



Short review

Application of biosurfactants in environmental biotechnology; remediation of oil and heavy metal

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Abstract: Many toxic substances have been introduced into environment through human activities. These compounds are danger to human health when they are ultimately or immediately in contact with soil particles. A conventional method to reduce, degrade and remove these substances is associated with some risk. In recent years, microorganisms have proved a unique role in the degradation and detoxification of polluted soil and water environments and, this process has been termed bio reclamation. The diversity of bioemulsifiers/biosurfactants makes them an attractive group and important key roles in various fields of industrial as well as biotechnological applications such as enhanced oil recovery, biodegradation of pollutants, and pharmaceuticals. Environmental application of microbial surfactant has been shown as a promising due to solubilization of low solubility compounds, low toxicity observed and efficacy in improving biodegradation. However, it is important to note that full scale tests and more information is require to predict the behavior and model of surfactant function on the remediation process with biosurfactants. The purpose of this review is to describe the state of art in the potential applications of biosurfactants in remediation of environmental pollution caused by oil and heavy metal.

Keywords: biodegradation; bioemulsifiers; biosurfactant; remediation; contamination

1. Introduction

Chemical substances released by human and those released in nature are of global concern now. Any undesirable substance released into the environment is termed as 'contaminant', deteriorating effects caused by the contaminant brings about 'pollution', a process whereby man-made and natural resource is made unfit to use [1]. Diverse treatment methods including biological, physicochemical, and thermal have been in use for remediation of polluted sites. Applications of strategies such as excavation, incineration are considered inefficient, costly and usually exchange a problem for other [2]. Alternatively, biological treatment strategy offers more environmentally friendly as well as low cost techniques [3,4], since organic components that account for toxicity may be converted to H₂O and CO₂ via familiar biological pathways [5]. Studies show that under condition with the presence of heavy metal and pesticides may cause multiple stresses to microorganism and may influence its bioremediation properties [6]. However these strategies have limitation as a result of low solubility exhibited by the contaminants in an aqueous medium, and this limiting the availability of the bio degraders microbes [7]. Two mechanisms are involved on how surfactants act; firstly, it acts by lowering the interfacial surface tension between oil-aqueous phases thereby lowering the mobility of the organic components. It's therefore capable of transferring the hydrophobic organic compounds to the mobile phase. Surfactants are able to form aggregates called micelles, hence solubilizing hydrophobic organic compound [8]. This review is aimed at providing an overview of characteristic features of biosurfactants and artificial surfactants, influence of biosurfactants on emulsification, sorption and environmentally-safe biodegradation organic pollutants that are hydrophobic in nature. The influences of biosurfactants on microbe (degraders) as well as mycoremediation via white rot fungi. Applications of biosurfactants in bioremediation processes are considered.

2. Biosurfactants

Biosurfactant is made up of a hydrophobic and hydrophilic component. The polar part of biosurfactant can be an amino acid, a carbohydrate, and/or a phosphate group. Long chain fatty acid constitutes the nonpolar portion. Biosurfactants or Natural surfactants can be produced extracellularly by a wide range of microorganisms including bacteria, fungi, and yeast. *Bacillus salmalaya* [9], *Candida lipolytica* [10], *Pseudomonas aeruginosa* [11], and *Saccharomyces lipolytica* [12] are examples of microorganism able to produce biosurfactant. The hydrophobic portion of biosurfactant is due to the presence of long chain fatty acids groups, and it can also be a phosphate, alcohol, carboxylic acid, carbohydrate, amino acid or cyclic peptide. Basically, the microbial surfactants are considered as the complex molecules with a diverse range of chemical structures [13,14]. Biosurfactants are grouped mainly based on their microbial origin or chemical contents/composition such as fatty acids, antibiotics, peptides, glycolipids, phospholipids, lipopeptides. Those microorganisms are able to synthesize surfactants in combination with many other chemicals. The yield of microbial surfactant varies depending on the nutritional requirements and environment for growing microorganism. In fact microbial cells that have high cell surface hydrophobicity are themselves surfactants. The most common types of biosurfactant are Glycolipids [15,16].

Glycolipids consist of monosaccharides, disaccharides, trisaccharides, and tetra saccharides including glucuronic acid, galactose sulphate, galactose, mannose, glucose, and rhamnose. The fatty

acid constituent usually has a composition similar to that of the phospholipids of the same microorganism. The glycolipids can be categorized as *Trehalose lipids*, *Sophorolipids* (produced by different strains of the yeast), and *Rhamnolipids* [15].

Moreover, biosurfactants can be classified into two main categories based on the molecular weight they have, high-molecular weight polymers or bioemulsans and low-molecular-weight molecules called biosurfactants. The low molecular weight biosurfactants with lower surface and interfacial tension includes groups of macromolecules such as proteins, lipopeptides, glycolipids, and phospholipids. Since this group consists of polymers of polysaccharides, lipoproteins, and particulate surfactants, so they are considered more effective as emulsion-stabilizing agents, such as they play an important role in stabilizing oil-in-water [17–19]. For example, surfactin and rhamnolipids are low-molecular mass biosurfactants with molecular weight of 1036 and 802 Da, respectively [20–22].

High molecular weight biosurfactant are generally polyanionic heteropolysaccharides containing proteins and polysaccharides. Extracellular lipopolysaccharide biosurfactant produced by *Acinetobacter calcoaceticus*, *Acinetobacter radioresistens* KA53 are a high-molecular-weight bioemulsifier (1000 kDa and 1MDa) [23].

Hydrocarbons, oil wastes, olive oil, vegetable oils and carbohydrates are used as carbon sources for biosurfactant production. Dadrasnia *et al.* [24] demonstrated a novel isolated *Bacillus salmalaya* strain 139SI from agricultural soil and was found potential for degradation of hydrocarbon from contaminated soil and wastewater. This bacterium produced biosurfactant in Brain-heart infusion broth media with various added hydrocarbons (lubricating, diesel and crude oils). Their research evaluated the effect and concentration of different sodium chloride, phosphates, and carbon source and the interaction between them. Results illustrated the highest surface tension (ST) reduction (71.1%) in optimized cultural conditions (pH 6.5, 36 °C, 1% sunflower oil). The phyto-genic surfactant (released from decaying roots) and cyclodextrins surfactant are another group of biosurfactants which are important in degradation of hydrophobic organic compounds in contaminated soil and aqueous solutions.

2.1. Structures and applications of biosurfactant

All surfactants consist of two ends which are hydrophobic and hydrophilic end respectively. For hydrophobic region, it is made up of a molecule which consists of hydrocarbon part which made up of a long-chain of fatty acid, hydroxy fatty acids, hydroxyl fatty acids or α -alkyl- β -hydroxy fatty acids which mainly found at the C8 to C22 alkyl chain or alkylaryl that usually either in linear or branched form. Meanwhile, hydrophilic region of the molecule is soluble in water that could be carbohydrate, amino acid, cyclic protein peptide, carboxylic acid, phosphate or alcohol [25]. This amphiphilic moiety of biosurfactants enabled it to lower the surface and interfacial tensions among individual molecules both at the surface and interface, respectively [26]. The amphiphiles that form micelles, bilayers or vesicles are believed potentially to be applied for surface chemical works as it defined as surface active agents or surfactant [27]. Biosurfactants were used to increase the surface area and the bioavailability of hydrophobic organic substrates, meanwhile regulate the attachment and removal of the microorganisms from the surfaces [16]. When the mixture containing oil, water and surfactant, the surfactant will lie at the water-oil interface; this emulsion characteristic provided

a remarkable foaming, dispersing capacity, detergency and emulsifying; that enable surfactants as one of the most utility chemical in industrial processes [27].

Surfactants can be grouped based on the characteristic of the charge on an individual polarity. Anionic surfactants possessed negative charge, mostly because of the presence of a sulphonate or a Sulphur group. Meanwhile, cationic surfactants are positively charged due to the presence of a quarternary ammonium group.

Biosurfactants are mostly glycolipids. Glycolipids are carbohydrates linked to hydroxyaliphatic fatty acids by ester group. Most commonly known glycolipids are rhamnolipids, trehalolipids and sophorolipids. First of all, rhamnolipids are considered the principal glycolipids produced by bacteria *Pseudomonas aeruginosa*, with one or two rhamnose molecules joined to one or two molecules of hydroxydecanoic acid [28]. It is a widely studied biosurfactant utilize for the eradication of hydrophobic compounds from polluted soil [25]. Second, trehalolipids are glycolipids which usually related with most species of *Corynebacterium*, *Mycobacterium*, and *Nocardia*. Trehalose lipids from *Rhodococcus erythropolis* and *Arthrobacter* spp. proved in lowering the surface and interfacial tensions in culture broth from 25–40 and 1–5mN m⁻¹ respectively [29]. Lastly, sophorolipids are glycolipids that usually produced by yeasts, *Torulopsis* sp. and made up of a dimeric carbohydrate sophorose linked by a glycosidic linkage to a long chain hydroxyl fatty acid [28]. Sophorolipid are effective emulsifying agents and could reduce the surface tensions among individual molecules at the surface [26].

A number of bacteria and yeast yielded vast amount of phospholipids and fatty acids surfactants when growing on n-alkanes through microbial oxidations [28]. Fatty acids help in lowering both the surface tension and interfacial tension and in fact most of the active form of saturated fatty acids are found placed in the range of Carbon 12-Carbon14 [18]. Phospholipids are the major components made up the microbial membranes. Phospholipids produced from *Thiobacillus thiooxidans* playing an important role in wetting elemental sulphur vital for growth [25]. Lipoproteins and lipopeptides are also known as cyclic surfactin which usually synthesized by *Bacillus* sp. which made up of seven amino acids that linked to a carboxyl (COO-) and hydroxyl (OH-) groups of C14 acid. The cyclic lipopeptide surfactin produced by *Bacillus subtilis* ATCC21332 is an example of one of the most stronger biosurfactants which could improve the yield of surfactin production up to 0.8g/l by constantly eradicating the surfactant by foam fractionation and iron or manganese addition to the growth medium [30]. Besides, there are also polymeric biosurfactants, mostly are polymeric heterosaccharide containing proteins which include emulsan, liposan, alas an, lipomanan and polysaccharide-protein complexes [28]. Emulsan usually synthesized by *Acinetobacter calcoaceticus* RAG-1 which is a potent polyanionic amphipathic heteropolysaccharide emulsifying agent for hydrocarbons in water whereas liposan is an extracellular emulsifier that able to dissolve in water are produced by *Candida lipolytica* which constituted of carbohydrate 83 % and protein composition of 17 % [25].

Studies showed that biosurfactants possess numerous advantages beyond chemically synthesized surfactants. First, biosurfactants have high biodegradability as they could easily degrade by bacteria and other microbes; therefore they produce lesser harm to the environment. Second, biosurfactants have lower toxicity compared to chemically synthesize surfactants, and productions from extremophiles have high efficiency at critical pH and temperature values [31]. Thirdly, the biosurfactants biocompatibility and digestibility guarantee their usage in cosmetics, pharmaceuticals, and oil and food industries. Besides, the accessibility of raw material in producing biosurfactant are

massive, cheap raw materials can be synthesized biosurfactants that can be accessed in huge quantities easily. For instance, cheaper agro industrial waste material like bagasse, molasses and plant material residues can be utilized to produce biosurfactants that are much more economically and show better environmental compatibility [31]. Depending upon its application, industrial wastes and by-products can be used to produce biosurfactants; hence this could be a premium interest for their large scale production [29]. In addition, biosurfactants can be employed in environmental control as they have high efficiency in industrial emulsions managing, oil spillage controlling, detoxification and biodegradation of industrial effluents and polluted soil bioremediation [32]. Furthermore, due to its specificity; biosurfactants would be a great attractive interest in detoxification of specific contaminants, de-emulsification of industrial emulsions, specific cosmetic, pharmaceutical and food applications due to its complex organic molecules with specific functional groups. Studies proved that the composition of the culture media have great influence in producing compounds with particular applications [25,31]. Moreover, biosurfactants can act as anti-adhesive agents. Biofilm is bacterial adherence which accumulated on any surface, however biosurfactants can alter the hydrophobicity of the surface which will affect the adhesion of microbes over the surface. For instance, a biosurfactant from *Streptococcus thermophilus* slows down the accumulation of other thermophilic strains of *Streptococcus* over the steel which caused fouling [16].

2.2. Environmental factors affecting biosurfactant production

Despite the fact that various forms of biosurfactant possess different structures, there exist some general phenomena regarding their biosynthesis. For instance, in the case of *Arthrobacter paraffineus*, no surface active agent could be extracted from the medium amended by using glucose as carbon source [14]. *Torulopsis petrophilum* is not producing any surfactant when grown on a single-phase medium [33]. Production of biosurfactant by *P. aeruginosa* was strongly decreased upon glucose addition, as carbon source [34].

The quality, quantity and type of biosurfactant produced are influenced by the concentration of the following elements; nitrogen, iron, phosphorus ions, and also medium, the nature of the carbon source, and the environmental conditions including dilution rate, temperature, pH and agitation [16].

Salinity condition will improve the biosurfactant production of *Pseudomonas* strains MEOR 171, while pH, Ca and Mg doesn't affect this production [25]. Biosurfactant production from *Arthrobacter paraffineus* ATCC 19558 prefers utilisation of ammonium as a source of inorganic nitrogen [35]. Addition of some multivalent cations could have positive effect on biosurfactant conditions. In addition, presence of some compounds such as Ethylenediaminetetraacetic acid (EDTA), antibiotic (penicillin) and ethambutol demonstrated the production of interracially active compounds in biosurfactant. The function of biosurfactant through these compounds is achieved either by increased production of water soluble substrates or by their effect on solubilization of nonpolar hydrocarbon substrates. Furthermore, pH and temperature are influenced the biosurfactant production. For example; temperature played important role in production of biosurfactant by *Pseudomonas* sp. DSM 2874 and *Arthrobacter paraffineus* ATCC 19558 [35,36], or pH has been shown vital role in production of biosurfactant by *Ustilago maydis*, *Pseudomonas* sp. and *Torulopsis bombicola* [37,38].

3. Role of Biosurfactants in Environmental Contamination by Oil Spills

3.1. Hydrocarbon degradation

The application of biosurfactants can enhance the processes of bioremediation by means of emulsification (improved by high molar mass), solubilization and mobilization (promoted low-molar mass) (Figure 1) [21–23]. The mobilization mechanism occurs at concentrations below the biosurfactant critical micelle concentration (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 solubilisation process takes place. At these concentrations biosurfactant molecules associate to form micelles, which dramatically increase the solubility of oil [39]. The various components of hydrophobic organic compounds (HOCs) are aromatics, resins, asphaltenes, alkanes, and cycloalkanes [23]. Biosurfactants can be enhanced the bioavailability of HOCs through the following mechanisms: facilitated transport of the pollutants from the solid phase [23] (this mechanism consist of many processes, such as interaction of surfactants with hydrocarbons, interaction of contaminants with single biosurfactant molecules, and the mobilization of pollutants in soil leading to lower surface tension of the soil particle pore water in soil particles), improvement on the apparent solubility of the contaminants (improve the apparent solubility of the HOCs), and emulsification of non-aqueous phase liquid contaminants (in this process biosurfactants can lower the interfacial tension between non-aqueous and aqueous phases, thus it lead to an increase in improving mass transport, the contact area, and mobilization liquid-phase contaminants). In fact, biosurfactants help microorganisms adsorb to soil particles occupied by the contaminant, thereby decreasing the path length of diffusion between the sites of adsorption and the site of bio-uptake process by the microorganisms [40,41].

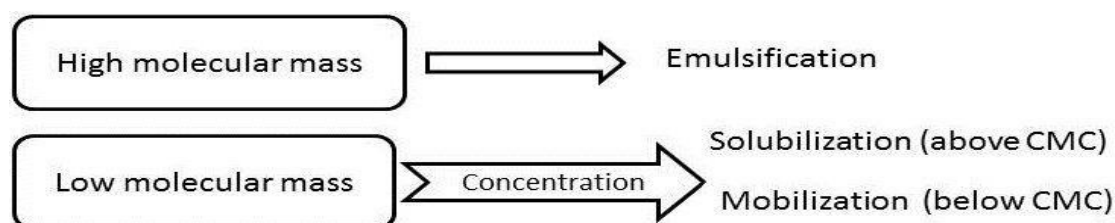


Figure 1. Mechanisms of hydrocarbon removal by biosurfactants.

Application biosurfactant in degradation of HOCs and heavy metal has been shown valuable results (Table 1). Basically, addition of microbial surfactant resulted in improving solubility of HOCs which has vital role for effective bioaugmentation. Degradation process is dependents on presence species of microorganisms, inorganic nutrients, water, pH, composition of hydrocarbon, temperature, and oxygen availability in soil [21]. Dadrasnia, *et al.* [9,24] demonstrated a process to decontaminating wastewater and polluted soil. In their study, a microbial population of 10^8 colony forming unit (CFU) ml^{-1} was used and the *Bacillus salmalaya* strain 139SI has shown degradation rate of 79% and 88% of the total petroleum hydrocarbons upon incubation in mineral salt media

having 2% and 1% of crude oil waste, respectively for a period of 42 days. Berg *et al.* reported recovery of 31 % of the compound in the aqueous phase by utilisation of biosurfactant synthesised by *Pseudomonas aeruginosa* UG2 due to an increase in the solubility of hexachlorobiphenyl added to soil slurries [42]. Application of *A. calcoaceticus* RAG-1 in the petroleum industry such as sludge from barges, clean oil has been shown to reduce viscosity of heavy oils, stabilize the water-in-oil emulsions in fuels and enhance oil recovery [43].

Table 1. Different type of biosurfactant producing during bioremediation process.

Biosurfactant Group	Microorganisms	Applications	Ref.
Glycolipid	<i>Nocardiopsis</i> sp. <i>Arthrobacter</i> sp. <i>Corynebacterium</i> sp. <i>R. wratislaviensis</i> BN38	Enhancement of the biodegradation of hydrocarbons in soil and marine environment	[40,44]
Lipopeptides	<i>Bacillus licheniformis</i> <i>Bacillus subtilis</i> <i>N. alba</i> strain MSA10	Enhancement of oil recovery; removal of heavy metals from a contaminated soil, sediment and water	[45–47]
Polymeric biosurfactants	<i>Saccharomyces cerevisiae</i> <i>Candida lipolytica</i>	Stabilization of hydrocarbon inwater emulsions	[48,49]
Fatty acids	<i>Acinetobacter</i> sp. <i>Rhodococcus erythropolis</i>	Increasing the tolerance of bacteria to heavy metals	[50]

3.2. Microbial enhanced oil recovery (MEOR)

One of the main potential of biosurfactant application is MEOR [51,52]. Microorganism population in tank are energised to synthesize surfactants and polymers so as to lower the interfacial tension at the oil–rock interface. Production of biosurfactant, *in situ*- microorganisms in the tank are usually supplied with low-cost substrates like inorganic nutrients and molasses in order to improve surfactant production and growth (Figure 2) [53]. *In situ*-bacteria must be able to survive under harsh conditions such as low level of oxygen, salinity, high temperature and pressure encountered in oil reservoirs and anaerobic and aerobic thermophiles that withstood pressure and moderate salinity have been isolated which are able to mobilize oil in the laboratory [43]. Banat [54,55] reviewed the effectiveness of MEOR by biosurfactants in field studies carried out in former Czechoslovakia, Hungary, the Netherlands, Poland, Romania, the United States and the former USSR, with a significant increment of oil recovery noted in only some cases. This re-affirm point shows that there is no such commonly used oil reservoir, in which the factors that entrap oil as well as the chemical and physical properties of oil reservoirs vary considerably [56]. Therefore, a generic microbial process might presumably not be fruitful when applied to a specific reservoir [57].

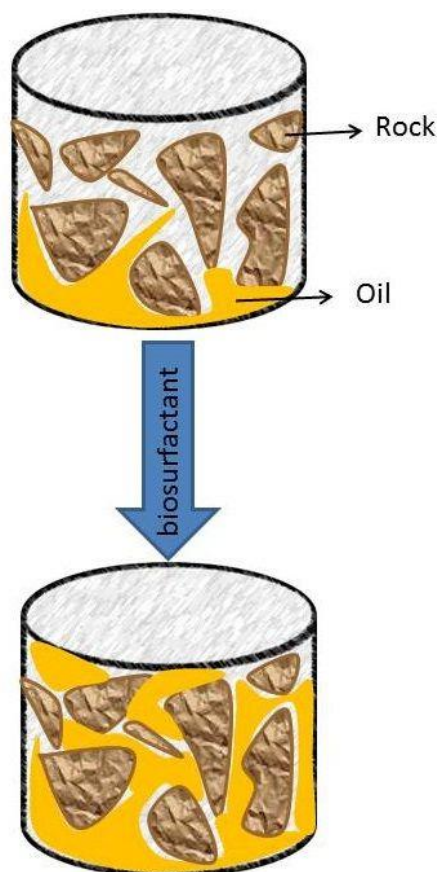


Figure 2. Application of biosurfactant in oil recovery.

3.2.1. Interaction between biosurfactant and microorganism

Biosurfactants possess the prospect for enhancing the bioavailability of hydrophobic organic compounds in polluted sites, which as result enhances efficient degradation processes. Environmental application of biosurfactants in industries are encouraging, due to their biodegradability, low toxicity shown as well as the efficacy in increasing biodegradation and solubilization of compounds with low rate of solubility [58]. In addition, biosurfactant has advantage over chemical-derived surfactant due to its effectiveness at extreme pH or temperature values [59,60]. It has been reported that artificial surfactant, Corexit exhibited a LC_{50} (lethal dose to 50%) against *Photobacterium phosphoreum*, which was found 10 times less compared to rhamnolipids (biosurfactant), indicating the higher toxicity shown by synthetic or chemical-derived surfactant [61]. Evaluation of acute toxicity of the biosurfactants, LBBMA111A, LBBMA155, LBBMA168, LBBMA191 and LBBMA201 was carried out against artificial surfactant, called sodium dodecyl sulfate (SDS) on *Vibrio fischeri* (bioluminescent bacterium) by determining the reduction in light emitted by this bacterium when exposed to different levels of surfactant concentration. In addition, toxic/adverse effects of the both biosurfactants and synthetic were evaluated on the growth of the pure cultures of the following isolates; *Acinetobacter junni* LBBMA36 and *Pseudomonas sp.* LBBMA101B. The effective concentration (EC_{50}) value obtained revealed that biological surfactant exhibited significantly lower toxicity to *Vibrio fischeri* than SDS. The reduction in growth of pure

bacterial cultures due to biosurfactants addition to the medium was lower compared than that observed by addition of SDS [62].

Gudiña *et al.* reported that, emulsifier from *Paenibacillus* strain isolated from crude oil exhibited similar or better emulsifying activity than the chemical surface active compounds, and its emulsifying activity was not hindered by exposure to high temperatures (ranging from 100-121 °C), high salinities (up to 300 g/l), or a wide pH values (ranging from 2-13). Moreover, it has demonstrated higher biodegradability and lower toxicity when compared to the chemical-derived surfactants, thus indicating a greater and greater environmental compatibility [63].

Biosurfactant has potential applications in medical and pharmaceutical areas. It inhibit bacterial growth, tumor growth and also inhibit attachment of pathogenic organisms on the solid surface [7]. In a heterogeneous system, biosurfactant tend to interact with the phase partition between two phases, which is defined as the interface. It has been established that organic molecules from aqueous phase incline to immobilize at the solid interface for all interfacial system. A firm called conditioning film is eventually formed there, leading to change in the properties of the original surface. In parallel to organic conditioning, in the presence of biosurfactant interacting with the interface, adhesion and attachment of the bacteria is affected [60].

3.2.2. Influence of biosurfactant on the breakdown of hydrophobic pollutant using white-rot fungi

Research in the area of bioremediation is mostly concentrated on bacteria, with mycoremediation attracting attention just within the last two decades. The choice of white rot fungi can be attributed to the fact that, they can withstand toxicity levels of most organic pollutant [64]. The interest of using white rot fungi in bioremediation arises due to its capability of degradation significantly of diverse range of toxic environmental contaminants. The nonspecific ability of white rot fungi to degrade wide range of pollutant is understood considering their ecological niche. White rot fungi are such organisms capable to breakdown lignin, a three dimensional polymer present in woody plants. Lignin consist of nonrepeating phenyl propanoid units joined by many carbon to carbon bonds [65]. Various forms of extracellular oxidases enzymes such as laccase, lignin peroxidase and Manganese peroxidase, that are taking part in the lignin degradation are produce by white rot fungi [66], and other enzymes taking part in production of free radicals (ROS and H₂O₂) that breaks down the carbon to carbon and carbon to hydrogen linkages of the lignin/xenobiotics through a mechanism involving free radicals [64], this mechanism involving free radicals provide and justified the reason for nonspecific degradation of extremely diverse structurally contaminants. A white rot fungus is well known for degradation of polyaromatic hydrocarbons (PAHs), polycyclic aromatics, polychlorinated dibenzo (p) dioxins, chlorinated aromatic hydrocarbons, pesticides (dichlorodiphenyltrichloroethane and lindane) and some azo dyes [67].

Breakdown of anthracene and pyrene in the presence of enzyme laccase was observed by addition of biosurfactant, Rhamnolipid at the concentration of 0.065mM and 0.075mM for anthracene and pyrene in reversed micelles respectively. The duration for degradation was 48 hours for both, the highest rates of degradation were found to be 37.52 % and 25.58 % for anthracene and pyrene respectively [68]. Lie *et al* demonstrated the effects of three surfactants dirhamnolipid (biosurfactant), SDS (anionic surfactant) and hexadecyltrimethyl ammonium bromide (cationic surfactant) on the removal of phenol catalyzed by laccase enzyme. Dirhamnolipid enhanced phenol removal, while sodium dodecyl sulfate and hexadecyltrimethyl ammonium bromide were detrimental.

Furthermore, addition of dirhamnolipid improved the removal of phenol at various concentrations, removal of phenol was also enhanced with variations over a wide range of temperature and pH [69]. Their studies suggested the potentiality of dirhamnolipid in bioremediation of phenols in the presence of laccase. The combined solubilization biodegradation process was applied using a rhamnolipid produced by *Pseudomonas* for remediation of soil polluted with phenanthrene. Result from the study demonstrated high percentage in solubilization and phenanthrene concentration was significantly decreased during biodegradation process [70].

4. Role of Biosurfactant in Metal Remediation

Heavy metals are persistent soil contaminants [71]. Remediation of soil contaminated with potentially toxic metal for example lead, zinc, cadmium and chromium has customarily included the exhuming and transport of contaminated soil to hazardous waste locales for landfilling [72]. Currently, great interest in utilizing microorganisms to *insitu* remediation of metal-contaminated surface and subsurface soils has been considered due to the immense cost of conventional remediation [40]. The goal of surfactants utilization for both organics and metals is similar; as to increase the solvency of the contaminant of interest to facilitate the evacuation by biodegradation or flushing. However, it ought to be noticed that there are some key differences between metal-contaminated and organic-contaminated soils that prior to be considered. First, heavy metals are not biodegradable; they can only be transformed from one chemical state to another, as a result changing in their mobility and toxicity state. Some forms of metals can be transformed either by redox processes or by alkylation. Metals can also be accumulated by microorganisms or intracellularly, through metabolism-dependent uptake. Microorganisms can influence the mobility of metal indirectly by adjusting the pH or by stimulating substances which could change the mobility of the metals. In some cases, transform regularly might increases the metal toxicity [73]. Studies show that increasing the pH would reduce the toxicity of nickel by a variety of different organisms, including bacteria (*Serratia marcescens*), filamentous fungi (*Arthrotrrys conoides*, *Penicillium vermiculatum*, *Rhizopus stolonifer*), and yeast (*Cryptococcus terreus*) [74,75]. Conceivable explanations behind this occurrence might be due to under high pH conditions, cells have the capacity being able to take up or adsorb great amount of the metal ions [76].

Second, organics are mostly made up of neutral molecules, meanwhile metals are most often found as cationic species. Since contaminant sorption relies on the chemical properties of both the soil and the contaminant, the choice of surfactant used for contaminant complexation will be essential. The addition of a biosurfactant could promote desorption of heavy metals from its solid phases in two different approaches. The first approach is through the complexation of the free form of metal ions residing in solution. This would decreases the solution-phase activity of the metal and, therefore, promotes desorption according to Le Chatelier's principle. The second approach is through the accumulation of biosurfactants at the solid-solution interface under the condition of reduced interfacial tension. This would allow the direct contact between the biosurfactant and the sorbed metal [77]. Since the utilization of microorganisms and microbial products, e.g., biosurfactants, in bioremediation of metal-contaminated soils shows promising results, consequently, the development of remedial technologies will require further study in several areas. For instance, soils contain numerous cations that may compete with metal contaminants for the biosurfactant complexation sites. Therefore, the selectivity of biosurfactants for metals both in solution and in soil systems must be

prior examined. There is also relatively scanty information regarding the biosurfactant structure and structure sizes, or the efficacy of biosurfactant-metal interactions on these structures. Clearly understood, biosurfactant structure size and charge will influence the movement of biosurfactant-metal complexes through the soil. Moreover, structure size and charge will influence the access of biosurfactants to soil pores and therefore, impact the interaction of biosurfactant with sorbed metals [73]. Next, the mechanisms of heavy metal removal by biosurfactants consist of three main steps: sorption and binding of the biosurfactant to the soil surface and also to the metal; separation of the metal from the soil to the solution; and lastly association of the heavy metal with micelles. Heavy metals are trapped within the micelles through electrostatic interactions and can be easily recovered through precipitation or membrane separation techniques [71].

5. Bioremediation Applications

The application of bioemulsifiers, biosurfactants or microorganisms producing surfactants can be employed in soil contaminants biodegradation methods, water/waste treatment and soil washing [7]. Biosurfactant is not only applicable in bioremediation of petroleum pollutants, but also in decreasing the viscosity of heavy oil, improving recovery of oil from wells, enhancing oil flow via pipelines, cleaning tanks for oil storage and fuel water-oil emulsion stabilization [78]. Liu and co-workers isolated a petroleum degrading strain of bacteria *Bacillus licheniformis* Y-1, capable of producing biosurfactant. Biosurfactant from this strain exhibited great emulsifying properties to different forms of oil, especially the crude oil [79]. *Pseudomonas aeruginosa* F-2, a rhamnolipid producing strain was used for recovery of refinery oily sludge in both laboratory experiment and pilot study, results from the study revealed 91.5% oil recovery during the pilot-scale study [80]. In Shengli oil field of northern China, more than 100 biosurfactant-producing microorganisms were isolated, sixteen which were found to produced biosurfactants that decreased the surface tension of the growth media from 71 to $< 30 \text{ mN m}^{-1}$ after 72 h. The oil recovery efficacies shown by different isolates range between 39 to 88% [81]. Saponin was also found very effective in removal of petroleum from polluted soil [82].

Polycyclic aromatic hydrocarbons (PAHs) is one of the major pollutants found in contaminated sites and are well known dangerous substances due to their mutagenic, carcinogenic and teratogenic effects [83]. Twenty three bacteria were isolated from soil polluted with petroleum waste, biosurfactant production was observed by decreased surface tension and emulsification activities from the ten of these strains. Phenanthrene and Naphthalene were employed as substrate in the study, where spraying of PAHs on the mineral agar demonstrated clearing zones formed by the isolates [84].

In recent years, soil washing is attracting attentions and it serve as one of the time-efficient and versatile technique. This method utilized liquids (usually aqueous) for pollutant removal from soil. The fact that contaminants stick to the surfaces of soil particles and normally are of low water solubility, usually additives such as surfactants acids, are added into the eluents in order to make contaminant soluble in the soil [85]. Electronic waste is one of the global environmental issues that need to be addressed urgently. Ye *et al.* demonstrated the effectiveness of tea saponin in removal of e-waste, the result revealed that 5.0g/L sapanin (natural biosurfactants found in plant) was found to be effectual in extracting 94.5% polybrominated diphenyl ethers, 97.1% polychlorinated biphenyl, 95.1% polycyclic aromatic hydrocarbons, 83.5% lead and 87.1% nickel after successive washing cycles [86].

6. Conclusion and Future Prospects

Human and natural processes resulted in continuous entry of pollutants into environment that contaminate the soil, sediments and water (both surface and ground). Several methods have been harnessed in order to contaminate and restore the affected sites. However, the efficiency these strategies are limited as a result of low solubility of the contaminants in the aqueous medium and also low availability of the microorganism degraders as well as low availability of physic-chemical techniques. Most biosurfactants are produced at laboratory scale and therefore need to be focused toward production in large or industrial scale and subsequent applications in field levels.

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Conflict of Interest

All authors declare no conflicts of interest in this paper

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