water systems. Due to the reduction of the interfacial force, contact of biosurfactants with soil/oil system increases the contact angle and reduces the capillary force holding oil and soil together. In turn, above the biosurfactant CMC the solubilization process takes place. At these concentrations biosurfactant molecules associate to form micelles, which dramatically increase the solubility of oil. The hydrophobic ends of biosurfactant molecules connect together inside the micelle while the hydrophilic ends are exposed to the aqueous phase on the exterior. Consequently, the interior of a micelle creates an environment compatible for hydrophobic organic molecules. The process of incorporation of these molecules into a micelle is known as solubilization [7].

4. Extraction of the Biosurfactant
The recovery and purification of biosurfactants from complex fermentation broth is a major problem in the commercialization of biosurfactants [12]. Bacterial cells were removed by centrifugation (12,000 x g, 4oC, and 30 min). Cultural supernatant was acidified with 6 N HCl to obtain the pH of 2.0. The extraction was performed twice with an equal volume of ethyl acetate. [9] Biosurfactant yield was expressed as g/l was measured in the cell-free culture medium. Known amounts of crude precipitate were re-suspended in distilled water and used for the determination of the critical micelle concentration (CMC) [11].

5. Industrial and Environmental Applications of Biosurfactants
The main commercial use of biosurfactants is in pollution remediation because of their ability to stabilize emulsions. This enhances the solubility and availability of hydrophobic pollutants, thus increasing their potential for biodegradation [12]. Biosurfactants (Microbial Surface Active Agents) have become recently an important product of biotechnology for industrial and medical applications [3,4].

6. Microbial De-emulsification of Oil Emulsions
Oilfield emulsions, both oil-in-water and water-in-oil, are formed at various stages of exploration, production and oil recovery and processing, represent a major problem for the petroleum industry. A process of de-emulsification is required to recover oil from these emulsions. Since the presence of water and sediments in oil causes corrosion and scaling in tanks and pipelines, a basic sediment and water (BS & W) content of 0.5 to 2.0% has been specified as the maximum allowable in crude oil for transportation through the existing...
pipelines. Factors that influence the stability of emulsions include viscosity, droplet size, phase volume ratio, temperature, pH, and age of emulsion, type of emulsifying agent present, density difference and agitation. Traditional de-emulsification methods include centrifugation, heat treatment, and electrical treatment and chemicals containing soap, fatty acids and long-chain alcohol.

7. Application of Biosurfactant Formulas for Recovering Hydrocarbons from Oil Sludge.

Chenggang Zheng et al. studied on Oil extraction from oil sludge with biosurfactant formulas was optimized by a Taguchi orthogonal array design of L16 (45) with five main factors, including biosurfactant type (surfactin, lichenysin, rhamnolipidandemulsan), biosurfactant concentration, pH, salinity and solvent. Oil recoveries obtained with the sixteen batch washing experiments with the selected levels of each factor were processed with DesignExpert/SPSS. The predicted optimal biosurfactant formula of 2.0 g/L rhamnolipid, pH 12.0, 10 g/L NaCl, and 5.0 g/L nbutanol were validated by a washing experiment that yielded an oil recovery of 74.55%, which was 27.28% higher than the grand average oil recovery of the whole experiment design. Based on the optimum biosurfactant formula, the oil extraction process followed first-order kinetics as the washing rate constant and final oil recovery increased with temperature [2].

In another study by P.J. Joseph et al. separated the oil from the petroleum sludge by induced biosurfactant production by bacteria. The sludge used for the investigation contained TPH in the concentration range of 850 ± 150 g·kg−1. The efficiency of removal of the various isolates ranged from 91.67% to 97.46%. Therefore, it has been observed that the biosurfactant produced by the primary inoculum remained in the supernatant and it was enough to continue the reaction. The biosurfactant displayed the property to reduce surface and interfacial tensions in both aqueous and hydrocarbon mixtures and hence had potential for oil recovery [7].

8. References:

