energies

MDPI

Review

Biosurfactants: Chemical Properties, Ecofriendly Environmental Applications, and Uses in the Industrial Energy Sector

Yslla Emanuelly da Silva Faccioli [1,2,3], Kaio Wêdann de Oliveira [2,3], Jenyffer Medeiros Campos-Guerra [4], Attilio Converti [2,5], Rita de Cássia F. Soares da Silva [2] and Leonie A. Sarubbo [1,2,3,*]

1 Rede Nordeste de Biotecnologia (RENORBIO), Universidade Federal Rural Pernambuco (UFRPE), Rua Dom Manuel de Medeiros, s/n—Dois Irmãos, Recife 52171-900, Brazil; ysfaccioli@hotmail.com
2 Instituto Avançado de Tecnologia e Inovação (IATI), Rua Potyra, n. 31, Prado, Recife 50751-310, Brazil; kaio.olliver@hotmail.com (K.W.d.O.); converti@unige.it (A.C.); rita.freire@iati.org.br (R.d.C.F.S.d.S.)
3 Escola de Tecnologia e Comunicação, Universidade Católica de Pernambuco (UNICAP), Rua do Príncipe, n. 526, Boa Vista, Recife 50050-900, Brazil
4 Departamento de Engenharia Química, Universidade Federal de Pernambuco, Av. Prof. Moraes Rego, 1235, Cidade Universitária, Recife 50670-901, Brazil; jenyffer.campos@ufpe.br
5 Department of Civil, Chemical and Environmental Engineering, Pole of Chemical Engineering, University of Genoa (UNIGE), Via Opera Pia 15, 16145 Genoa, Italy
* Correspondence: leonie.sarubbo@unicap.br

Abstract: The exploitation of nature and the increase in manufacturing production are the cause of major environmental concerns, and considerable efforts are needed to resolve such issues. Oil and petroleum derivatives constitute the primary energy sources used in industries. However, the transportation and use of these products have huge environmental impacts. A significant issue with oil-related pollution is that hydrocarbons are highly toxic and have low biodegradability, posing a risk to ecosystems and biodiversity. Thus, there has been growing interest in the use of renewable compounds from natural sources. Biosurfactants are amphipathic microbial biomolecules emerging as sustainable alternatives with beneficial characteristics, including biodegradability and low toxicity. Biosurfactants and biosurfactant-producing microorganisms serve as an ecologically correct bioremediation strategy for ecosystems polluted by hydrocarbons. Moreover, synthetic surfactants can constitute additional recalcitrant contaminants introduced into the environment, leading to undesirable outcomes. The replacement of synthetic surfactants with biosurfactants can help solve such problems. Thus, there has been growing interest in the use of biosurfactants in a broad gamut of industrial sectors. The purpose of this review was to furnish a comprehensive view of biosurfactants, classifications, properties, and applications in the environmental and energy fields. In particular, practical applications of biosurfactants in environmental remediation are discussed, with special focus on bioremediation, removal of heavy metals, phytoremediation, microbial enhanced oil recovery, metal corrosion inhibition, and improvements in agriculture. The review also describes innovating decontamination methods, including nanobioremediation, use of genetically modified microorganisms, enzymatic bioremediation, modeling and prototyping, biotechnology, and process engineering. Research patents and market prospects are also discussed to illustrate trends in environmental and industrial applications of biosurfactants.

Keywords: biosurfactant; environmental contamination; remediation; industrial applications; environmental biotechnology

check for updates

Citation: Faccioli, Y.E.d.S.; de Oliveira, K.W.; Campos-Guerra, J.M.; Converti, A.; Soares da Silva, R.d.C.F.; Sarubbo, L.A. Biosurfactants: Chemical Properties, Ecofriendly Environmental Applications, and Uses in the Industrial Energy Sector. *Energies* **2024**, *17*, 5042. https://doi.org/10.3390/en17205042

Academic Editor: Antonio Zuorro

Received: 13 September 2024
Revised: 5 October 2024
Accepted: 8 October 2024
Published: 10 October 2024

1. Introduction

Environmental contamination by complex pollutants is a problem that threatens numerous forms of life and results from human activities [1]. Oil and petroleum derivatives are the most widely used energy sources. The transport and use of these products often leads to diverse forms of contamination, especially in underground aquatic environments [2]. Oil spills are examples of such contamination and have harmed millions of km^2 of environmental protection areas throughout the world [3,4], altering the biological and physical-chemical properties of contaminated sites due to the potential for bioaccumulation, resistance to biodegradation, toxicity, and carcinogenicity [5]. Petroleum, which is the most abundant energy source worldwide, is composed of a mixture of hydrocarbons, mainly alkanes, saturated hydrocarbons, aromatic compounds, resins, asphaltene, naphthene, and natural gas [6].

The various methods adopted to diminish the effects of contamination related to the petroleum sector include remediation processes based on the utilization of chemical surface-active agents, most of which, however, are nonbiodegradable and may lead to secondary pollution [7]. Such chemicals mainly serve as emulsifying or surface tension-reducing agents, especially at the oil–water interface. The suitability of a surfactant for a given application is established on the basis of solubility, tension-reducing capacity, micellar concentration, and wetting characteristics. Chemical surfactants are widely used petro- or oleo-chemical derivatives [8], whose negative effect on humans and the environment has stimulated research into novel technologies that can assist in the reduction of both inorganic and organic pollutants, including metals and hydrocarbons [9].

As "greener" natural materials, biosurfactants are currently gaining significant importance in ecologically correct biotechnological degradation and remediation processes. The advantages of biosurfactants over their chemical counterparts include high selectivity, eco-acceptability, biocompatibility, and greater effectiveness under extreme conditions in terms of temperature and salt concentration. Studies have described the development and use of biosurfactants for restoring contaminated environments as well as remediating inorganic and organic contaminants. Biosurfactants have been successful in microbial enhanced oil recovery (MEOR) and as components in cosmetics and pharmaceuticals, as well as in the treatment of oily sludge and wastewaters. Moreover, these natural surfactants constitute an emerging technology for the removal of heavy metals from soil and aquatic environments [10,11].

2. Biosurfactants

Biosurfactants are sustainable, ecologically correct bioproducts characterized by high selectivity and stability across a wide range of pH values, temperatures, and salinities. These natural compounds have emerged as an important category of surfactants, as their characteristics and structural variability enable use in diverse fields, including manufacturing, biotechnology, and environmental protection. The chemistry and cost of biosurfactants are determined by the microorganisms used, substrates, and purification strategies. The amphipathic nature of biosurfactants enables their partition in two immiscible phases, thus lowering surface and interfacial tensions [12].

Based on the producing organism, biosurfactants are classified as saponins, which are derived from plants, or microbial, which are mainly synthesized by bacteria or yeasts. Saponins generally receive the name of the producing plant; thus, more than one biosurfactant can have the same name. Most microbial biosurfactants are glycolipids, such as rhamnolipids, sophorolipids, and trehalolipids. Rhamnolipids are produced by the bacterium *Pseudomonas aeruginosa* and have excellent surface activity. Especially in terms of sustainability, biosurfactants provide important advantages over petrochemical-based synthetic surfactants and are produced under moderate conditions (in bioreactors or extracted from plants), generally less toxic, and more biocompatible. Moreover, saponins have pharmacological action, including antiviral properties [13].

Sustainability requires considering social, environmental, and economic aspects throughout the production chain of a product to ensure a fully positive impact. With biosurfactants, sustainability not only refers to the way these biomolecules are produced but also to the materials used during production and post-production. For a surfactant to be considered sustainable, sustainability must be present from its conception to its disposal [14]. The design of a new biosurfactant must involve the selection of raw materials that satisfy the properties of the product in a sustainable manner. The extraction and selection of sustainable raw materials must be prioritized. Several aspects must be observed in the selection of raw materials, which must be natural and renewable. Biosurfactants can be obtained from agro-industrial substrates. Other aspects also need to be considered in the production process, such as energy and water consumption and the emission of pollutants into waterbodies and the air. In this regard, the production of biosurfactants can significantly reduce CO_2 emissions, and the use of the crude extract without costly purification steps helps to reduce water and energy consumption as well as other waste emissions [15]. The packaging phase also plays an important role in terms of sustainability. Reusable packaging can reduce the environmental impact of surfactants. Environmental sustainability can also be affected in the product use phase, which results in the generation of waste in the form of rinse water. Biosurfactants have the capacity to reduce the toxicity of the waste generated, as these natural compounds are capable of stimulating the degradation of petroleum hydrocarbons in this waste [14].

Surfactants are usually qualified according to the effect on surface/interfacial tension and the critical micelle concentration (CMC), which is the minimum surfactant concentration required to achieve the lowest surface tension. Surface tension depends on the forces at play among the molecules of a liquid. Surfactants are able to break such forces and reduce the tension between phases, enabling the interaction of two immiscible liquids [16]. Surface tension diminishes more as the concentration of surfactant increases (Figure 1) until the formation of surfactant molecular clusters denominated micelles (Figure 2) [17]. The efficiency of a biosurfactant is measured by the CMC, which ranges from 1 to 2000 mg/L; ranges of oil/water surface and interfacial tensions are respectively about 30–35 and 1–10 mN/m [18].

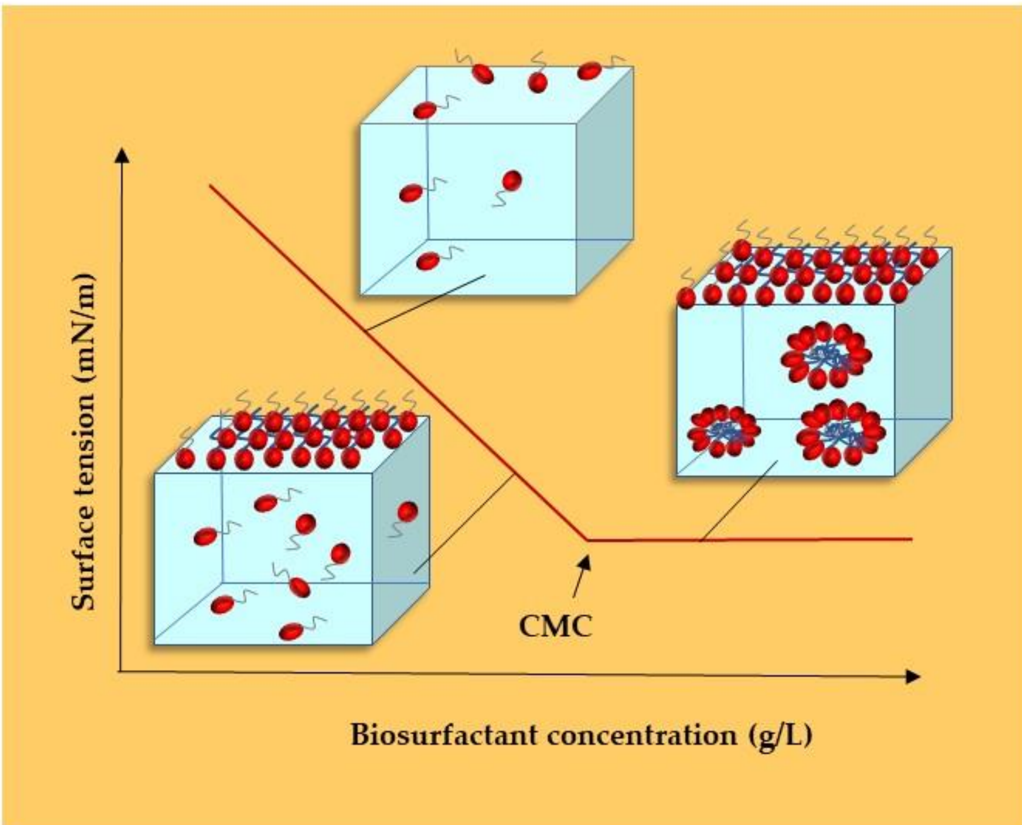

Figure 1. Surfactant concentration increases until critical micelle concentration (CMC) is reached.

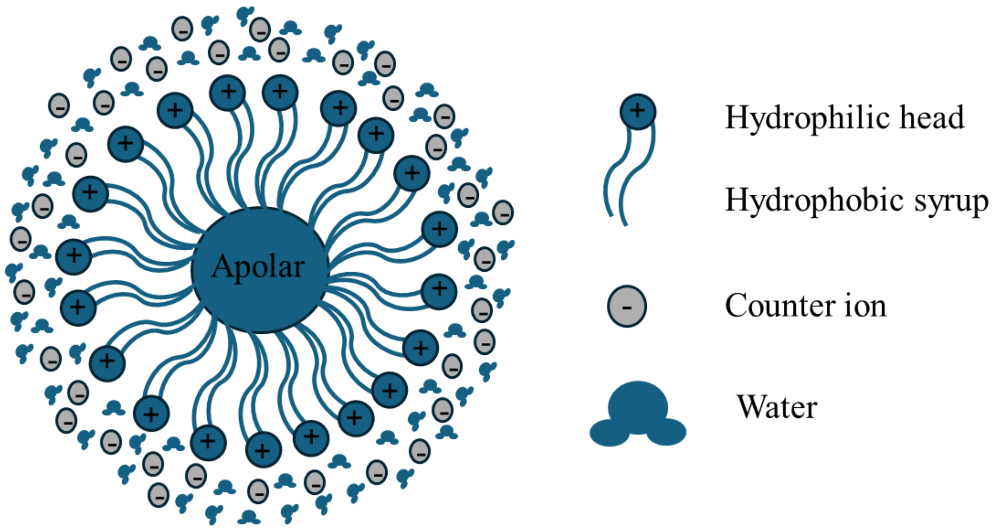

Figure 2. Representation of micellar structure.

The global demand for biosurfactants as raw materials has increased considerably. Taking into consideration the different physical-chemical properties, these natural compounds are more stable than chemical surface-active agents. Various industrial sectors are currently using biosurfactants in formulations of cosmetics, food additives, and detergents or combined with enzymes for the treatment of wastewater. However, the economics of the bioprocess determines the level at which any product will be commercially successful. The incurred costs can be lowered by optimizing the composition of the culture media and mode of production as well as using effective biosurfactant-producing strains. Moreover, the selection of cheaper raw materials can exert a positive impact on the overall production cost [19].

3. Classification of Biosurfactants

Biosurfactants have an amphipathic nature. The hydrophilic portion may be a carbohydrate, amino acid, cyclic peptide, phosphate, alcohol, or carboxylic acid, while the hydrophobic portion may be unsaturated, saturated, linear, or branched fatty acids, which assist in reducing interfacial and surface tensions between two immiscible phases with different degrees of polarity and hydrogen bonds, such as the interphase of water and oil [20]. Bacteria, yeasts, and filamentous fungi are used for the production of phospholipids, glycolipids, fatty acids, lipopeptides, alkyl polyglycosides, and polymeric surfactants. Biosurfactants with low molecular weight are more effective at lowering surface and interfacial tension (air–water); those of high molecular weight are more effective at stabilizing oil-in-water emulsions [21].

3.1. Glycolipids

Glycolipids constitute the most widely investigated class of low-molecular-weight biosurfactants [22]. These microbial molecules are composed of a carbohydrate unit linked to one or more fatty acids and have been receiving greater interest in research due to the green production paths, environmental benefits, and variety of applications. Trehalolipids, rhamnolipids, mannosylerythritol lipids, and sophorolipids are among the best-characterized glycolipids. The emulsifying and antibacterial properties give glycolipids considerable potential in different applications [23]. Polyol lipids are produced by fungi and yeasts and constitute a group of microbial lipids also classified as glycolipids. Polyol esters of fatty acids and liamocins are the two main categories of polyols. These compounds are less studied than other glycolipids but have good potential for commercialization [24].

Rhamnolipids are a combination of α-L-rhamnopyranosyl-α-L-rhamnopyranosyl-β-hydroxydecanoate (Rha-Rha-C10) and α-L-rhamnopyranosyl-α-L-rhamnopyranosyl-βhydroxydecanoyl-β-hydroxydecanoate (Rha-Rha-C10-C10) and their mono-rhamnolipid congeners (Rha-C10 and Rha-C10-C10) [25]. The type produced depends on the strain, carbon source, and culture conditions. Due to their advantageous characteristics, rhamnolipids are among the most useful biosurfactants. Various renewable substrates serve as adequate carbon sources for the production of these biosurfactants, such as used oils and waste from the food industry. The critical micelle concentration of pure rhamnolipids and mixtures ranges from 50 to 200 mg/L, depending on the chemical composition [25]. Although produced mainly by the bacterium *Pseudomonas aeruginosa*, production by congeners and even other genera is also possible. These natural compounds serve as efficient anionic surface-active agents that reduce the surface tension of water from 72 mN/m to approximately 24–27 mN/m [26], enabling the pseudo-solubilization of organic compounds in the aqueous phase, a change in the hydrophobicity of the cell surface, and the formation of emulsions [27].

The hydrophilic moiety of trehalolipids is the disaccharide trehalose. The main trehalolipid-producing bacteria belong to the genera *Nocardia*, *Mycobacterium*, *Corynebacterium*, and *Rhodococcus* [28]. Most of these bacteria breakdown alkanes, and trehalolipid production is induced in the presence of hydrocarbons [29]. Trehalolipids from *Arthrobacter* spp. and *Rhodococcus erythropolis*, respectively, reduce interfacial and surface tensions to 1–5 and 25–40 mN/m [25]. The marine strain *Rhodococcus* sp. PML026 produced trehalose using hexadecane as the substrate [30].

Sophorolipids are produced by different species of yeasts—mainly those of the genus *Starmerella* (initially *Candida*)—and have applications in various industrial processes [25]. These glycolipids have a dimeric carbohydrate (sophorose) linked to a long-chain hydroxylated fatty acid through a glycosidic bond. *Starmerella bombicola* is one of the best producers of these biosurfactants, which can achieve surface tension values of around 33 mN/m and interfacial tension of 5 mN/m between water and *n*-hexadecane [25]. Sophorolipids provide numerous benefits over their chemical counterparts and are useful in pharmaceutical products as well as oil recovery and bioremediation processes. Moreover, the unique composition and molecular structure of sophorolipids confer a diversified gamut of biological attributes as well as functional and physicochemical properties [31].

Mannosylerythritol lipids (MELs) can interact with heavy metals (Pb^{2+}, Cd^{2+}, Hg^{2+}, and Zn^{2+}) and increase the solubility of pesticides, thus reducing environmental toxicity and serving as dispersing agents that can reduce pathogenic microorganisms on animals and leaves [32]. Yeasts of the genus *Moesziomyces* and fungi of the genus *Ustilago* are the main producers of MELs [33,34]. MELs also have antimicrobial activities, especially against Gram-positive bacteria and phytopathogenic fungi, demonstrating considerable potential for use as a safer green option for the partial replacement of synthetic pesticides [35].

3.2. Lipopeptides

Lipopeptides are a subgroup of microbial surfactants that include fengycin, surfactin, iturin, kurstaki, and lichenysin. The type depends on the sequence of amino acids and producing species, such as *Bacillus cereus*, *B. subtilis*, *B. globigii*, *B. thuringiensis*, *B. licheniformis*, *B. amyloliquefaciens*, *B. pumilus*, and *B. megaterium* [36]. Surfactin is one of the most potent biosurfactants ever reported and is able to reduce the surface tension of water from 72 to 27–25 mN/m. This compound is composed of seven L- and D-amino acid residues and a fatty acid residue containing 13 to 15 carbon atoms. The literature reports more than 30 types of surfactin, each with different amino acids and fatty acid residues, although the surfactin molecules remain identical [37]. Surfactin has antibacterial, antiviral, antifungal, and anti-mycoplasma activities, with applications in the health field as well as the food industry as an efficient emulsifier, stabilizer, and surface modifier [38]. Lichenysin was first discovered in the supernatant of a *B. licheniformis* culture and is quite similar to surfactin, the only difference being the presence of glutamine rather than glutamic acid in the amino acid 1 position [39]. Lichenysin is highly stable in a broad range of pH values as well as at high temperatures and at high concentrations of salt [40].

3.3. Phospholipids

Phospholipids have a phosphate group head and fatty acid tails. The fats are long-chain compounds composed mainly of hydrogen and carbon, whereas the phosphate groups have a phosphorus atom and four connected oxygen atoms. The two portions are connected by glycerol as a third constituent. Phospholipids are the main components of microbial membranes. The production of phospholipids increases considerably when certain hydrocarbon-degrading yeasts or bacteria are grown in alkane substrates [41]. *Thiobacillus thiooxidans* and *Acinetobacter* spp. produce phospholipid biosurfactants [42]. When grown in *n*-alkanes as substrates, these microorganisms have potent surface-active properties. Phospholipids are capable of forming microemulsions as well as diminishing the interfacial tension between hexadecane and water to less than 1 mN/m [43,44].

3.4. Polymeric Surfactants

Polymeric biosurfactants are combinations of compounds with different chemical structures, such as exopolysaccharides, heteropolysaccharides, other polysaccharide-protein complexes, and carbohydrate–lipid–protein mixtures [45]. Liposan, emulsan, and alasan are the most widely investigated polymeric biosurfactants and are respectively produced by *Candida lipolytica*, *Acinetobacter calcoaceticus*, and *Acinetobacter radioresistens* [21,46,47].

Biosurfactants with high molecular weight include proteins containing heterosaccharides (polymeric surfactants) and particulate surfactants used for emulsification [48]. Particulate biosurfactants reduce interfacial tension between two immiscible fluids that form stable emulsions. However, comparatively fewer studies have been published on these molecules. Emulsans are heterolipopolysaccharide biosurfactants produced mainly by *A. calcoaceticus* that have a fatty acid linked through ester and amide bonds and a molecular weight of 1000 kDa [49].

Figure 3 illustrates the chemical structure of the most widely studied biosurfactants.

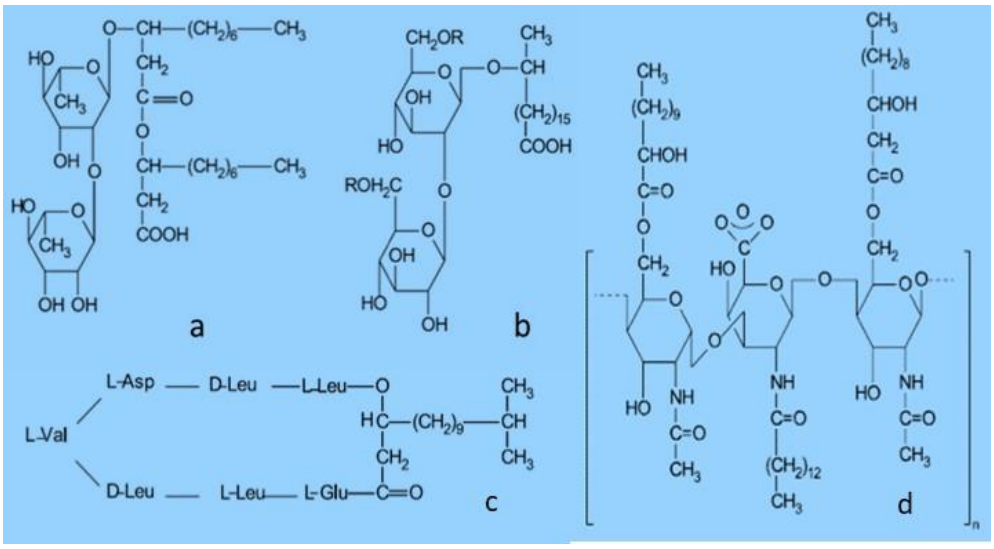

Figure 3. Chemical structure of biosurfactants. (**a**) Rhamnolipid; (**b**) Sophorolipids; (**c**) Surfactin; (**d**) Emulsan.

4. Properties of Biosurfactants

The unique properties of biosurfactants differentiate these natural compounds from their synthetic chemical counterparts and make them the preferred choice for the development of formulations and aggregation studies [50,51]. Biosurfactants preferentially partition liquids of different polarities (water/oil/air), improving the bioavailability of substrates through the reduction in surface and interfacial tensions. Other advantages include broad substrate specificity, low toxicity, structural diversity, biodegradability, environmental compatibility, functional stability in extreme ranges of pH, salinity, temperature, and low CMC.

Microbial biosurfactants have superior foam formation, wetting capacity, phase separation, detergency, micro-emulsification, and selective tension properties compared to various synthetic surfactants [43].

4.1. Surface and Interface Activity

The effectiveness and efficiency of biosurfactants with regards to surface and interfacial activity are greater than those of chemical surfactants, and biosurfactants have significantly lower CMCs [52]. As stated above, surfactin lowers the surface tension of water to 25 mN/m and the interfacial tension to less than 1 mN/m between water and hexadecane. *P. aeruginosa* produces rhamnolipids that reduce the surface tension of water to 26 mN/m and the water/hexadecane interfacial tension to less than 1 mN/m. The greater effectiveness and often lower CMCs of biosurfactants compared to chemical surfactants mean that less surfactant is needed for maximum surface tension reduction [53].

4.2. Biodegradability

As recalcitrant and xenobiotic compounds, chemical surfactants are resistant to the natural degradation process, which leads to their accumulation in the environment and causes ecotoxicity. In contrast, microbial surfactants are biodegradable and do not accumulate in water and soil. These natural compounds are broken down by the enzymatic action of microorganisms that cleave and inactivate the monomers of the surfactant. For example, emulsan polymerase cleaves the polysaccharide skeleton of emulsan, inactivating the molecule [43]. Moreover, the isolation and purification of these surfactant-degrading enzymes are simple processes. Although little research has been conducted on the biodegradation of biosurfactants, data published to date indicate that biosurfactants are more easily biodegraded than their chemical counterparts [54]. In a study investigating the biodegradability of sophorolipids produced by a non-pathogenic strain of *C. bombicola*, the degradation of the biosurfactants was instantaneous, whereas the synthetic surfactants tested remained active even after eight days [55]. A mannosylerythritol lipid (MEL) from *Candida antarctica* was found to biodegrade in five days [56]. Cappello et al. [57] found an exopolysaccharide biosurfactant to be easily biodegradable in marine environments by certain bacterial strains. The biodegradability of sophorolipids from *C. bombicola* was investigated using the Organisation for Economic Co-operation and Development Guidelines for testing of chemicals, and the results showed that the biosurfactants began to biodegrade immediately after cultivation [58]. Mohan et al. [59] showed that rhamnolipid biosurfactants are biodegradable under both aerobic and anaerobic conditions.

4.3. Low Toxicity

The low toxicity or even absence of toxicity makes biosurfactants suitable for use in the cosmetic, food, and pharmaceutical industries [60]. High concentrations of chemical surfactants can cause toxic reactions and other side effects. In contrast, biosurfactants are generally metabolized to form nontoxic substances and are therefore widely used in these industries. Poremba et al. [61] conducted comparative toxicity tests on chemicals and biosurfactants, reporting that rhamnolipids were tenfold less toxic than the chemical surfactant Corexit. The ecotoxicity of a green detergent containing the biosurfactant from *S. bombicola* ATCC 22214 was investigated using the marine recruitment test on metal plates covered with paint into which the biosurfactant was incorporated. Tests with microcrustacean and vegetable seeds yielded promising results and revealed the safety of the natural detergent [62]. The biosurfactant from *C. bombicola* URM 3712 had no toxic effect on vegetable seeds or on *Eisenia fetida* used as a bioindicator [63], while the biosurfactant from *B. cereus* UCP1615 exhibited low toxicity to the microcrustacean *Artemia salina* and vegetable seeds [64].

4.4. Stability at Extreme Temperatures, High Salt Concentrations and in a Broad pH Range

The surface activity of numerous biosurfactants remains unaltered by environmental conditions. Biosurfactants maintain their physicochemical activity in a broad pH range (3–12) and at high temperatures. Moreover, biosurfactants can tolerate saline concentrations of up to 10% (w/v), whereas synthetic surfactants become inactivated in the presence of ≥2% NaCl [25]. In a study conducted by Santos et al. [65], the emulsification capacity and reduction in surface tension achieved by the biosurfactant produced by *C. lipolytica* remained unaltered for 120 days in the presence of NaCl (1–5%), at temperatures of 40 and 50 °C, and in a pH range of 5 to 9. Researchers also demonstrated that the biosurfactant produced by *Streptomyces* sp. was effective in a broad range of temperatures (4–120 °C), pH values (2–12), and salinities (2–12%), as well as for up to 120 min at 90 °C [66]. The stability of the biosurfactant from *Pseudomonas cepacia* CCT6659 was demonstrated by the maintenance of its surface-active properties throughout an entire storage period of 120 days [67]. The biosurfactant from *S. bombicola* ATCC 22214 grown in a mineral medium containing 10% sucrose, 1.2% canola oil, and 0.5% corn steep liquor emulsified 96.25% of used motor oil and exhibited stability under extreme conditions with no significant loss of its properties [15].

4.5. Emulsification and De-Emulsification

An emulsion is the formation of micro-droplets of an immiscible liquid dispersed in another immiscible liquid, generating solubilized particles of micelles measuring >0.1 mm. De-emulsification is a process that disturbs the stability of the surface layer between the internal phase and bulk phase. The two main types of heterogeneous emulsion systems are water in oil (w/o) and oil in water (o/w). The addition of a biosurfactant can extend the stability of the system from a few days to several weeks [26].

Many glycolipids have noteworthy emulsification activity, solubilizing hydrocarbons in water. Rhamnolipids and sophorolipids have higher emulsification indices. In one study, congener mono-rhamnolipids from *P. aeruginosa* exhibited different emulsification activities for hydrocarbons of varied complexity [68]. Biosurfactants with a high molecular weight are suitable for emulsification but are not particularly effective at reducing surface tension [69]. Liposan, which is excreted by *C. lipolytica*, can stabilize o/w emulsions and is used in cosmetics and the food industry [65]. The use of de-emulsifiers has been recommended to treat emulsions generated by the crude oil industry [70]. Studies have also reported the use of rhamnolipid compounds as possible destabilizers of crude oil residues [71].

5. Practical Applications of Biosurfactants in Environmental Remediation

The problem of industrial pollution faced by various countries around the world is different in several aspects. In developed countries, pressures created by environmental assets, i.e., the emission of traditional pollutants from iron and steel as well as the manufacturing of metals and petrochemicals, have been growing slowly. On the other hand, issues such as soil contamination and the subsequent increase in treatment costs have received growing attention [25]. In developing countries, the environmental pressure from traditional pollutants created by industry remains heavy. For both, the growing technology-based industry has created new problems due to the use of concentrated toxic material in production processes, causing soil and water contamination. At the same time, industrial activities are a source of pressure on the environment in the form of emissions of gases and waste into the atmosphere and the ecosystem, generating waste and consuming natural resources. In addition, industries are major contributors to the global pollution burden. According to the Organization for Economic Cooperation and Development, industrial activities account for about one-third of global energy and water consumption in its member states. The relative contribution to the total pollution burden is highest in the industrial sector, which generates both traditional pollutants, such as organic substances, sulphur dioxide, particulate matter, and nutrients, and pollutants recently recognized as specific toxic substances [72].

In recent years, industrial activities have led to an increase in the accidental or purposeful release of organic and inorganic waste into the environment. Environments contaminated with pollutants are often difficult to remediate. Biosurfactants are structurally versatile, enabling these compounds to enhance the bioavailability of different organic compounds and contaminant ions for biological activities or mobilize such contaminants for collection, concentration, and/or treatment. Such approaches assist in resolving environmental problems. To ensure that the overall effect is positive, however, the environmental impact of the value chain of biosurfactants also needs to be assessed [73].

Environmental applications of biosurfactants are based on two main interaction mechanisms: biosurfactants increase the bioavailability of the substrate and promote interactions with the cell surface, increasing its hydrophobicity and enabling hydrophobic substrates to interact with bacterial cells [74,75]. Figure 4 illustrates the use of biosurfactants in environmental applications.

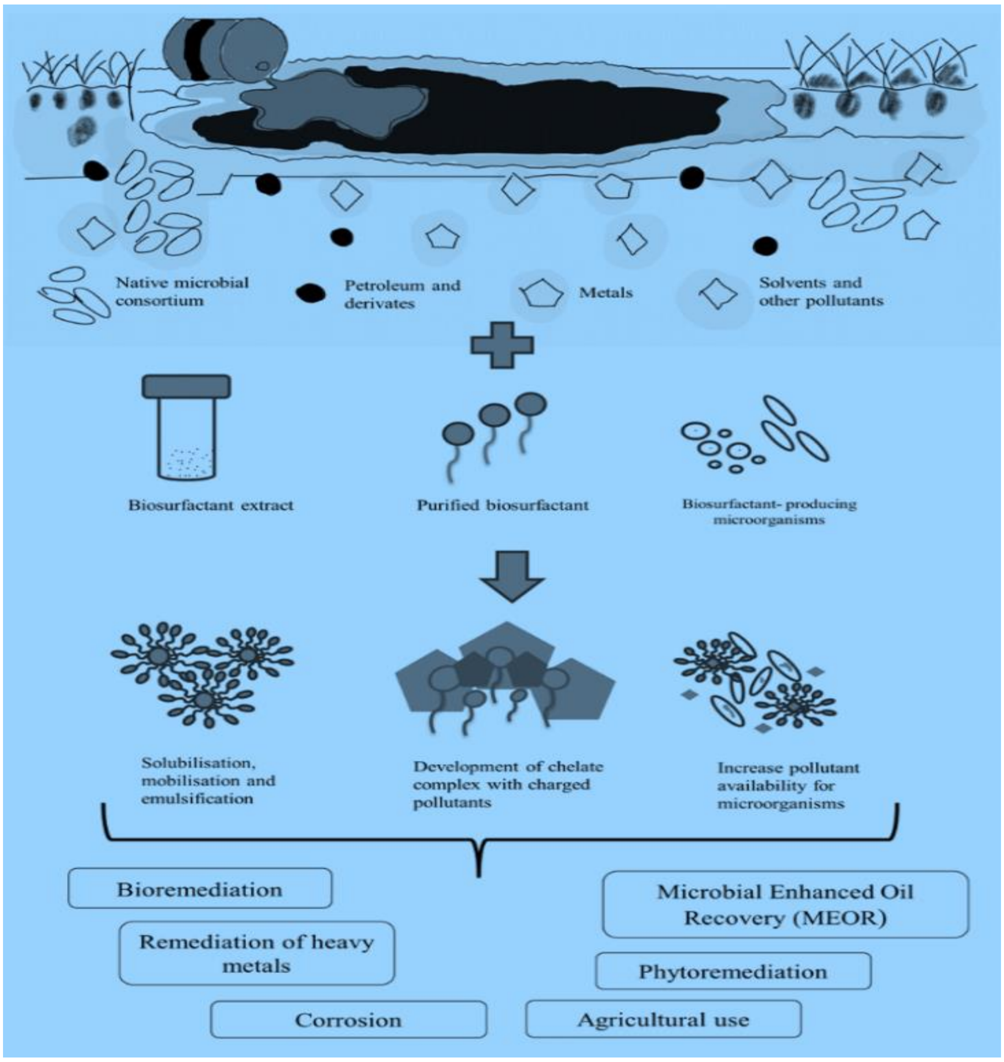

Figure 4. Environmental applications of biosurfactants [25].

The study of patents is an important strategy for identifying innovations and the degree of development of technological processes for environmental applications of biosurfactants. Patent documents do indeed provide essential information, such as claims for the identification of the novelty, inventive activity, and industrial application of the product or process to be protected [76]. Thus, a search was performed of patents to show the trend in this scenario of applications of biosurfactants in the environmental field, as displayed in Table 1. This search was performed on different patent search websites (https://worldwide.espacenet.com/, accessed on 23 June 2024, http://www.uspto.gov/, accessed on 3 June 2024, http://www.ipo.gov.uk/, accessed on 23 June 2024, https://www.google.com/?tbm=pts, accessed on 24 June 2024 and https://patentscope.wipo.int/search/pt/search.jsf, accessed on 24 June 2024) using combinations of the keywords remediation, bioremediation, microbial surfactant, biosurfactant, and environmental applications.

Based on data retrieved from international databases, China and the United States together maintain the leadership in the publication of patents. Different methods using biosurfactants can be seen in environmental applications for bioremediation, such as bioflocculation, the use of microbial flora, or even genetically modified microorganisms. Compared to other environmental applications, phytoremediation is difficult to explore and generate patents for. Biosurfactants are explored for diverse agricultural applications, mainly the formulation of pesticides and agrochemicals. These products can serve as biopesticides for controlling pests, pathogens, phytopathogenic fungi, and weeds. Plants can also benefit from biosurfactants and microorganisms as nutrients [77]. The remediation of soil contaminated with heavy metals involves the flushing of the soil with surfactants [78]. In industrial environments, biosurfactants inhibit metal corrosion in aggressive pickling, de-fouling, acidification, alkaline, and saline environments by adsorption to the surface of metals. The use of biosurfactants for the inhibition of corrosion appears to be a future trend [79]. The summary of patents presented below demonstrates the promising growing exploration and commercial interest in different environmental fields.

Table 1. Patents of biosurfactants in the industrial field.

Environmental Applications	Title of Patent	Description	Reference
Bioremediation	A process for the bioremediation of hydrocarbons in contaminated soil or sediment	Invention involving bioremediation of soil and sludge contaminated with hydrocarbons using microorganisms, nutrients, and biosurfactant.	[80]
	Bacillus sp. producing bioflocculant and biosurfactant and use thereof	Invention involving *Bacillus* sp. (*Bacillus* sp. SS15) that produces bioflocculant and biosurfactant for application in remediation of fracturing flowback liquid and effective simultaneous removal of chroma, COD, suspended solids, polycyclic aromatic hydrocarbons, and *n*-alkanes	[81]
	Method for degrading *n*-hexadecane and fermenting rhamnolipid biosurfactant	Invention discloses a strain (*Pseudomonas aeruginosa* H2-4) capable of using the pollutant *n*-hexadecane as a carbon source and producing a rhamnolipid surfactant.	[82]
	High-efficiency composite degrading bacterial agent and process for bioremediation of oil-containing soil	Invention regards soil remediation and discloses a high-efficiency composite degrading bacterial agent that comprises *P. aeruginosa*, *Rhodococcus honghuengensis*, *Bacillus subtilis*, and *Candida tropicalis*. The efficient microbial flora constructed by the invention can metabolize a biosurfactant by taking petroleum hydrocarbon as a unique carbon source, can greatly reduce the content of petroleum substances in oily sludge (soil), and has the advantages of a short degradation period, low cost, and no secondary pollution.	[83]

Table 1. *Cont.*

Environmental Applications	Title of Patent	Description	Reference
	Genetically modified *Burkholderia kururiensis*, method for rhamnolipid-type biosurfactants and uses	Invention describes genetically modified *Burkholderia kururiensis* (LMM21) and a method of using genetic engineering as a tool for the production of rhamnolipid-type biosurfactants in a non-pathogenic strain, *B. kururiensis* KP23T, as a heterologous host. The mono-rhamnolipids are used for the bioremediation of soils and waters contaminated by hydrocarbons.	[84]
Microbial enhanced oil recovery (MEOR)	*Brevibacillus agri*, preparation thereof, method for preparing surfactant, and use thereof	Invention discloses the preparation of a strain of *Brevibacillus agri* and a surfactant-producing method and use thereof. The bacterial strain and its preparation may enhance the recovery of crude oil; the surfactant preparation method confers the lipopeptide biosurfactant with satisfactory physical properties with a reduction in surface tension and has adequate emulsification of petroleum, lipids, and various hydrocarbons.	[85]
	Microbial products and uses thereof to improve oil recovery	Invention regards compositions of biochemical-producing microbes and methods for microbially enhanced oil recovery. Specifically, biosurfactant-producing bacteria and/or by-products of the growth of the bacteria are applied to an oil-producing site. The bacteria can also be applied with a yeast fermentation product, polymer, non-biological surfactant, alkaline compound, and/or one or more chelating agents. The advantage of the invention is its usefulness in stimulating the flow of oil from a well.	[86]
Bioremediation of polycyclic aromatic hydrocarbons (PAHs)	Method for synergistic remediation of soil polluted by high-ring polycyclic aromatic hydrocarbons by using biosurfactant	Invention discloses a method for synergistic remediation of soil polluted by high-ring polycyclic aromatic hydrocarbons using a biosurfactant and belongs to the technical field of soil remediation. Its advantages are that the biosurfactant is added to promote the solubilization of the high-ring PAHs, the selected strains can synthesize the biosurfactant during the growth process, the dispersibility of the high-ring PAHs in soil particles is further promoted, the added exogenous carbon source can be used as a growth substrate and as a co-metabolism substrate for the growth of degrading bacteria, and the degradation efficiency of the high-ring PAHs is improved.	[87]

Table 1. *Cont.*

Environmental Applications	Title of Patent	Description	Reference
Remediation of heavy metals	Biosurfactant produced by *Candida bombicola* with potential application in the removal of heavy metals	Invention regards a novel biodegradable bioproduct (Bombisan), which is obtained by yeast from industrial waste. Bombisan has high emulsifying capacity, stability over a wide range of temperatures, pH values, and salinities, in addition to the ability to remove heavy metals from contaminated soil and effluents.	[88]
	Environmentally-friendly compositions and methods for extracting minerals and metals from ore	Invention enables extracting minerals and/or metal from ore through safe, environmentally-friendly compositions and methods. Bioleaching is achieved using a composition composed of one or more biosurfactant-producing microorganisms and/or microbial growth by-products.	[89]
	Application and method of lipopeptide in removal of heavy metal ions	Invention discloses an application and method of biosurfactant lipopeptide in heavy metal ion removal. Micelles with a certain particle size are formed using the electrostatic binding effect of -COOH residues of surfactin and metal ions and reaching the critical micelle concentration (CMC). Micelles are intercepted by an ultrafiltration membrane with a certain pore size so that the lipopeptide can be used for removing heavy metal ions. Therefore, the effect of removing the metal ions is achieved.	[90]
	Bio-leaching compositions and methods for mining metals	Bioleaching compositions for processing ores or other matter, including metal or metal salt, are presented. Bioleaching composition includes a biosurfactant and metal solubilizing reagents. The biosurfactant can be a sophorolipid biosurfactant, and the metal-solubilizing reagents include an acid and an oxidant or a microorganism. In methods using the bioleaching composition, the metals from ores can be isolated from either a solution or non-solution phase.	[91]

Table 1. *Cont.*

Environmental Applications	Title of Patent	Description	Reference
Phytoremediation	Method for reinforcing phytoremediation of polycyclic aromatic hydrocarbon-contaminated soil with phytohormones and biosurfactants	Invention discloses a method for reinforcing phytoremediation of soil contaminated with polycyclic aromatic hydrocarbons using phytohormones and a biosurfactant. The method involves (1) adding a biosurfactant to the surface layer of the contaminated soil; (2) dissolving the phytohormone in ethanol and then adding distilled water for dilution; (3) putting *Medicago sativa* seeds in H_2O_2 for soaking, then performing flushing with sterile distilled water and planting the treated seeds in soil contaminated with polycyclic aromatic hydrocarbons; and (4) conducting conventional watering management on *M. sativa*: spraying the phytohormone ethanol aqueous solution 2–3 times within the plant growth period, harvesting the plant after 90–12 days growth, and conducting low-temperature drying and centralized treatment.	[92]
Agriculture	Method of using biosurfactant-producing bacteria against fungal and bacterial pathogens	Disclosure regards use of a bacterium (*Streptomyces*, *Bacillus*, *Microbacterium*, *Rhodococcus*, *Staphylococcus*, *Micrococcus*, *Arthrobacter*, or *Pseudomonas*) and/or extract containing a biosurfactant isolated from said bacterium as an antimicrobial agent against a foodborne or a plant bacterial or fungal pathogen. The bacterium optionally comprises at least 3 of difficidin, bacilysin, bacillaene, macrolactin h, fengycin, bacillomycin d, bacillibactin, and surfactin.	[93]
	Biosurfactant producing microorganisms	Invention discloses *Burkholderia thailandensis* DIS2 bacterium and a *B. thailandensis* DIS2.1 bacterium, as well as bacteria having all the identifying characteristics thereof and mutants thereof. There is also provided *Starmerella bombicola* DIS4 yeast and a yeast having all the identifying characteristics thereof and mutants thereof, along with a method for producing rhamnolipids and a method for producing sophorolipids.	[94]
	Antimicrobial compositions and related methods of use	Invention discloses antimicrobial compositions with one or more compounds generally recognized as safe for human consumption and related methods of use. The compositions and methods have applications in agricultural, pharmaceutical, building, industrial, and/or personal care products.	[95]

Table 1. *Cont.*

Environmental Applications	Title of Patent	Description	Reference
	Sanitization method and related formulation	Invention relates to an aqueous formulation comprising at least one surfactant of microbial origin and at least one organic acid in a weight ratio between 1:1000 and 10:1 and methods for sanitizing the internal surfaces of plants and products subject to biofilm formation using an aqueous solution. The latter is obtained by dosing the above formulation in water so that the aqueous solution contains at least one biosurfactant in an amount between 0.0001 and 10% by weight and at least one organic acid in an amount between 0.001 and 10% by weight.	[96]
	Bacillus strain for applications in agriculture, livestock health, and environmental protection	A bacterial strain with enhanced biosurfactant-production capabilities is provided, as well as methods of its use in agriculture, livestock husbandry, and environmental protection. In a specific embodiment, the invention is directed to a strain of *Bacillus amyloliquefaciens* that has novel properties for producing a mixture of lipopeptides, which is unique to its genus and species.	[97]
Corrosion	Method of using biosurfactants as acid corrosion inhibitors in well treatment operations	Corrosion during well treatment is inhibited by introducing a composition into the well containing a biosurfactant selected from glycolipids (other than mannosylerythritol lipids or sophorolipids), polyol lipids, phospholipids, lipopeptides, lipoproteins, carbohydrate-lipids, ornithine lipids, amino acid lipids, neutral lipids, liposan, exolipids, protein polyamines, diglycosyl diglycerides, siderolipids, saponified triglycerides, fatty acids, and fimbriae. Composition may also contain a corrosion inhibitor intensifier.	[98]
	Multifunctional composition for enhanced oil recovery, improved oil quality, and prevention of corrosion	Invention provides compositions and methods for simultaneously enhancing oil recovery, improving quality of oil and gas through reduction in sulphur-containing compounds, and preventing and/or reducing corrosion of production equipment.	[99]

Table 1. *Cont.*

Environmental Applications	Title of Patent	Description	Reference
	Environment-friendly industrial oil stain cleaning agent and preparation method thereof	Invention provides an environment-friendly industrial oil stain cleaning agent. The cleaning agent is prepared from the following components in percentage by weight: 1–5% of biological enzyme, 5–20% of a biosurfactant, 20–40% of a plant extract, 1–10% of a washing aid, and 25–73% of deionized water. The cleaning agent has the advantages of having high oil removal capability and being non-corrosive to various types of equipment, non-irritative to humans, safe, non-toxic, and environmentally friendly.	[100]

5.1. Bioremediation

The biodegradation of petroleum compounds can be a very slow process. Biosurfactants increase the bioavailability of pollutants, accelerating biodegradation and enabling the remediation of soil and aquatic environments contaminated with oil [101]. The bioavailability of crude oil is enhanced by the increase in the area of contact provided by biosurfactants to enable microbial action. The molecules of biosurfactants cluster due to the amphiphilic nature of the natural compound, thus enhancing the solubility and bioavailability of hydrophobic pollutants. Moreover, biosurfactants can interact directly with bacteria to increase their hydrophobicity and accelerate the absorption of oil pollutants by bacterial cells [102]. Rhamnolipids significantly enhance the solubility of saturated and aromatic hydrocarbons in water [103,104] in addition to improving the composition of bacterial communities and significantly increasing the abundance of oil-degrading bacteria [105], making rhamnolipids the most widely used biosurfactants in the field of bioremediation.

Oil spills can also occur in places other than the ocean, such as on land or in dry soil, directly contaminating the ecosystem with polycyclic aromatic hydrocarbons. Oil spills in soil clog porous spaces and significantly diminish both the aeration of the soil and penetration of water, which impedes nutrients and water from reaching the roots of plants, thus stunting growth. Moreover, some compounds in spilt oil are denser than water and can limit soil permeability [106,107]. Biosurfactants can also be used in the bioremediation of oil-contaminated soil. A strain of *B. subtilis* (Al-Dhabi-130) produced a biosurfactant that increased the emulsification of the crude oil in soil and also assisted in the degradation of the oil [108]. The novel biosurfactant produced by the bacterium *Bacillus invictae* UCP1617 cultivated in an alternative substrate was used in the formulation of an eco-friendly detergent. A detergent formulation containing the biosurfactant at the CMC completely dispersed motor oil in seawater and removed 99.21% of motor oil contained in clayey soil [109].

The application of biosurfactants in bioremediation processes involves two strategies: biostimulation and bioaugmentation. Biostimulation refers to the use of a biosurfactant or final fermentation extract that can be applied alone or together with other compounds [110]. Bioestimulation is one of the most widely used bioremediation strategies involving biosurfactants, with biodegradation efficiency ranging from 50 to 97%. Most biostimulation studies perform comparisons of biosurfactants and chemical reference surfactants in the bioremediation of oil [111]. Chaprão et al. [112] demonstrated greater motor oil removal efficiency from sand using a crude extract of biosurfactants from *Bacillus* sp. and *Candida sphaerica* (43% and 93%, respectively) compared to Tween 80 and Triton X-100 (40 to 80%).

Using concentrations of 0.05 to 2 g/L of a biosurfactant produced by *B. amyloliquefaciens* AN6, Ayed et al. [74] made comparisons to chemical surfactants, such as sodium dodecyl sulphate and Tween 80, with regards to the removal of diesel oil, reporting the high emulsification capacity of the biosurfactant and the greater solubilization of diesel (71.54%) at a concentration of 1 g/L.

Bioaugmentation involves the introduction of microorganisms into the soil to enhance the bioremediation process [110]. Biosurfactant-producing microorganisms added to a contaminated system enhanced the solubilization and bioavailability of hydrocarbons, with biodegradation efficiency ranging from 32.67 to 87.54%. According to Machado et al. [101], however, bioaugmentation can lead to competition between native and introduced microorganisms, reporting similar diesel oil removal rates with bioaugmentation (57.92%) and control treatments (approximately 58%). Other researchers point out that foreign microorganisms need time to adapt to the new environment and may not survive if the new environment is highly contaminated. To circumvent this situation, a consortium containing native microorganisms can be used to stimulate the adaptation of external microorganisms [113,114].

Figure 5 shows the differences between bioaugmentation and biostimulation strategies.

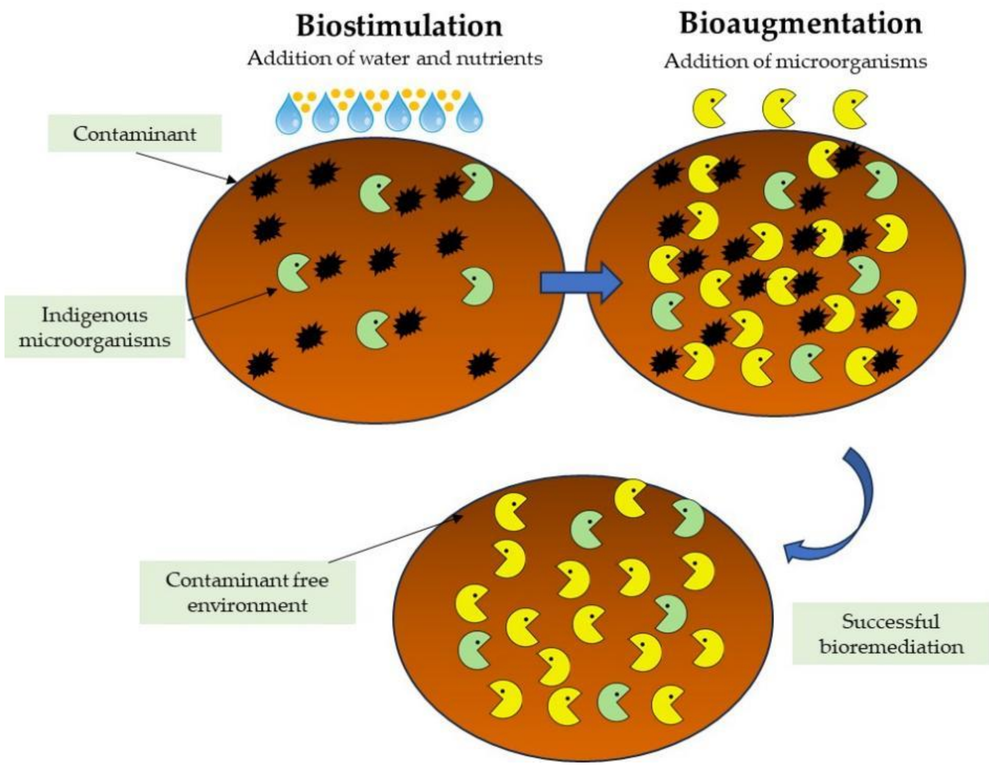

Figure 5. Comparison between bioaugmentation and biostimulation techniques.

With ex situ soil washing, a biosurfactant solution is placed into a glass column with contaminated soil to flush out heavy metal ions [115]. Soil washing methods involve the solubilization and mobilization of metals, and the reduction in interfacial tension assists in the removal of toxic contaminants [116,117]. Rhamnolipids can easily flush positively charged heavy metal ions from soil, such as Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} [118,119]. The sequential flushing of contaminated soil with a biosurfactant solution constitutes an adequate method for recovering and eliminating toxic heavy metals and increasing the availability of minerals in soil [120].

With in situ soil washing, the surfactant-containing washing solution is injected directly into the soil for the solubilization and mobilization of contaminants through the formation of micelles or chemical interactions. After percolation, the solution containing the contaminants is collected from the injection wells for treatment, discarding, or reinjection into the same site [115]. Unlike their synthetic counterparts, biosurfactants can be produced in situ, which reduces the treatment cost [121]. Two types of green surfactants—a chemically synthesized biobased surfactant and a biosurfactant produced by *S. bombicola*—were used in soil decontamination tests with a mobile soil remediation system (MSRS), which operates like a concrete mixer. The optimized experimental conditions enabled the commercial biosurfactant to remove 92.4% of the motor oil absorbed in the sand within the system [122].

Polycyclic aromatic hydrocarbons (PAHs) have complex ring-shaped chemical structures and are highly harmful to health [123]. These pollutants are mainly the result of human activities, such as the burning of fossil fuels, the use of wood preservers (e.g., creosote, the composition of which is approximately 85% PAHs), and other industrial activities [124]. Biosurfactants can be used to remediate soil contaminated with PAHs. In one study, the addition of biosurfactants led to an 86.5% PAH degradation rate compared to 57% in the control treatment without biosurfactants. According to the authors of the study, complete PAH removal was impeded due to mass transport limitations, as the increase in the dissolution rate promoted by the introduction of the biosurfactants increased the bioavailability of PAHs to microorganisms [125]. The bacteria *Azotobacter vinelandii* and *Streptomyces* sp. produce biosurfactants that can be used in the bioremediation of soil contaminated with hydrocarbons [3]. Yeast biosurfactants also play important roles in bioremediation processes. The biosurfactant from *S. bombicola* ATCC 222214, for example, removed 82.30%, 96.65%, and 98.25% of exhaust motor oil from sand, silty soil, and clayey soil under kinetic conditions, while in static tests (packed columns), removal rates were 66.62%, 63.03%, and 58.45%, respectively [126].

Among the advantages of biosurfactants, bacterial strains capable of producing them do not need to have the capacity to survive in soils contaminated with heavy metals [127]. However, the isolated use of biosurfactants requires the continual addition of these compounds. The application of microbial surfactants for the remediation of heavy metals has received some attention recently due to the high emulsification and surface activity [128,129]. The usefulness of biosurfactants for the bioremediation of soil contaminated with heavy metals is mainly due to their capacity to form complexes with metals. With anionic biosurfactants, such complexes are formed through ionic bonds that are stronger than those formed between the soil and metal. Metal-biosurfactant complexes are desorbed from soil due to the lowering of interfacial tension. Metal ions can be replaced with cationic biosurfactants by competition for some negatively charged surfaces (ionic exchange). The micelles of the biosurfactant can also remove metal ions from the surface of soils.

Figure 6 shows the mechanism of heavy metal removal by biosurfactants. The polar head of micelles binds to metals in water [130]. The removal rate is dependent upon the properties and structure of the metal-biosurfactant interactions. The biosurfactant produced by *Bacillus* sp. is used at twice its CMC achieved high removal rates for Hg (75.5%), Mn (89.5%), Pb (97.73%), and Cd (99.93%), with the formation of co-precipitates [131]. The biosurfactant from *C. bombicola* URM3712 cultivated in a low-cost medium demonstrated potential in removing Fe, Zn, and Pb, with removal rates ranging from 70% to 88%, while in packed column tests, Fe, Zn, and Pb removal rates ranged from 40% to 65%. The removal kinetics revealed increasing rates, with greater removal efficiency at the end of 24 h [63]. In another study, the authors reported the gradual increase in removal efficiency with the increase in the concentration of the biosurfactant [132].

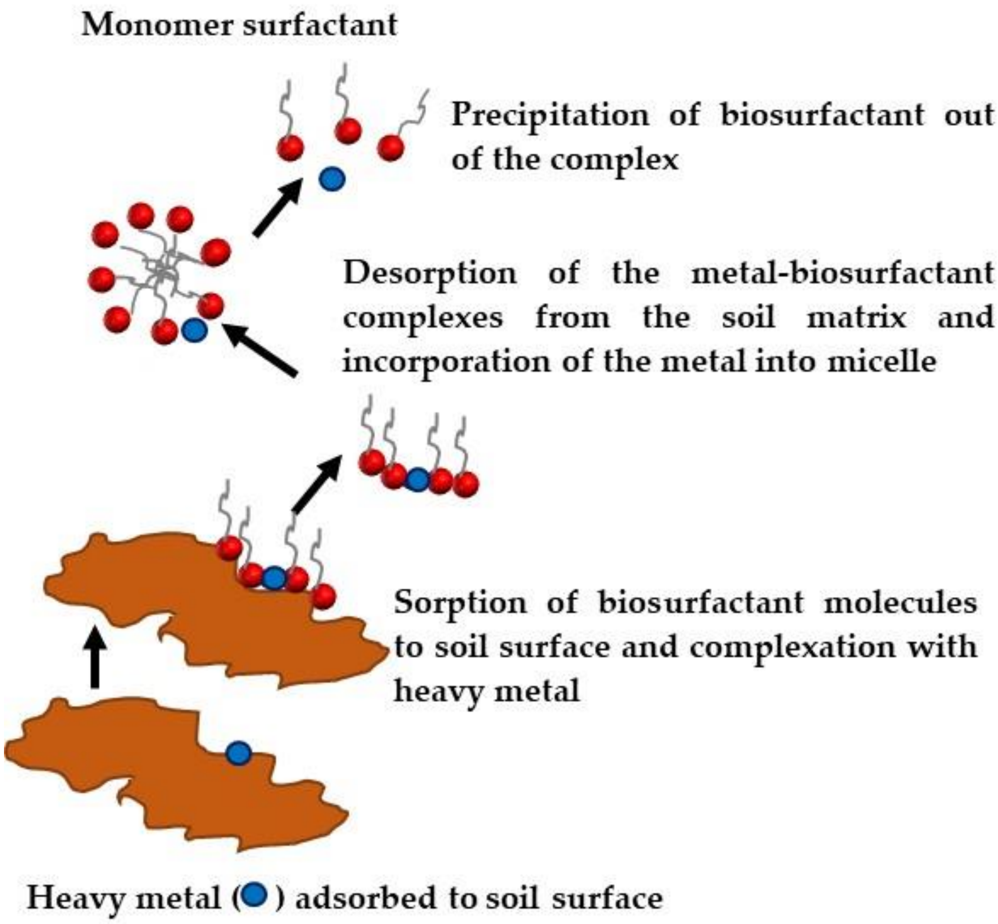

Figure 6. Mechanism of heavy metal removal by biosurfactants.

Phytoremediation is considered a sustainable remediation option applicable to organic and inorganic contaminants, with the additional advantage of using microorganisms to increase the remediation rate [133,134]. Biosurfactants can be used to support plant growth and improve soil quality, as illustrated in Figure 7. Shah and Daverey [135] reported the use of a sophorolipid in cadmium-contaminated soil. The authors reported a reduction in proline concentrations in a metal-accumulating plant (*Bidens pilosa*), with 18.2 µmoles of proline/g found in the treated soil vs. 40.2 µmoles/g in the control group. Moreover, a significant reduction was found in the toxic effects of Cd. The sophorolipid also improved the growth of the shoot and roots and increased the permeability of the roots of the plants *Medicago sativa* and *B. pilosa*, consequently enhancing the absorption of nutrients and phytobiomass. These cases demonstrate that an increase in biosurfactant concentration in phytoremediation processes can reduce the toxicity of pollutants as well as promote the respiration of the soil and the absorption of nutrients, enhancing microbial activity and plant growth [115]. Due to their binding capacity, biosurfactants can form complexes with metals through different attraction and repulsion forces. Thus, biosurfactants can replace persistent chemical chelating agents. Biosurfactants should be considered in phytoremediation processes to reduce the toxicity of metals and enhance plant growth [7].

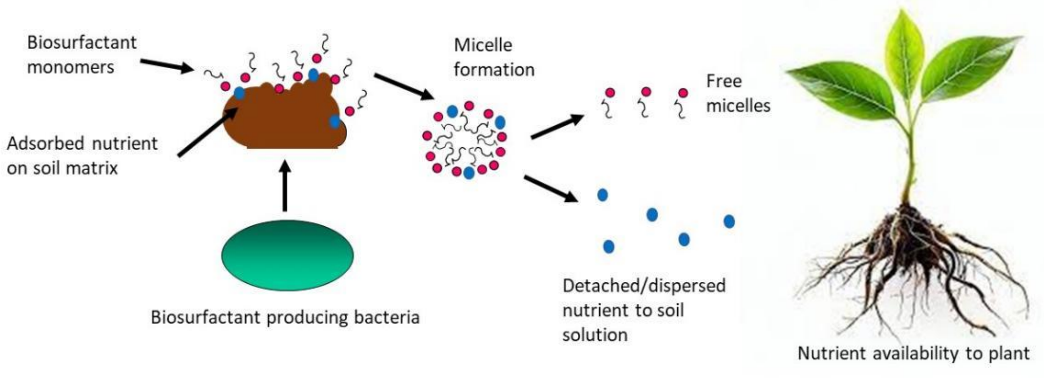

Figure 7. Mechanism of biosurfactant-assisted phytoremediation.

5.2. Microbial Enhanced Oil Recovery

Microbial enhanced oil recovery (MEOR) involves primary, secondary, and tertiary extraction. The first two stages remove up to 40% of the oil, whereas the tertiary stage recovers part of the oil that remained in the reservoir. For tertiary methods that do not depend on temperature, chemical and biological methods are employed to facilitate the recovery process. Biosurfactant-mediated MEOR may be in situ or ex situ. With the in situ approach, microbes are injected into the oil well together with nutrients and left to incubate for months. With the ex situ approach, previously produced biosurfactants are injected into the well. The control of undesirable and beneficial microbes (e.g., sulphide producers and sulphate reducers) can be difficult, and the production of biosurfactants cannot be easily controlled with in situ approaches, but the investment costs are lower. In contrast, ex situ approaches are easier because field tests and applications are performed using the same device [114]. A schematic of MEOR is displayed in Figure 8.

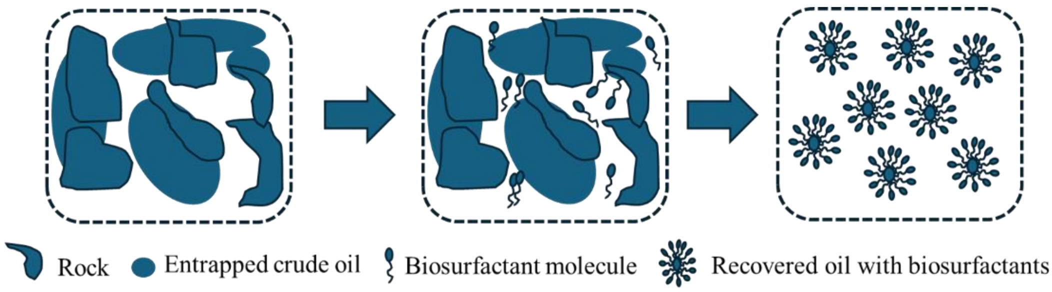

Figure 8. Schematic of mechanisms involved in biosurfactant-mediated microbial enhanced oil recovery (adapted from Santos et al. [23]).

5.3. Metal Corrosion Inhibition

Corrosion on metals is caused by moisture, alkalis, acids, gases, salts, and chemical products. The ambient temperature also exerts a significant effect, and some species of bacteria within a biofilm on steel can promote the progression of existing corrosion [136]. Corrosion affects a large variety of structures and activities, such as drinking water systems, sewage pipes, oil refineries, marine transportation, construction, etc. [137].

Corrosion occurs due to the oxidation of the atoms of a metal, compromising the mineralized structure of the surface. The initial step is the adsorption of protons, which is followed by an electrochemical reaction with the atoms of the metal. Metallic cations dissolved in the aqueous phase react with anions, leading to greater surface corrosion [138].

The avoidance of metallic corrosion is sought through corrosion inhibitors with a good benefit–cost ratio. However, corrosion inhibitors are often both highly effective and highly toxic, which has led to the banning of such products by environmental agencies. Thus, researchers have been investigating the use of ecologically friendly compounds. Surfactants and biocompatible corrosion inhibitors are suitable for long-term industrial use and constitute a novel approach in the field of chemical science [139]. Biosurfactants have proven to be the best ecologically correct substances for the inhibition of biocorrosion processes and the protection of materials from corrosion and have recently become one of the important products of the bioeconomy, with multiple applications, although knowledge on their use in the treatment of biocorrosion is scarce [140]. Ali et al. [140] assessed the ability of plant-derived biosurfactants to inhibit corrosion. Extracts from *Citrus sinensis* contributed to the inhibition of corrosion on carbon steel surfaces in 0.5 M sulfuric acid (H_2SO_4). The metallic structure was composed of C, Mn, P, Fe, and S. The interaction between the biosurfactants and metallic structure was determined by Fourier transform infrared spectroscopy, and roughness was assessed using atomic force microscopy, which revealed that the surfactants formed a smooth protective layer on the surface of the carbon steel in the H_2SO_4 medium. The biosurfactant from *P. cepacia* proved to be an excellent inhibitor of the formation of biofilm and metallic corrosion in a recent study [67].

5.4. Improvements in Agriculture

The exponential increase in the use of biosurfactants in agriculture is mainly due to the improvement in seed fertility and the control of plant pathogens. Biosurfactants have been used to improve soil quality, assist in the absorption of fertilizers and nutrients by roots, and eliminate plant pathogens [141]. Biosurfactants have been used as antifungal agents to control tip-over disease and enhance the hydrophilicity and wettability of deteriorated soil. In pesticide formulations, biosurfactants facilitate the movement of toxic agents to the respective targets and increase the surface contact area, which enables pesticides to reach target organisms and pests. Lipopeptides are reported to be effective antipathogen agents against *Fusarium verticillioides* and *Botrytis cinerea*, which are commonly found in labyrinths. Another study reported the inhibition of the germination of spores and the growth of mycelium on plants [142]. Akladious et al. [143] assessed the antifungal activity of the biosurfactant produced by *B. licheniformis* on two different varieties of *Vicia faba*, reporting a reduction in the infection rate from 62.11 to 20% and 38.93 to 16.51% on the Nubaria 1 and Sakha 1 varieties, respectively. Reports suggest that biosurfactants can enhance the health of agricultural soil through soil remediation processes [77]. For example, surfactin can facilitate the biodegradation of pesticides [144], and glycolipids can aid in the degradation of hydrocarbons [145]. Additionally, biosurfactants produced by species of *Burkholderia* isolated from oil-contaminated soil show potential for remediating pesticide contamination [146].

5.5. Methods and Innovations in Environmental Remediation

Some studies developed in recent years have demonstrated the application of biosurfactants as adjuvants of various remediation technologies, as described in previous sections. Table 2 displays examples of studies in the literature that describe the practical application of biosurfactants to increase degradation/removal efficiency in different remediation technologies. Despite the benefits provided by biosurfactants in the remediation of contaminated soils and aquatic environments, these natural compounds may also delay or have no effect on the biodegradation of organic hydrocarbons, as shown in the table below. This demonstrates the importance of basic research considering the most diverse variables to achieve success in applications.

Table 2. Examples of applications of biosurfactants as adjuvants in remediation processes.

Remediation Strategy	Contaminants	Description	Reference
Bioaugmentation + biosurfactant/surfactant-assisted biodegradation	Pyrene (10 mg/kg)	Successful bioaugmentation. Highly efficient biodegradation in uncorrected soil samples and with synthetic surfactants (Brij-35). Inhibition of biodegradation process when supplementation was performed with rhamnolipids, which were used as a preferential carbon source.	[147]
Biosurfactant-assisted biodegradation	Phenanthrene (0.1–1.0 mg/L)	Supplementation with rhamnolipids affected phenanthrene sorption kinetics, but exerted no influence on pollutant biodegradation kinetics.	[148]
Biosurfactant-assisted biodegradation	Hexadecane (2% *v*/*v*)	*Pseudomonas aeruginosa* produced rhamnolipids that increased availability of hexadecane; availability of hexadecane was reduced in the presence of *Pseudomonas putida*, which was not capable of producing rhamnolipids. Blocking effect by rhamnolipids caused reduction. Rhamnolipid dissipation also occurred.	[149]
Natural attenuation + bioaugmentation + biostimulation	Crude oil (3% *w*/*v*)	Bioaugmentation combined with biostimulation enabled achieving biodegradation faster and more efficiently.	[27]
Bioreactor (ex situ)	Crude oil (47.5 g kg)	Combined treatment with rhamnolipids + nutrients + a bacterial consortium led to an oil degradation efficiency of 77% in 90 days.	[150]
Phytoremediation (in situ)	Cadmium (39.06 mg/kg)	Higher levels of the phytoextraction of cadmium (Cd) occurred with the addition of biosurfactants on the 30th day of corn planting.	[151]
Ex-situ remediation using a Mobile Soil Remediation System (MSRS)	Motor oil (10% *w/w*)	Commercial biosurfactant from *Starmerella bombicola* enabled removing 92.4% of motor oil adsorbed to sand.	[122]
Biosurfactant-assisted biodegradation	Motor oil (10% *w*/*w*)	Addition of biosurfactant produced by *Pseudomonas cepacia* increased degradation of motor oil adsorbed to sand over a 70-day period. Increase in biosurfactant concentration increased pollutant solubilization, influencing removal rate.	[67]

Table 2. *Cont.*

Remediation Strategy	Contaminants	Description	Reference
Biosurfactant-assisted biodegradation	Motor oil (10% *w*/*w*)	*Bacillus cereus* produced biosurfactant that increased biodegradation of motor oil up to 96% compared to control over 27 days of incubation in seawater.	[152]

Biostimulation and bioaugmentation are the most widely used in situ bioremediation methods, whereas bioreactors are widely used in ex situ methods. Ex situ bioremediation methods have the additional costs of excavation and transportation and, thus, tend to be more expensive. However, such methods can be used for the controlled treatment of a broad gamut of pollutants. While not having the additional cost of excavation, the effectiveness of in situ methods is considerably reduced by the cost of on-site equipment installation and the inability to visualize and effectively control the subsurface of the polluted site. Consequently, the cost of remediation apparently has no main factor that would determine the bioremediation method to be applied at a given site [121]. Thus, the applicability of a remediation method is influenced by the site and type of contamination, objectives, efficiency, time, benefit/cost ratio, and acceptability by the public. Studies and planning to assist in selecting the most viable method should be conducted prior to the implementation of a large-scale operation.

The classifications of novel methods in the field of remediation are described in the next sections.

5.5.1. Nanobioremediation

Nanobioremediation is the use of nanomaterials coupled to biosurfactants to assist in reducing the toxicity of the pollutant to microorganisms. Nanomaterials increase the surface area and diminish activation energy, enhancing the efficiency of the degradation of toxic waste by microorganisms and resulting in a general reduction in remediation time and cost.

5.5.2. Multiple Bioremediation Methods

The simultaneous application of multiple bioremediation methods assists in enhancing remediation effectiveness by minimizing the individual disadvantages of each method [153].

5.5.3. Genetically Modified Microorganisms

The measured use of genetically modified microorganisms is a promising and innovative way to enhance the effectiveness of bioremediation. This method enables designing a biocatalyst for the effective degradation of a target pollutant, such as recalcitrant compounds, by broadening the substrate range of existing pathways, incorporating novel effective metabolic pathways, and increasing the stability of catabolic activity [154].

5.5.4. Enzymatic Bioremediation

Enzymatic bioremediation is another effective way to degrade pollutants. Their smaller size compared to microbial cells enables enzymes to come into direct contact with contaminants [155]. Researchers have reported in detail the role of oxygenases, peroxidases, laccases, carboxylesterases, haloalkane dehalogenases, phosphothriesterases, cellulases, and lipases in the degradation of various pollutants [156].

5.5.5. Modelling and Prototyping

The development of models and prototypes with artificial neural networks, artificial intelligence, machine learning, fuzzy logic, and statistical modeling [155,157] provides a new set of powerful tools to improve biodegradation and bioremediation.

5.5.6. Biotechnology and Process Engineering

Recent advances in biotechnology and process engineering are expected to expand the production scale of biosurfactants and reduce the costs of obtaining these biomolecules to promote their extensive use in the market.

6. Industrial Application and Market Prospects

The use of biosurfactants in the industrial energy sector involves their application in various stages of the oil industry, ranging from exploration, production, refining, and transportation to the consumption of petroleum derivatives. Biosurfactants can be used in oil recovery to reduce contamination in soil and groundwater and in the formulation of new products to increase the yield of the extracted crude oil [126]. Although most studies concentrate on environmental applications of biosurfactants, these biomolecules have found numerous applications in nearly all sectors of the market, from petroleum to foods, cosmetics, and medications. This commercial diversity is mainly related to the capacity of biosurfactants to reduce surface and interfacial tensions at very low CMC. Moreover, the advancement of the technology increases environmental awareness. Indeed, there has been an exponential increase in the demand for nontoxic, biodegradable constituents in new products [26].

Table 3 lists examples of the application of biosurfactants in enhanced oil recovery, oil biotechnology, the mining of precious metals, agriculture, food processing, medicine/pharmaceutical/bioprocessing, protection of foam rubber/textiles/paper/painting/coating, chemical synthesis, and production of detergents.

Table 3. Industrial applications of biosurfactants.

Industry	Field	Biosurfactants	Mechanism/Functioning/ Property Used	Reference
Oil biotechnology	Extraction from crude oil reservoirs	Glycolipids and Lipopeptides	Biosurfactants enhance the formation of stable water-oil emulsions, break the film of oil on rock, and reduce interfacial tension, which reduces capillary forces that impede the movement of oil through the pores of rock	[158,159]
	Transportation of oil through pipelines	Emulsan, alasan, biodispersan	Biosurfactants with high molecular weight form stable water-in-oil emulsions, assisting in the mobility of oil, reducing viscosity, and avoiding the coalescence of droplets	[160,161]

Table 3. *Cont.*

Industry	Field	Biosurfactants	Mechanism/Functioning/ Property Used	Reference
	Cleaning of oil storage tanks	Rhamnolipids	A well-circulated biosurfactant forms an oil-in-water emulsion, raises/mobilizes the sludge at the bottom of the tank, and solubilizes it in the previously formed emulsion	[162,163]
Metallic corrosion	Anticorrosive agents	Rhamnolipids, lipopeptides, and glycolipids	Biosurfactants form a protective layer, impeding the occurrence of corrosion	[147]
Nanotechnology mining	Recovery of precious metals Silver and gold nanoparticles	Biodispersan exopolysaccharide from algae	Reduces energy needed to cleave the microstructure of ground limestone, solubilizes, and serves as a sequestering agent Biosurfactant-producing organisms convert (Ag-Au) NO_3 into silver/gold particles using enzymes such as nitrate reductase	[162–164]
Medications/pharmaceuticals	Gene delivery Antimicrobial activity	Mannosylerythritol lipids (MEL) Anionic isoform of surfactin rhamnolipids	Cationic liposomes containing MEL-A effectively increases the transfection of genes in mammal cells Antimicrobial effect of biosurfactants manifests through activity similar to detergents	[165–167]
	Anticancer activity	Sophorolipids	Biosurfactants as antiviral agents interrupt cell replication, favoring cell differentiation	[168]
	Immunological adjuvants	Surfactin	Immunomodulating biosurfactants increase the migration of polymorphic nuclear cells and the lymphocyte transformation rate, stimulating the immune system	[169]
	Antiviral activity	Ethyl ester of diacetate sophorolipid, surfactin	Biosurfactants inactivate viral lipid capsules and envelopes	[170]

Table 3. *Cont.*

Industry	Field	Biosurfactants	Mechanism/Functioning/ Property Used	Reference
	Antiadhesive agents	Sophorolipids	Adsorption of biosurfactants to a substrate modifies hydrophobicity of surface, affecting microbial adhesion and the desorption process	[171]
Bioprocessing	Recovery of product	Sophorolipids Rhamnolipids	Surfactant properties contribute to the reverse micellar extraction of antibiotics and proteins	[172,173]
Leather	Stabilizer, dispersant, humectant	Biodispersan	Degreasing agent used as detergent for the skin, emulsifier, tanning and dying, wetting, and penetration	[174]
Textiles	Dispersants, penetrating agents	Nonspecific trehalote-traestercHAL2	Removal of lipophilic components and oils from fibers as pretreatment; improved dispersion of dyes for uniform penetration into fibers	[174]
Paper	Cellulose processing	Biodispersan	Used for washing and de-resinification of pulp by de-foaming, dispersion, and evening of color	[174]
	Paper manufacturing	Biodispersan	Chalk was effectively buried using biodispersan and used as filter in manufacturing of paper. Biosurfactant also used in calendaring through wetting, levelling, coating, and dying	[174]
Paint protection/coating	Stabilizers, dispersants	Biodispersan	Employed as dispersant as humectant agent during milling and stabilization to improve the mixture properties	[175]
Food industry	Food emulsifiers	Polymeric biosurfactants	Alteration of rheological characteristics for desired consistency and texture of foods using emulsification properties	[176]

Table 3. *Cont.*

Industry	Field	Biosurfactants	Mechanism/Functioning/ Property Used	Reference
	Food stabilizer	Rhamnolipids	Alteration of rheological characteristics of foods for desired consistency and texture	[176]
Cosmetic industry	Emulsifiers, humectants, moisturizers, foaming agents	Sophorolipids Rhamnolipids MELs	Application of biosurfactants in cosmetics due to cytoprotective effect, low irritability, antiaging and antioxidant effects, moisturizing properties, wettability, tonifying of skin, and healing properties	[177–179]
Detergent for clothes	Foaming agent, dirt removal	Sophorolipids MEL	Properties such as formation of foam, reduction of surface tension, and solubilization are suitable for the fabrication of detergents	[180]

In the year 2020, the market of green surfactants was estimated at around USD 2.54 billion, and the global market is expected to increase at a compound annual growth rate of 5.7%, reaching USD 3.56 billion by the year 2026. The expansion of the sector is due to the growing demand for green surfactants made from biomass residues and agricultural raw materials [181].

The biosurfactant market in Brazil is quite promising, with the presence of companies specializing in these products. Despite the noteworthy growth in the industry in recent decades, large-scale production continues to pose an economic challenge, mainly due to the high financial investment and limited industrial production. Scaling up the production of biosurfactants from the laboratory to the industrial and commercial scale is currently the biggest challenge in industrial biotechnology. This is due to the fact that, under normal circumstances, microbial cells produce low concentrations of surfactants, which hinder large-scale production. To overcome this obstacle, it is important to select cost-effective raw materials that can improve the overall conditions for commercial production. While the production process has been studied and improved to meet the growing demand for biosurfactants, challenges still exist for industrial-scale production, such as excessive foam formation, the availability of suitable raw materials, and the costs involved in processing and cleaning, especially during the extraction and purification steps, which involve technologies such as foam fractionation, membrane filtration, gravity separation (e.g., acid precipitation, crystallization), and ultrafiltration, all of which have high capital and operating costs. Despite efforts to address these economic issues, few strategies have been developed to make the production process more viable. Baccile et al. [182] conducted a life cycle assessment for the production of glycolipids and found that the environmental impact was surprisingly similar to that of chemical surfactants derived from fossil resources. This impact was mainly attributed to the use of rapeseed oil and glucose as substrates, which accounted for 78% of the harm to ecosystems and resources. The remaining impact was caused largely by the use of electricity throughout the production chain (15%). Other factors that need to be considered for viable production include the type of microorganisms, design of industrial bioreactors, target markets, purification processes, properties of the biosurfactants, production conditions, and the time required for fermentation and achievable production yields [25].

Novel molecules and structures with unique properties could be produced with a combination of safe biosurfactant producers and waste materials rich in nutrients. The screening and monitoring of microbial producers, clarification of intrinsic paths, and integration of the perspective of the green economy, low-carbon economy, bioeconomy, and circular economy would provide safe, sustainable biosurfactants. The use of agricultural waste and aquatic residues would ensure the cheap, large-scale production of healthy-quality biosurfactants. Moreover, the genetic engineering and the adjustment of the downstream process would ensure constant supplies of safe-quality biosurfactants. Biosurfactant production processes need to be optimized. The yield, technical-economic viability, form of consumption, level of purity, and shelf life could be improved by altering the processes [183].

7. Conclusions

The use of biosurfactants as part of a new generation of biomolecules in industrial and environmental applications has increased in recent years. They can address the challenges of the oil industry by reducing its economic, social, and environmental impacts. Biosurfactants, which have been especially exploited for application in the industrial sector, have high specificity due to their considerable molecular variability and structural diversity, enabling the selection of the best biosurfactant for a given application based on the results of previous studies. Furthermore, the use of these microbial biomolecules with decontamination capabilities is essential to the offer of new, attractive biotechnological products. This enables reducing environmental impacts and obtaining greater economic gains compared to the toxic products normally used in industries. Many properties, such as emulsification/de-emulsification, dispersion, foam formation, wetting, and coating, make them useful in physicochemical and biological remediation technologies for organic and metallic contaminants. Biosurfactants increase the bioavailability of hydrocarbons, resulting in greater growth and contaminant degradation by hydrocarbon-degrading bacteria found in polluted soil. In soil contaminated with heavy metals, biosurfactants form complexes with the metals at the interface of the soil, which is followed by the desorption of the metal and removal from the soil, leading to an increase in the concentration of metal ions and their bioavailability in the soil solution. Biosurfactants can also be used as anti-corrosion agents to protect metallic surfaces from atmospheric interactions and reduce microbial contamination, thus inhibiting the development of corrosive biofilms. Despite their advantages over surfactants derived from petroleum, they are sometimes more expensive than those commonly used in the industrial sector. Such an economic issue could hinder their use in the industrial sectors; so, research has been focusing on more affordable means to produce them. Technological advances and large-scale production are able to lower costs, and this trend is likely to go on in the future. Therefore, it can be concluded that using biosurfactants on an industrial scale represents a promising alternative to current oil-based counterparts. Nonetheless, additional efforts are necessary to obtain cheap and sustainable biosurfactants capable of performing satisfactorily under the conditions required for a given application. The coming years are very promising for biosurfactant applications, but they will only be commercially viable if the same challenges are overcome. Certainly, the use of biosurfactants will make an important contribution to a more sustainable and environmentally friendly industry.

Author Contributions: Conceptualization, L.A.S. and R.d.C.F.S.d.S.; writing—original draft preparation, Y.E.d.S.F., R.d.C.F.S.d.S., K.W.d.O. and J.M.C.-G.; writing—review and editing, L.A.S. and A.C.; visualization, L.A.S. and A.C.; supervision, L.A.S. and A.C.; project administration, L.A.S. and A.C.; funding acquisition, L.A.S. and A.C. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the following Brazilian fostering agencies: Foundation for the Support of Science and Technology of the State of Pernambuco (FACEPE), the Research and Development Program from National Agency of Electrical Energy (ANEEL), the National Council for Scientific and Technological Development (CNPq), and the Coordination for the Improvement of Higher Level Education Personnel (CAPES).

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article.

Acknowledgments: The authors are grateful to the laboratories of the School of Technology and Communication, the Catholic University of Pernambuco (UNICAP) and the Advanced Institute of Technology and Innovation (IATI), Brazil.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Ali, M.; Song, X.; Ding, D.; Wang, Q.; Zhang, Z.; Tang, Z. Bioremediation of PAHs and heavy metals co-contaminated soils: Challenges and enhancement strategies. *Environ. Pollut.* **2022**, *295*, 118686. [CrossRef]
2. Singh, R.; Rathore, D. Effects of fertilization with textile effluent on germination, growth and metabolites of chilli (*Capsicum annum* L.) cultivars. *Environ. Process.* **2021**, *8*, 1249–1266. [CrossRef]
3. Bezza, F.A.; Chirwa, E.M.N. Biosurfactant-enhanced bioremediation of aged polycyclic aromatic hydrocarbons (PAHs) in creosote contaminated soil. *Chemosphere* **2016**, *144*, 635–644. [CrossRef]
4. Wei, Z.; Wang, J.J.; Gaston, L.A.; Li, J.; Fultz, L.M.; DeLaune, R.D.; Dodla, S.K. Remediation of crude oil-contaminated coastal marsh soil: Integrated effect of biochar, rhamnolipid biosurfactant and nitrogen application. *J. Hazard. Mater.* **2020**, *396*, 122595. [CrossRef]
5. Zahed, M.A.; Matinvafa, M.A.; Azari, A.; Mohajeri, L. Biosurfactant, a green and effective solution for bioremediation of petroleum hydrocarbons in the aquatic environment. *Discov. Water* **2022**, *2*, 5. [CrossRef]
6. Pereira, E.; Napp, A.; Allebrandt, S.; Barbosa, R.; Reuwsaat, J.; Lopes, W.; Kmetzsch, L.; Staats, C.C.; Schrank, A.; Dallegrave, A.; et al. Biodegradation of aliphatic and polycyclic aromatic hydrocarbons in seawater by autochthonous microorganisms. *Int. Biodeterior. Biodegrad.* **2019**, *145*, 104789. [CrossRef]
7. Eras-Muñoz, E.; Farré, A.; Sánchez, A.; Font, X.; Gea, T. Microbial biosurfactants: A review of recent environmental applications. *Bioengineered* **2022**, *13*, 12365–12391. [CrossRef]
8. Ambaye, T.G.; Vaccari, M.; Prasad, S.; Rtimi, S. Preparation, characterization and application of biosurfactant in various industries: A critical review on progress, challenges and perspectives. *Environ. Technol. Innov.* **2021**, *24*, 102090. [CrossRef]
9. Pacwa-Płociniczak, M.; Płaza, G.A.; Piotrowska-Seget, Z.; Cameotra, S.S. Environmental applications of biosurfactants: Recent advances. *Int. J. Mol. Sci.* **2011**, *12*, 633–654. [CrossRef]
10. Bezerra, K.G.O.; Rufino, R.D.; Luna, J.M.; Sarubbo, L.A. Saponins and microbial biosurfactants: Potential raw materials for the formulation of cosmetics. *Biotechnol. Prog.* **2018**, *34*, 1482–1493. [CrossRef]
11. Sun, S.; Wang, Y.; Zang, T.; Wei, J.; Wu, H.; Wei, C.; Qiu, G.; Li, F. A biosurfactant-producing *Pseudomonas aeruginosa* S5 isolated from coking wastewater and its application for bioremediation of polycyclic aromatic hydrocarbons. *Bioresour. Technol.* **2019**, *281*, 421–428. [CrossRef]
12. Medhi, M.K.; Ambust, S.; Kumar, R.; Das, A.J. Characterization and purification of biosurfactants. In *Advancements in Biosurfactants Research*; Aslam, R., Mobin, M., Aslam, J., Zehra, S., Eds.; Springer: Cham, Switzerland, 2023; pp. 79–93. [CrossRef]
13. Bailly, C.; Vergoten, G. Glycyrrhizin: An alternative drug for the treatment of COVID-19 infection and the associated respiratory syndrome? *Pharmacol. Ther.* **2020**, *214*, 107618. [CrossRef]
14. Furman, A.C.; Veit, M.; Palácio, S.; Gonçalves, G.; Barbieri, J.C.Z. Sustainability in the production process of the cosmetic industry: A literature review. *Res. Soc. Dev.* **2022**, *11*, e586111335852. [CrossRef]
15. Silva, I.A.; Fortunato, J.G.L.A.; Almeida, F.C.G.; Alves, R.N.; Cunha, M.C.C.; Rufino, R.D.; Fernandes, M.L.B.; Sarubbo, L.A. Production and application of a new biosurfactant for solubilisation and mobilisation of residual oil from sand and seawater. *Processes* **2024**, *12*, 1605. [CrossRef]
16. Twigg, M.S.; Baccile, N.; Banat, I.M.; D'eziel, E.; Marchant, R.; Roelants, S.; Van Bogaert, I.N.A. Microbial biosurfactant research: Time to improve the rigour in the reporting of synthesis, functional characterization and process development. *Microbiol. Biotechnol.* **2021**, *14*, 147–170. [CrossRef]
17. Silva, R.C.F.S.; Almeida, D.G.; Rufino, R.D.; Luna, J.M.; Santos, V.A.; Sarubbo, L.A. Applications of biosurfactants in the petroleum industry and the remediation of oil spills. *Int. J. Mol. Sci.* **2014**, *15*, 12523–12542. [CrossRef]
18. Shakeri, F.; Babavalian, H.; Amoozegar, M.A.; Ahmadzadeh, Z.; Zuhuriyanizadi, S.; Afsharian, M.P. Production and application of biosurfactants in biotechnology. *Biointerface Res. Appl. Chem.* **2021**, *11*, 10446–10460. [CrossRef]
19. Alara, O.R.; Abdurahman, N.H.; Alara, J.A.; Tade, M.O.; Ali, H.A. Commercialization of biosurfactants. In *Advancements in Biosurfactants Research*; Aslam, R., Mobin, M., Aslam, J., Zehra, S., Eds.; Springer: Cham, Switzerland, 2023; pp. 525–549. [CrossRef]

20. Kumari, K.; Nandi, A.; Sinha, A.; Ghosh, A.; Sengupta, S.; Saha, U.; Singh, P.K.; Panda, P.K.; Raina, V.; Verma, S.K. The paradigm of prophylactic viral outbreaks measures by microbial biosurfactants. *J. Infect. Public Health* **2023**, *16*, 575–587. [CrossRef]
21. Uzoigwe, C.; Burgess, J.G.; Ennis, C.J.; Rahman, P.K.S.M. Bioemulsifiers are not biosurfactants and require different screening approaches. *Front. Microbiol.* **2015**, *6*, 245. [CrossRef]
22. Abdel-Mawgoud, A.M.; Lépine, F.; Déziel, E. Rhamnolipids: Diversity of structures, microbial origins and roles. *Appl. Microbiol. Biotechnol.* **2010**, *86*, 1323–1336. [CrossRef]
23. Ashby, R.D.; Wan Muhammad Zulkifli, W.N.F.; Yatim, R.; Ren, K.; Mustafa, A. Glycolipid biosurfactants: Biosynthesis and related potential applications in food industry. In *Applications of Next Generation Biosurfactants in the Food Sector*; Inamuddin, C.O.A., Ed.; Academic Press: London, UK, 2023; pp. 307–334. [CrossRef]
24. Garay, L.A.; Sitepu, I.R.; Cajka, T.; Xu, J.; Teh, H.E.; German, J.B.; Pan, Z.; Dungan, S.R.; Block, D.E.; Boundy-Mills, K.L. Extracellular fungal polyol lipids: A new class of potential high value lipids. *Biotechnol. Adv.* **2018**, *36*, 397–414. [CrossRef]
25. Santos, D.K.F.; Rufino, R.D.; Luna, J.M.; Santos, V.A.; Sarubbo, L.A. Biosurfactants: Multifunctional biomolecules of the 21st century. *Int. J. Mol. Sci.* **2016**, *17*, 401. [CrossRef]
26. Kashif, A.; Rehman, R.; Fuwad, A.; Shahid, M.K.; Dayarathne, H.N.P.; Jamal, A.; Aftab, M.N.; Mainali, B.; Choi, Y. Current advances in the classification, production, properties and applications of microbial biosurfactants–A critical review. *Adv. Colloid Interface Sci.* **2022**, *306*, 102718. [CrossRef]
27. Varjani, S.J.; Upasani, V.N. Critical review on biosurfactant analysis, purification and characterization using rhamnolipid as a model biosurfactant. *Bioresour. Technol.* **2017**, *232*, 389–397. [CrossRef]
28. Shao, Z. Trehalolipids. In *Biosurfactants. Microbiology Monographs*; Soberón-Chávez, G., Ed.; Springer: Berlin/Heildelberg, Germany, 2011; Volume 20, pp. 121–143. [CrossRef]
29. Satpute, S.K.; Banat, I.M.; Dhakephalkar, P.K.; Banpurkar, A.G.; Chopade, B.A. Biosurfactants, bioemulsifiers and exopolysaccharides from marine microorganisms. *Biotechnol. Adv.* **2010**, *28*, 436–450. [CrossRef]
30. Bages-Estopa, S.; White, D.A.; Winterburn, J.B.; Webb, C.; Martin, P.J. Production and separation of a trehalolipid biosurfactant. *Biochem. Eng. J.* **2018**, *139*, 85–94. [CrossRef]
31. Pal, S.; Chatterjee, N.; Das, A.K.; McClements, D.J.; Dhar, P. Sophorolipids: A comprehensive review on properties and applications. *Adv. Colloid Interface Sci.* **2023**, *313*, 102856. [CrossRef]
32. Arutchelvi, J.I.; Bhaduri, S.; Uppara, P.V.; Doble, M. Mannosylerythritol lipids: A review. *J. Ind. Microbiol. Biotechnol.* **2008**, *35*, 1559–1570. [CrossRef]
33. Fukuoka, T.; Morita, T.; Konishi, M.; Imura, T.; Sakai, H.; Kitamoto, D. Structural characterization and surface-active properties of a new glycolipid biosurfactant, mono-acylated mannosylerythritol lipid, produced from glucose by *Pseudozyma antarctica*. *Appl. Microbiol. Biotechnol.* **2007**, *76*, 801–810. [CrossRef]
34. Saika, A.; Koike, H.; Yamamoto, S.; Kishimoto, T.; Morita, T. Enhanced production of a diastereomer type of mannosylerythritol lipid-B by the basidiomycetous yeast *Pseudozyma tsukubaensis* expressing lipase genes from *Pseudozyma antarctica*. *Appl. Microbiol. Biotechnol.* **2017**, *101*, 8345–8352. [CrossRef]
35. Matosinhos, R.D.; Cesca, K.; Carciofi, B.A.M.; de Oliveira, D.; de Andrade, C.J. Mannosylerythritol lipids as green pesticides and plant biostimulants. *J. Sci. Food Agric.* **2023**, *103*, 37–47. [CrossRef]
36. Nihorimbere, V.; Cawoy, H.; Seyer, A.; Brunelle, A.; Thonart, P.; Ongena, M. Impact of rhizosphere factors on cyclic lipopeptide signature from the plant beneficial strain *Bacillus amyloliquefaciens* S499. *FEMS Microbiol. Ecol.* **2012**, *79*, 176–191. [CrossRef]
37. Cochrane, S.A.; Vederas, J.C. Lipopeptides from *Bacillus* and *Paenibacillus* spp.: A gold mine of antibiotic candidates. *Med. Res. Rev.* **2016**, *36*, 4–31. [CrossRef] [PubMed]
38. Sałek, K.; Euston, S.R. Sustainable microbial biosurfactants and bioemulsifiers for commercial exploitation. *Process Biochem.* **2019**, *85*, 143–155. [CrossRef]
39. Grangemard, I.; Wallach, J.; Maget-Dana, R.; Peypoux, F. Lichenysin: A more efficient cation chelator than surfactin. *Appl. Biochem. Biotechnol.* **2001**, *90*, 199–210. [CrossRef] [PubMed]
40. McInerney, M.J.; Javaheri, M.; Nagle, D.P. Properties of the biosurfactant produced by *Bacillus licheniformis* strain JF-2. *J. Ind. Microbiol.* **1990**, *5*, 95–101. [CrossRef]
41. Hazaimeh, M.D.; Ahmed, E.S. Bioremediation perspectives and progress in petroleum pollution in the marine environment: A review. *Environ. Sci. Pollut. Res. Int.* **2021**, *28*, 54238–54259. [CrossRef]
42. Rawat, G.; Dhasmana, A.; Kumar, V. Biosurfactants: The next generation biomolecules for diverse applications. *Environ. Sustain.* **2020**, *3*, 353–369. [CrossRef]
43. Soares dos Santos, A.; Pereira, J.N.; Freire, D.M.G. Strategies for improved rhamnolipid production by *Pseudomonas aeruginosa* PA1. *PeerJ* **2016**, *4*, 2078. [CrossRef]
44. Paulino, B.N.; Pessôa, M.G.; Mano, M.C.R.; Molina, G.; Neri-Numa, I.A.; Pastore, G.M. Current status in biotechnological production and applications of glycolipid biosurfactants. *Appl. Microbiol. Biotechnol.* **2016**, *100*, 10265–10293. [CrossRef]
45. Vijayakumar, S.; Saravanan, V. Biosurfactants types, sources and applications. *Res. J. Microbiol.* **2015**, *10*, 181–192.
46. Shekhar, S.; Sundaramanickam, A.; Balasubramanian, T. Biosurfactant producing microbes and their potential applications: A review. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45*, 1522–1554. [CrossRef]
47. Karlapudi, A.P.; Venkateswarulu, T.C.; Tammineedi, J.; Kanumuri, L.; Ravuru, B.K.; Dirisala, V.R.; Kodali, V.P. Role of biosurfactants in bioremediation of oil pollution-a review. *Petroleum* **2018**, *4*, 241–249. [CrossRef]

48. Brumano, L.P.; Soler, M.F.; Silva, S.S. Recent advances in sustainable production and application of biosurfactants in Brazil and Latin America. *Ind. Biotechnol.* **2016**, *12*, 31–39. [CrossRef]
49. De, S.; Malik, S.; Ghosh, A.; Saha, R.; Saha, B. A review on natural surfactants. *RSC Adv.* **2015**, *5*, 65757–65767. [CrossRef]
50. Abbot, V.; Paliwal, D.; Sharma, A.; Sharma, P. A review on the physicochemical and biological applications of biosurfactants in biotechnology and pharmaceuticals. *Heliyon* **2022**, *8*, 10149. [CrossRef]
51. Madankar, C.S.; Meshram, A. Review on classification, physicochemical properties and applications of microbial surfactants. *Tenside Surf. Deterg.* **2022**, *59*, 1–16. [CrossRef]
52. Corazza, E.; Abruzzo, A.; Giordani, B.; Cerchiara, T.; Bigucci, F.; Vitali, B.; di Cagno, M.P.; Luppi, B. Human *Lactobacillus* biosurfactants as natural excipients for nasal drug delivery of hydrocortisone. *Pharmaceutics* **2022**, *14*, 524. [CrossRef]
53. Cooper, D.G.; Macdonald, C.R.; Duff, S.J.B.; Kosaric, N. Enhanced production of surfactin from *Bacillus subtilis* by continuous product removal and metal cation additions. *Appl. Environ. Microbiol.* **1981**, *42*, 408–412. [CrossRef]
54. Patel, S.; Kharawala, K. Biosurfactants and their biodegradability: A review and examination. *Int. J. Eng. Adv. Technol.* **2022**, *11*, 4–11. [CrossRef]
55. Ahn, C.; Morya, V.K.; Kim, E.-K. Tuning surface-active properties of bio-surfactant sophorolipids by varying fatty-acid chain lengths. *Korean J. Chem. Eng.* **2016**, *33*, 2127–2133. [CrossRef]
56. Kim, H.-S.; Jeon, J.-W.; Kim, S.-B.; Oh, H.-M.; Kwon, T.-J.; Yoon, B.-D. Surface and physico-chemical properties of a glycolipid biosurfactant, mannosylerythritol lipid, from *Candida antarctica*. *Biotechnol. Lett.* **2022**, *24*, 1637–1641. [CrossRef]
57. Cappello, S.; Crisari, A.; Denaro, R.; Crescenzi, F.; Porcelli, F.; Yakimov, M.M. Biodegradation of a bioemulsificant exopolysaccharide (EPS2003) by marine bacteria. *Water Air Soil Poll.* **2011**, *214*, 645–652. [CrossRef]
58. Hirata, Y.; Ryu, M.; Oda, Y.; Igarashi, K.; Nagatsuka, A.; Furuta, T.; Sugiura, M. Novel characteristics of sophorolipids, yeast glycolipid biosurfactants, as biodegradable low-foaming surfactants. *J. Biosci. Bioeng.* **2009**, *108*, 142–146. [CrossRef] [PubMed]
59. Mohan, P.K.; Nakhla, G.; Yanful, E.K. Biokinetics of biodegradation of surfactants under aerobic, anoxic and anaerobic conditions. *Water Res.* **2006**, *40*, 533–540. [CrossRef]
60. Mallik, T.; Banerjee, D. Biosurfactants: The potential green surfactants in the 21st century. *J. Adv. Sci. Res.* **2022**, *13*, 97–106. [CrossRef]
61. Poremba, K.; Gunkel, W.; Wagner, F. Toxicity testing of synthetic and biogenic surfactants on marine microorganisms. *Environ. Toxicol. Water Qual.* **1991**, *6*, 157–163. [CrossRef]
62. da Silva, I.A.; de Almeida, F.C.G.; Alves, R.N.; Cunha, M.C.C.; de Oliveira, J.C.M.; Fernandes, M.L.B.; Sarubbo, L.A. The formulation of a natural detergent with a biosurfactant cultivated in a low-cost medium for use in coastal environmental remediation. *Fermentation* **2024**, *10*, 332. [CrossRef]
63. da Silva, R.R.; Santos, J.C.V.; Meira, H.M.; Almeida, S.M.; Sarubbo, L.A.; Luna, J.M. Microbial biosurfactant: *Candida bombicola* as a potential remediator of environments contaminated by heavy metals. *Microorganisms* **2023**, *11*, 2772. [CrossRef]
64. Durval, I.J.B.; Rufino, R.D.; Sarubbo, L.A. Biosurfactant as an environmental remediation agent: Toxicity, formulation, and application in the removal of petroderivate in sand and rock walls. *Biointerface Res. Appl. Chem.* **2022**, *12*, 34–48. [CrossRef]
65. Santos, D.K.F.; Resende, A.H.M.; De Almeida, D.G.; Soares da Silva, R.C.F.; Rufino, R.D.; Luna, J.M.; Banat, I.M.; Sarubbo, L.A. *Candida lipolytica* UCP0988 biosurfactant: Potential as a bioremediation agent and in formulating a commercial related product. *Front. Microbiol.* **2017**, *8*, 767. [CrossRef] [PubMed]
66. Santos, E.F.; Teixeira, M.F.S.; Converti, A.; Porto, A.L.F.; Sarubbo, L.A. Production of a new lipoprotein biosurfactant by *Streptomyces* sp. DPUA1566 isolated from lichens collected in the Brazilian Amazon using agroindustry wastes. *Biocatal. Agric. Biotechnol.* **2019**, *17*, 142–150. [CrossRef]
67. Faccioli, Y.E.S.; Silva, G.O.; Soares da Silva, R.C.F.; Sarubbo, L.A. Application of a biosurfactant from *Pseudomonas cepacia* CCT 6659 in bioremediation and metallic corrosion inhibition processes. *J. Biotechnol.* **2022**, *351*, 109–121. [CrossRef]
68. Perfumo, A.; Banat, I.M.; Canganella, F.; Marchant, R. Rhamnolipid production by a novel. thermophilic hydrocarbon-degrading *Pseudomonas aeruginosa* AP02-1. *Appl. Microbiol. Biotechnol.* **2006**, *72*, 132–138. [CrossRef] [PubMed]
69. Smyth, T.; Perfumo, A.; McClean, S.; Marchant, R.; Banat, I. Isolation and analysis of lipopeptides and high molecular weight biosurfactants. In *Handbook of Hydrocarbon and Lipid Microbiology*; Timmis, K.N., Ed.; Springer: Berlin/Heidelberg, Germany, 2010; pp. 3687–3704. [CrossRef]
70. Mohebali, G.; Kaytash, A.; Etemadi, N. Efficient breaking of water/oil emulsions by a newly isolated de-emulsifying bacterium, *Ochrobactrum anthropi* strain RIPI5-1. *Colloids Surf. B* **2012**, *98*, 120–128. [CrossRef]
71. Aparna, A.; Srinikethan, G.; Smitha, H. Production and characterization of biosurfactant produced by a novel *Pseudomonas* sp. 2B. *Colloids Surf. B* **2012**, *95*, 23–29. [CrossRef]
72. Synergia Consultoria. Available online: https://www.synergiaconsultoria.com.br/ (accessed on 24 September 2024).
73. Manga, E.B.; Celik, P.A.; Cabuk, A.; Banat, I.M. Biosurfactants: Opportunities for the development of a sustainable future. *Curr. Opin. Colloid Interface Sci.* **2021**, *56*, 101514. [CrossRef]
74. Ayed, B.H.; Jemil, N.; Maalej, H.; Bayoudh, A.; Hmidet, N.; Nasri, M. Enhancement of solubilization and biodegradation of diesel oil by biosurfactant from *Bacillus amyloliquefaciens* AN6. *Int. Biodeterior. Biodegrad.* **2015**, *99*, 8–14. [CrossRef]
75. Reis, R.S.; Pacheco, G.J.; Pereira, A.G.; Freire, D.M.G. Biosurfactants: Production and applications. In *Industrial Applications of Biosurfactants and Microorganisms*; Chamy, R., Rosenkranz, F., Eds.; Intech Open: Valparaiso, Chile, 2013; pp. 277–305. [CrossRef]

76. Instituto Nacional da Propriedade Industrial (INPI). 2017. Available online: http://www.inpi.gov.br/ (accessed on 25 November 2023).
77. Silva, M.D.G.C.; Medeiros, A.O.; Converti, A.; Almeida, F.C.G.; Sarubbo, L.A. Biosurfactants: Promising biomolecules for agricultural applications. *Sustainability* **2024**, *16*, 449. [CrossRef]
78. Liu, J.; Xue, J.; Yuan, D.; Wei, X.; Su, H. Surfactant washing to remove heavy metal pollution in soil: A review. *Recent Innov. Chem. Eng.* **2020**, *13*, 3–16. [CrossRef]
79. Wang, Q.H.; Yan, Z. Potential of biosurfactants in corrosion inhibition. In *Industrial Applications of Biosurfactants and Microorganisms*; Aslam, R., Aslam, J., Hussain, C.M., Eds.; Academic Press: Boca Raton, FL, USA, 2024; pp. 277–305. [CrossRef]
80. Wang, Z. A Process for the Bioremediation of Hydrocarbons in Contaminated Soil or Sediment. AU Patent 2,016,101,966, 9 November 2016.
81. Zhang, C.; Zeng, F.; Zhou, H.; Jiang, L.; Zhang, D.; Li, Y.; Li, S. *Bacillus* sp. Producing Bioflocculant and Biosurfactant and Use Thereof. U.S. Patent 20,230,159,959, 23 November 2023.
82. Zhuan, X.; Wang, Y.; Wu, S.; Wang, H. Method for Degrading n-Hexadecane and Fermenting Rhamnolipid Biosurfactant. CN Patent 116,426,590, 1 April 2022.
83. Sun, W.; Ke, C.; Zhai, W.; Wang, S.; Sun, R.; Zhang, Q.; Qin, F. High-Efficiency Composite Degrading Bacterial Agent and Process for Bioremediation of Oil-Containing Soil. CN Patent 115,537,353, 30 December 2022.
84. Neves, B.C.; Mariano, D.C.O.; Tavares, L.F.D.; Lima, P.S.F. Genetically Modified Burkholderia kururiensis, Method for Raminolipid-Type Biosurfactants and Uses. PI Patent 1102193-4, 23 May 2011.
85. She, Y.; Zhang, F.; Zhang, Z.; Yao, P.; Li, F.; Dong, H.; Sun, S.; Yu, G.; Yi, S.; Zhang, W.; et al. Brevibacillus agri, Preparation Thereof, Method for Preparing Surfactant and Use Thereof. U.S. Patent 20,220,049,165, 17 February 2022.
86. Farmer, S.; Alibek, K.; Mazumder, S.; Adams, K.; Dixon, T.; Chen, Y.; Milovanovic, M. Microbial Products and Uses Thereof to Improve Oil Recovery. U.S. Patent 20,220,389,303, 8 December 2022.
87. Cao, F.; Zhu, H.; Chen, J.; Liao, C.; Wei, X.; Zhou, Y.; Yan, D.; Yang, Y.; Xie, D.; Chen, S.; et al. Method for Synergistic Remediation of Soil Polluted by High-Ring Polycyclic Aromatic Hydrocarbon by Using Biosurfactant. CN Patent 112,620,342, 20 October 2020.
88. Silva, R.R.; Sarubbo, L.A.; Luna, J.M. Biosurfactant Produced by Candida bombicola with Potential Application in the Removal of Heavy Metals. BR Patent 1,020,220,046,115, 19 September 2023.
89. Farmer, S.; Karathur, K.N. Environmentally-Friendly Compositions and Methods for Extracting Minerals and Metals from Ore. U.S. Patent 20,230,322,556, 7 November 2023.
90. Long, X.; Yu, F. Application and Method of Lipopeptide in Removal of Heavy Metal Ions. CN Patent 116655085, 25 June 2023.
91. Mahmoudkhani, A.; Rogers, J.; Farmer, S.; Knesel, G. Bio-Leaching Compositions and Methods for Mining Metals. WO Patent 2,023,141,456, 18 January 2023.
92. Qi, L.; Wang, Q.; Wu, W.; Han, C.; Gan, F.; Xie, W.; Zhang, R.; Guan, Y.; Cheng, T. Method for Reinforcing Phytoremediation of Polycyclic Aromatic Hydrocarbon Contaminated Soil with Phytohormone and Biosurfactant. CN Patent 108,817,054, 31 July 2018.
93. Jabaji, S. Method of Using Biosurfactant-Producing Bacteria against Fungal and Bacterial Pathogens. WO Patent 2,021,163,810, 26 August 2021.
94. Martinez, S.; Balendra, N.; Benaissa, H. Biosurfactant Producing Microorganisms. WO Patent 2,023,184,025, 10 May 2023.
95. Gandhi, N.R.; Skebba, V.P.; Strobel, G.A. Antimicrobial Compositions and Related Methods of Use. U.S. Patent 20,230,172,199, 23 June 2023.
96. Garusi, G.; Garusi, F.; Fermi, B.; Doniselli, N. Sanitization Method and Related Formulation. EP Patent 4,206,148, 29 December 2021.
97. Farmer, S.; Alibek, K. Bacillus Strain for Applications in Agriculture, Livestock Health and Environmental Protection. U.S. Patent 20,230,029,570, 13 April 2021.
98. Gunawan, S.; Vorderbruggen, M.A.; Armstrong, C.D. Method of Using Biosurfactants as Acid Corrosion Inhibitors in Well Treatment Operations. U.S. Patent 20,160,237,334, 4 October 2015.
99. Farmer, S.; Alibek, K.; Adams, K.; Karathur, K.N.; Moldakozhayev, A.; Nerris, A. Multifunctional Composition for Enhanced Oil Recovery, Improved Oil Quality and Prevention of Corrosion. U.S. Patent 20,230,159,814, 1 October 2023.
100. Hao, Z.; Li, C. Environment-Friendly Industrial Oil Stain Cleaning Agent and Preparation Method Thereof. CN Patent 109,762,669, 25 February 2019.
101. Machado, T.S.; Decesaro, A.; Cappellaro, Â.C.; Machado, B.S.; Reginato, K.V.S.; Reinehr, C.O.; Thomé, A.; Colla, L.M. Effects of homemade biosurfactant from *Bacillus methylotrophicus* on bioremediation efficiency of a clay soil contaminated with diesel oil. *Ecotoxicol. Environ. Saf.* **2020**, *201*, 110798. [CrossRef] [PubMed]
102. Dell'Anno, F.; Sansone, C.; Ianora, A.; Dell'Anno, A. Biosurfactant-induced remediation of contaminated marine sediments: Current knowledge and future perspectives. *Mar. Environ. Res.* **2018**, *137*, 196–205. [CrossRef] [PubMed]
103. Mahanty, B.; Pakshirajan, K.; Dasu, V.V. Understanding the complexity and strategic evolution in PAH remediation research. *Crit. Rev. Environ. Sci. Technol.* **2011**, *41*, 1697–1746. [CrossRef]
104. Kiran, G.S.; Ninawe, A.S.; Lipton, A.N.; Pandian, V.; Selvin, J. Rhamnolipid biosurfactants: Evolutionary implications, applications and future prospects from untapped marine resource. *Crit. Rev. Biotechnol.* **2016**, *36*, 399–415. [CrossRef]
105. Ambaye, T.G.; Formicola, F.; Sbaffoni, S.; Franzetti, A.; Vaccari, M. Insights into rhamnolipid amendment towards enhancing microbial electrochemical treatment of petroleum hydrocarbon contaminated soil. *Chemosphere* **2022**, *307*, 136126. [CrossRef]

106. Abosede, E.E. Effect of crude oil pollution on some soil physical Properties. *IOSR J. Agric. Vet. Sci.* **2013**, *6*, 14–17. [CrossRef]
107. Klamerus-Iwan, A.; Błońska, E.; Lasota, J.; Kalandyk, A.; Waligórski, P. Influence of oil contamination on physical and biological properties of forest soil after chainsaw use. *Water Air Soil Pollut.* **2015**, *226*, 389. [CrossRef] [PubMed]
108. Al-Dhabi, N.A.; Esmail, G.A.; Valan Arasu, M. Enhanced production of biosurfactant from *Bacillus subtilis* strain Al-Dhabi-130 under solid-state fermentation using date molasses from Saudi arabia for bioremediation of crude-oil-contaminated soils. *Int. J. Environ. Res. Public Health* **2020**, *17*, 8446. [CrossRef] [PubMed]
109. Barata, M.I.C.; Cavalcanti, M.H.C.; Rufino, R.D.; Almeida, F.C.G.; Sarubbo, L.A. Optimized production and properties of biosurfactant from *Bacillus invictae* UCP1617 and its performance in a detergent formulation for environmental applications. *J. Surfact. Deterg.* **2024**, 1–15. [CrossRef]
110. Imam, A.; Kanaujia, P.K.; Ray, A.; Suman, S.K. Removal of petroleum contaminants through bioremediation with integrated concepts of resource recovery: A review. *Indian J. Microbiol.* **2021**, *61*, 250–261. [CrossRef]
111. Gautam, K.K.; Tyagi, V.K. Microbial surfactants: A review. *J. Oleo Sci.* **2006**, *55*, 155–166. [CrossRef]
112. Chaprão, M.J.; Ferreira, I.N.; Correa, P.F.; Rufino, R.D.; Luna, J.M.; Silva, E.J.; Sarubbo, L.A. Application of bacterial and yeast biosurfactants for enhanced removal and biodegradation of motor oil from contaminated sand. *Electron. J. Biotechnol.* **2015**, *18*, 471–479. [CrossRef]
113. Pérez Vargas, J.; Viguera Carmona, S.E.; Zamudio Moreno, E.; Rivera Casado, N.A.; Calva, G. Bioremediation of soils from oil spill impacted sites using bioaugmentation with biosurfactants producing, native, free-living nitrogen fixing bacteria. *Rev. Int. Contam. Ambient.* **2017**, *33*, 105–114. [CrossRef]
114. Geetha, G.; Banat, I.M.; Joshi, S.J. Biosurfactants: Production and potential applications in microbial enhanced oil recovery (MEOR). *Biocatal. Agric. Biotechnol.* **2018**, *14*, 23–32. [CrossRef]
115. Sarubbo, L.A.; Rocha Junior, R.B.; Luna, J.M.; Rufino, R.D.; Santos, V.A.; Banat, I.M. Some aspects of heavy metals contamination remediation and role of biosurfactants. *Chem. Ecol.* **2015**, *31*, 707–723. [CrossRef]
116. Chang, S.; Wang, K.; Kuo, C.; Chang, C.; Chou, C. Remediation of metal contaminated soil by an integrated soil washing electrolysis process. *Soil Sediment Contam. Int. J.* **2005**, *14*, 559–569. [CrossRef]
117. Kumar, R.; Das, A.J.; Juwarkar, A. Reclamation of petrol oil contaminated soil by rhamnolipids producing PGPR strains for *Withania somnifera* a medicinal shrub. *World J. Microbiol. Biotechnol.* **2015**, *31*, 307–313. [CrossRef]
118. Juwarkar, A.A.; Nair, A.; Dubey, K.V.; Singh, S.K.; Devotta, S. Biosurfactant technology for remediation of cadmium and lead contaminated soils. *Chemosphere* **2007**, *68*, 1996–2002. [CrossRef] [PubMed]
119. Diaz, M.A.; De Ranson, I.S.; Dorta, B.D. Metal removal from contaminated soils, through bioleaching with oxidizing bacteria and rhamnolipid biosurfactant. *Soil Sediment Contam.* **2015**, *24*, 16–29. [CrossRef]
120. Liu, Z.; Li, Z.; Zhong, H.; Zeng, G.; Liang, Y.; Chen, M.; Wu, Z.; Zhou, Y.; Yu, M.; Shao, B. Recent advances in the environmental applications of biosurfactant saponins: A review. *J. Environ. Chem. Eng.* **2017**, *5*, 6030–6038. [CrossRef]
121. Sales da Silva, I.G.; Almeida, F.C.G.; Rocha e Silva, N.M.P.; Casazza, A.A.; Converti, A.; Sarubbo, L.A. Soil bioremediation: Overview of technologies and trends. *Energies* **2020**, *13*, 4664. [CrossRef]
122. Silva, I.G.S.D.; Pappalardo, J.R.; Rocha e Silva, N.M.P.D.; Converti, A.; Almeida, F.C.G.D.; Sarubbo, L.A. Treatment of motor oil-contaminated soil with green surfactant using a mobile remediation system. *Processes* **2023**, *11*, 1081. [CrossRef]
123. Patel, A.B.; Shaikh, S.; Jain, K.R.; Desai, C.; Madamwar, D. Polycyclic aromatic hydrocarbons: Sources, toxicity, and remediation approaches. *Front. Microbiol.* **2020**, *11*, 562813. [CrossRef]
124. Hu, J.; Nakamura, J.; Richardson, S.D.; Aitken, M.D. Evaluating the effects of bioremediation on genotoxicity of polycyclic aromatic hydrocarbon-contaminated soil using genetically engineered, higher eukaryotic cell lines. *Environ. Sci. Technol.* **2012**, *46*, 4607–4613. [CrossRef]
125. Bezza, F.A.; Chirwa, E.M.N. The role of lipopeptide biosurfactant on microbial remediation of aged polycyclic aromatic hydrocarbons (PAHs)-contaminated soil. *Chem. Eng. J.* **2017**, *309*, 563–576. [CrossRef]
126. Selva Filho, A.A.P.; Faccioli, Y.E.; Converti, A.; da Silva, R.D.C.F.S.; Sarubbo, L.A. Maximization of the production of a low-cost biosurfactant for application in the treatment of soils contaminated with hydrocarbons. *Sustainability* **2024**, *16*, 7970. [CrossRef]
127. Devianto, L.A.; Latunussa, C.E.L.; Helmy, Q.; Kardena, E. Biosurfactants production using glucose and molasses as carbon sources by *Azotobacter vinelandii* and soil washing application in hydrocarbon-contaminated soil. *IOP Conf. Ser. Earth Environ. Sci.* **2020**, *475*, 012075. [CrossRef]
128. Meenakshisundaram, M.; Pramila, M. Detoxification of heavy metals using microbial biosurfactant. *Int. J. Curr. Microbiol. Appl. Sci.* **2017**, *6*, 402–411. [CrossRef]
129. Lal, S.; Ratna, S.; Said, O.B.; Kumar, R. Biosurfactant and exopolysaccharide-assisted rhizobacterial technique for the remediation of heavy metal contaminated soil: An advancement in metal phytoremediation technology. *Environ. Technol. Innov.* **2018**, *10*, 243–263. [CrossRef]
130. Aşçı, Y.; Nurbaş, M.; Açıkel, Y.S. A comparative study for the sorption of Cd(II) by soils with different clay contents and mineralogy and the recovery of Cd(II) using rhamnolipid biosurfactant. *J. Hazard. Mater.* **2008**, *154*, 663–673. [CrossRef]
131. Ravindran, A.; Sajayan, A.; Priyadharshini, G.B.; Selvin, J.; Kiran, G.S. Revealing the efficacy of thermostable biosurfactant in heavy metal bioremediation and surface treatment in vegetables. *Front. Microbiol.* **2020**, *11*, 222. [CrossRef] [PubMed]
132. Haryanto, B.; Chang, C. Removing adsorbed heavy metal ions from sand surfaces via applying interfacial properties of Rhamnolipid. *J. Oleo Sci.* **2015**, *64*, 161–168. [CrossRef] [PubMed]

133. Futughe, A.E.; Purchase, D.; Jones, H. Phytoremediation using native plants. In *Phytoremediation. Concepts and Strategies in Plant Sciences*; Shmaefsky, B., Ed.; Springer: Berlin/Heildelberg, Germany, 2020; pp. 285–327. [CrossRef]
134. Gabriele, I.; Race, M.; Papirio, S.; Esposito, G. Phytoremediation of pyrene-contaminated soils: A critical review of the key factors affecting the fate of pyrene. *J. Environ. Manag.* **2021**, *293*, 112805. [CrossRef]
135. Shah, V.; Daverey, A. Effects of sophorolipids augmentation on the plant growth and phytoremediation of heavy metal contaminated soil. *J. Clean. Prod.* **2021**, *280*, 124406. [CrossRef]
136. Zakeri, A.; Bahmani, E.; Aghdam, A.S.R. Plant extracts as sustainable and green corrosion inhibitors for protection of ferrous metals in corrosive media: A mini review. *Corros. Comum.* **2022**, *5*, 25–38. [CrossRef]
137. Beech, I.B.; Gaylarde, C.C. Recent advances in the study of biocorrosion—An overview. *Rev. Microbiol.* **1999**, *30*, 177–190. [CrossRef]
138. El-din, M.R.N.; Farag, R.K.; Elazbawy, O.E. Utilization of new anionic polymeric surfactants for corrosion inhibition enhancement in petroleum industries. *Int. J. Electrochem. Sci.* **2016**, *11*, 815–835. [CrossRef]
139. Pal, A.; Sarkar, R.; Karmakar, K.; Mondal, M.; Saha, B. Surfactant as an anti-corrosive agent: A review. *Tenside Surfactants Deterg.* **2022**, *59*, 363–372. [CrossRef]
140. Ali, A.E.; Badr, G.E.; Founda, A.E.S. *Citrus sinensis* extract as a green inhibitor for the corrosion of carbon steel in sulphuric acid solution. *Biointerface Res. Appl. Chem.* **2021**, *11*, 14007–14020. [CrossRef]
141. Chen, J.; Wu, Q.; Hua, Y.; Chen, J.; Zhang, H.; Wang, H. Potential applications of biosurfactant rhamnolipids in agriculture and biomedicine. *Appl. Microbiol. Biotechnol.* **2017**, *101*, 8309–8319. [CrossRef]
142. Hussain, T.; Haris, M.; Shakeel, A.; Ahmad, G.; Khan, A.A.; Khan, M.A. Bio-nematicidal activities by culture filtrate of *Bacillus subtilis* HussainT-AMU: New promising biosurfactant bioagent for the management of Root Galling caused by *Meloidogyne incognita*. *Vegetos* **2020**, *33*, 229–238. [CrossRef]
143. Akladious, S.A.; Gomaa, E.Z.; El-Mahdy, O.M. Efficiency of bacterial biosurfactant for biocontrol of *Rhizoctonia solani* (AG-4) causing root rot in faba bean (*Vicia faba*) plants. *Eur. J. Plant Pathol.* **2019**, *153*, 1237–1257. [CrossRef]
144. Mata-Sandoval, J.C.; Karns, J.; Torrents, A. Influence of rhamnolipids and Triton X-100 on the biodegradation of three pesticides in aqueous phase and soil slurries. *J. Agric. Food Chem.* **2001**, *49*, 3296–3303. [CrossRef] [PubMed]
145. Odukkathil, G.; Vasudevan, N. Enhanced biodegradation of endosulfan and its major metabolite endosulfate by a biosurfactant producing bacterium. *J. Environ. Sci. Health B* **2013**, *48*, 462–469. [CrossRef]
146. Wattanaphon, H.T.; Kerdsin, A.; Thammacharoen, C.; Sangvanich, P.; Vangnai, A.S. A biosurfactant from *Burkholderia cenocepacia* BSP3 and its enhancement of pesticide solubilization. *J. Appl. Microbiol.* **2008**, *105*, 416–423. [CrossRef] [PubMed]
147. Wolf, D.C.; Gan, J. Influence of rhamnolipid biosurfactant and Brij-35 synthetic surfactant on 14C-Pyrene mineralization in soil. *Environ. Pollut.* **2018**, *243*, 1846–1853. [CrossRef]
148. Crampon, M.; Cébron, A.; Portet-Koltalo, F.; Uroz, S.; Le Derf, F.; Bodilis, J. Low effect of phenanthrene bioaccessibility on its biodegradation in diffusely contaminated soil. *Environ. Pollut.* **2017**, *225*, 663–673. [CrossRef]
149. Liu, Y.; Zeng, G.; Zhong, H.; Wang, Z.; Liu, Z.; Cheng, M.; Liu, G.; Yang, X.; Liu, S. Effect of rhamnolipid solubilization on hexadecane bioavailability: Enhancement or reduction? *J. Hazard. Mater.* **2017**, *322*, 394–401. [CrossRef]
150. Tahseen, R.; Afzal, M.; Iqbal, S.; Shabir, G.; Khan, Q.M.; Khalid, Z.M.; Banat, I.M. Rhamnolipids and nutrients boost remediation of crude oil-contaminated soil by enhancing bacterial colonization and metabolic activities. *Int. Biodeterior. Biodegradation* **2016**, *115*, 192–198. [CrossRef]
151. Mekwichai, P.; Tongcumpou, C.; Kittipongvises, S.; Tuntiwiwattanapun, N. Simultaneous biosurfactant-assisted remediation and corn cultivation on cadmium-contaminated soil. *Ecotoxicol. Environ. Saf.* **2020**, *192*, 110298. [CrossRef]
152. Durval, I.B.; Resende, A.; Ostendorf, T.; Oliveira, K.G.O.; Luna, J.M.; Rufino, R.D.; Sarubbo, L.A. Application of *Bacillus cereus* UCP 1615 biosurfactant for increase dispersion and removal of motor oil from contaminated seawater. *Chem. Eng. Trans.* **2019**, *74*, 319–324. [CrossRef]
153. Martínez-Pascual, E.; Grotenhuis, T.; Solanas, A.M.; Viñas, M. Coupling chemical oxidation and biostimulation: Effects on the natural attenuation capacity and resilience of the native microbial community in alkylbenzene-polluted soil. *J. Hazard. Mater.* **2015**, *300*, 135–143. [CrossRef] [PubMed]
154. Janssen, D.B.; Stucki, G. Perspectives of genetically engineered microbes for groundwater bioremediation. *Environ. Sci. Process Impacts* **2020**, *22*, 487–499. [CrossRef] [PubMed]
155. Kumar, P.T.; Vinod, P.T.; Phoha, V.V.; Iyengar, S.S.; Iyengar, P. Design of a smart biomarker for bioremediation: A machine learning approach. *Comput. Biol. Med.* **2011**, *41*, 357–360. [CrossRef] [PubMed]
156. Sharma, B.; Dangi, A.K.; Shukla, P. Contemporary enzyme based technologies for bioremediation: A review. *J. Environ. Manag.* **2018**, *210*, 10–22. [CrossRef]
157. Nasr, M. Modeling applications in bioremediation of hydrocarbon pollutants. In *Microbial Action on Hydrocarbons*; Kumar, V., Kumar, M., Prasad, R., Eds.; Springer: Singapore, 2019; pp. 181–197. [CrossRef]
158. De Almeida, D.G.; Soares da Silva, R.D.; Luna, J.M.; Rufino, R.D.; Santos, V.A.; Banat, I.M.; Sarubbo, L.A. Biosurfactants: Promising molecules for petroleum biotechnology advances. *Front. Microbiol.* **2016**, *7*, 1718. [CrossRef] [PubMed]
159. Crecente, C.; Rasmussen, K.; Torsaeter, O.; Storm, A.; Kowalewski, E. An experimental study of microbial improved oil recovery by using *Rhodococcus* sp.094. In Proceedings of the International Symposium of the Society of Core Analysts, Toronto, ON, Canada, 21–25 August 2005. Paper no. SCA2005-45.

160. Perfumo, A.; Rancich, I.; Banat, I.M. Possibilities and challenges for biosurfactants use in petroleum industry. *Adv. Exp. Med. Biol.* **2010**, *672*, 135–145. [CrossRef]
161. Mulligan, C.N.; Sharma, S.K.; Mudhoo, A. *Biosurfactants: Research Trends and Applications*; CRC Press: Boca Raton, FL, USA, 2014; 352p. [CrossRef]
162. Plaza, G.A.; Chojniak, J.; Banat, I.M. Biosurfactant mediated biosynthesis of selected metallic nanoparticles. *Int. J. Mol. Sci.* **2014**, *15*, 13720–13737. [CrossRef]
163. Banat, I.M.; Makkar, R.S.; Cameotra, S.S. Potential commercial applications of microbial surfactants. *Appl. Microbiol. Biotechnol.* **2000**, *53*, 495–508. [CrossRef]
164. Eswari, J.S.; Dhagat, S.; Mishra, P. Biosurfactant assisted silver nanoparticle synthesis: A critical analysis of its drug design aspects. *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2018**, *9*, 045007. [CrossRef]
165. Sil, J.; Dandapat, P.; Das, S. Health care applications of different biosurfactants: Review. *Int. J. Sci. Res.* **2017**, *6*, 41–50. [CrossRef]
166. Kitamoto, D.; Isoda, H.; Nakahara, T. Functions and potential applications of glycolipid biosurfactants—From energy-saving materials to gene delivery carriers. *J. Biosci. Bioeng.* **2002**, *94*, 187–201. [CrossRef]
167. Lee, D.S.; Song, H.G. Antibacterial activity of isolated bacteria against *Propionibacterium acnes* causing acne vulgaris. *Korean J. Microbiol.* **2018**, *54*, 272–279. [CrossRef]
168. Yuewen, L.; Ran, L.; Zhifei, L.; Jing, C.; Xinli, L. Comparison of the pharmaceutical activities of sophorolipids and nano-hydroxyapatite sophorolipids on cervical cancer cells. *Chin. J. Appl. Environ. Biol.* **2017**, *3*, 386–490.
169. Al-wazni, W.S. Immunomodulator activity of biosurfactant extract from *Serratia marcescens*. *Int. J. Microbiol. Res.* **2016**, *7*, 36–42. [CrossRef]
170. Muthusamy, K.; Gopalakrishnan, S.; Ravi, T.K.; Sivachidambaram, P. Biosurfactants: Properties, commercial production and application. *Curr. Sci.* **2008**, *94*, 736–747.
171. Rufino, R.D.; Luna, J.M.; Campos-Takaki, G.M.; Ferreira, S.R.; Sarubbo, L.A. Application of the biosurfactant produced by *Candida lipolytica* in the remediation of heavy metals. *Chem. Eng. Trans.* **2012**, *27*, 61–66. [CrossRef]
172. Chai, T.; Yan, H.; Zhang, Z.; Xu, M.; Wu, Y.; Jin, L.; Huang, G.; Fu, H. Optimization of enhanced ultrafiltration conditions for cd with mixed biosurfactants using the Box-Behnken response surface methodology. *Water* **2019**, *11*, 442. [CrossRef]
173. Shoeb, E.; Akhlaq, F.; Badar, U.; Akhter, J.; Imtiaz, S. Classification and industrial applications of biosurfactants. *AR Int.* **2013**, *4*, 243.
174. Fracchia, L.; Ceresa, C.; Franzetti, A.; Cavallo, M.; Gandolfi, I.; van Hamme, J.; Gkorezis, P.; Marchant, R.; Banat, I.M. Industrial applications of biosurfactants. In *Biosurfact: Production and Utilization—Processes, Technologies, and Economics*; Kosaric, N., Sukan, F.V., Eds.; CRC Press: Boca Raton, FL, USA, 2014; Volume 3, pp. 245–360.
175. Kosaric, N. Biosurfactants and their application for soil bioremediation. *Food Technol. Biotechnol.* **2001**, *39*, 295–304.
176. Campos, J.M.; Stamford, T.L.; Sarubbo, L.A.; de Luna, J.M.; Rufino, R.D.; Banat, I.M. Microbial biosurfactants as additives for food industries. *Biotechnol. Prog.* **2013**, *29*, 1097–1108. [CrossRef] [PubMed]
177. Morita, T.; Konishi, M.; Fukuoka, T.; Imura, T.; Kitamoto, D. Physiological differences in the formation of the glycolipid biosurfactants, mannosylerythritol lipids, between *Pseudozyma antarctica* and *Pseudozyma aphidis*. *Appl. Microbiol. Biotechnol.* **2007**, *74*, 307–315. [CrossRef] [PubMed]
178. Maeng, Y.; Kim, K.T.; Zhou, X.; Jin, L.; Kim, K.S.; Kim, Y.H.; Lee, S.; Park, J.H.; Chen, X.; Kong, M.; et al. A novel microbial technique for producing high-quality sophorolipids from horse oil suitable for cosmetic applications. *Microb. Biotechnol.* **2018**, *11*, 917–929. [CrossRef] [PubMed]
179. Roy, A. A review on the biosurfactants: Properties, types and its application. *J. Fundam. Renew. Energy Appl.* **2017**, *8*, 100248. [CrossRef]
180. Vecino, X.; Cruz, J.M.; Moldes, A.B.; Rodrigues, L.R. Biosurfactants in cosmetic formulations: Trends and challenges. *Crit. Rev. Biotechnol.* **2017**, *37*, 911–923. [CrossRef]
181. Green Surfactants Market Size, Share, Price Analysis. Expert Market Research; 2022–2027. Available online: https://www.expertmarketresearch.com/reports/green-surfactants-market (accessed on 15 April 2023).
182. Baccile, N.; Babonneau, F.; Banat, I.M.; Ciesielska, K.; Cuvier, A.-S.; Devreese, B.; Everaert, B.; Lydon, H.; Marchant, R.; Mitchell, C.A.; et al. Development of a cradle-to-grave approach for acetylated acidic sophorolipid biosurfactants. *ACS Sustain. Chem. Eng.* **2017**, *5*, 1186–1198. [CrossRef]
183. Mgbechidinma, C.L.; Akan, O.D.; Zhang, C.; Huang, M.; Linus, N.; Zhu, H.; Wakil, S.M. Integration of green economy concepts for sustainable biosurfactant production—A review. *Bioresour. Technol.* **2022**, *364*, 128021. [CrossRef]