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Review

Biosurfactants: Promising Biomolecules for Agricultural Applications

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Abstract: Population growth and the need for increased agricultural productivity pose a global problem. Therefore, the development of green compounds to ensure agricultural sustainability is an urgent necessity. Surfactant compounds hold significant commercial importance due to their diverse industrial uses. However, the synthetic origin of these agents limits their commercial application due to their toxicity. As a result, extensive research has focused on the production of microbial-originated green surfactants, known as biosurfactants, over the past fifteen years. These biomolecules not only offer a green alternative for agriculture but also exhibit reduced toxicity and excellent stability under specific environmental conditions. Biosurfactants can lower surface tension more effectively than synthetic surfactants. With properties such as detergency and foam formation, biosurfactants are suitable for various agricultural applications, particularly in pesticide and agrochemical formulations. They can function as biopesticides to manage pests, pathogens, phytopathogenic fungi, and weeds due to their antimicrobial activity. Moreover, plants can benefit from biosurfactant molecules and microorganisms as nutrients. They can also aid efficiently in the distribution of micronutrients and metals in the soil. They also stimulate plant immunity and are utilized for soil hydrophilization to ensure proper moisture levels and uniform fertilizer distribution. This review aims to provide valuable insights into the role and properties of biosurfactants as agricultural adjuvants, fostering the development of sustainable formulations to replace the chemical surfactants used in pesticides. For this purpose, the general aspects of global agricultural activity are initially described, followed by a discussion of pesticides, including herbicides, fungicides, and insecticide products. Next, the properties of chemical surfactants are discussed and the use of green surfactants, with emphasis on microbial biosurfactants, is demonstrated. The application of biosurfactants in the agricultural industry and trends are addressed and prospects for the application of these agents are discussed.

Keywords: biosurfactants; sustainable agriculture; adjuvant; pesticide; plant pathogen; remediation

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1. Introduction

The demand for food and agricultural products has significantly increased since the 1990s due to population growth, urbanization, rising income, and production incentives. According to the United Nations average projection, the population is expected to reach around 10 billion people by 2050. As a result, international agreements and regulatory frameworks for sustainable development in the coming decades have been established to promote the sustainable use of natural resources, mitigation of climate change impacts, and sustainable utilization of their components, among others. Many efforts are being made to intensify and sustainably meet the world's agricultural production needs to accommodate population expansion. It will be necessary to increase current food production levels in a manner that is more than proportional to population growth to provide an adequate diet for a larger human population [1,2].

The incorporation of new laboratory techniques, statistics, computer science, and genetically modified crops has driven recent agricultural advancements, resulting in a significant increase in productivity per hectare for various crops. In this context, combating pests and weeds using pesticides is of utmost importance in modern agricultural practices [3,4].

Agrochemicals used worldwide are chemical substances that can control biological weeds or unwanted plants (herbicides) [5], protect agricultural products against fungi (fungicides) [6], and combat pests such as rodents and insects (pesticides) [7]. Among the top five most widely used agrochemicals, glyphosate and 2,4-D herbicides hold the first and second positions. Glyphosate was banned in Germany and Australia in 2008 due to its potential link to cancer in children [8].

The use of agrochemicals brings significant problems as they are non-biodegradable and pose great difficulty in breaking down into non-toxic elements. Many of these products are discharged into bodies of water, leading to the contamination of fish through bioaccumulation in their tissues or maintaining their presence in food items such as vegetables [5,9,10]. There are reports of workers directly involved in handling these agrochemicals in crops who have developed various illnesses, with many of them resulting in death due to their high toxicity [11].

Given this scenario, one of the strategies used has been the development of genetically modified crops to reduce the use of agrochemicals. Genetically modified crops are organisms that have been genetically altered to enhance productivity and/or exhibit resistance to pathogens [12]. However, even with the use of genetically modified crops, there has not been a decrease in the use of agrochemicals but rather an increase. While these crops may be resistant to specific pathogens, they have become more susceptible to other injuries, leading to a significant rise in the demand for agrochemicals [13]. Since it is no longer possible to remove genetically modified foods from the market due to the high demand for food worldwide, government agencies have decided to invest in environmental policies and increase the demand for natural agricultural defenses.

Thus, the search for bioproducts or green products for the development of agrochemicals becomes necessary to reduce the presence of toxic agrochemicals in agribusiness [9].

One of the main representatives of natural agriproducts is natural agricultural defenses. These are biologically derived agrochemicals that can be obtained from plant extracts, fungal or bacterial extracts, and similar sources. Due to their natural origin, these defenses exhibit reduced toxicity and high biodegradability [14–16].

Agrochemical formulations require the use of surfactants, which are essential for their preparation, maintenance of physical stability, and enhancement of biological performance. Chemical surfactants are widely used in agriculture as aids in agricultural production [17,18].

Therefore, the importance of sustainability using renewable resources and product improvement brings forth the possibility of replacing chemical surfactants with their biological counterparts. Green surfactants are amphiphilic and antimicrobial substances that can be extracted from plants and/or obtained through the metabolism of microorganisms (biosurfactants) or chemical synthesis using natural extracts (natural-based surfactants) [19,20].

These biomolecules, due to their desirable characteristics for agro-industrial activities, have been investigated for use as biopesticides, biofertilizers, biostimulants, bio dispersants, and bioremediators of soil, among other applications. However, compared with research in environmental, health, cosmetic, and food-related fields, studies on the use of biosurfactants in agriculture are still relatively limited [14,16,21–23].

Given the above issues and the scarcity of information regarding the utilization of biosurfactants in agriculture, this review aims to describe the importance of microbial surfactants in the agricultural sector. The search method comprised an analysis of 1493 publications, including articles, book chapters, and patents sourced from databases such as Scopus, ScienceDirect, Google Scholar, and Google Patents using the PRISMA methodology [24]. This review focused on studies published from 1994 to 2024, aimed at comprehensively evaluating the evolution of biosurfactant application research. Specific keywords such as biosurfactant, agriculture, plant protection, crop, and soil improvement were used, ensuring the scope's relevance. Criteria were set to include the literature explicitly addressing biosurfactant use in agriculture, experimental articles, relevant book chapters, and patents reflecting advancements. All the literature not relevant to our study was excluded, such as conference proceedings, articles in languages other than English, difficult-to-access literature, low-quality or inconsistent information studies, and materials discussing biosurfactants for applications other than agriculture. Finally, following the application of the inclusion and exclusion criteria, we obtained 287 publications, including relevant articles and patents. The PRISMA flow diagram is shown in Figure 1.

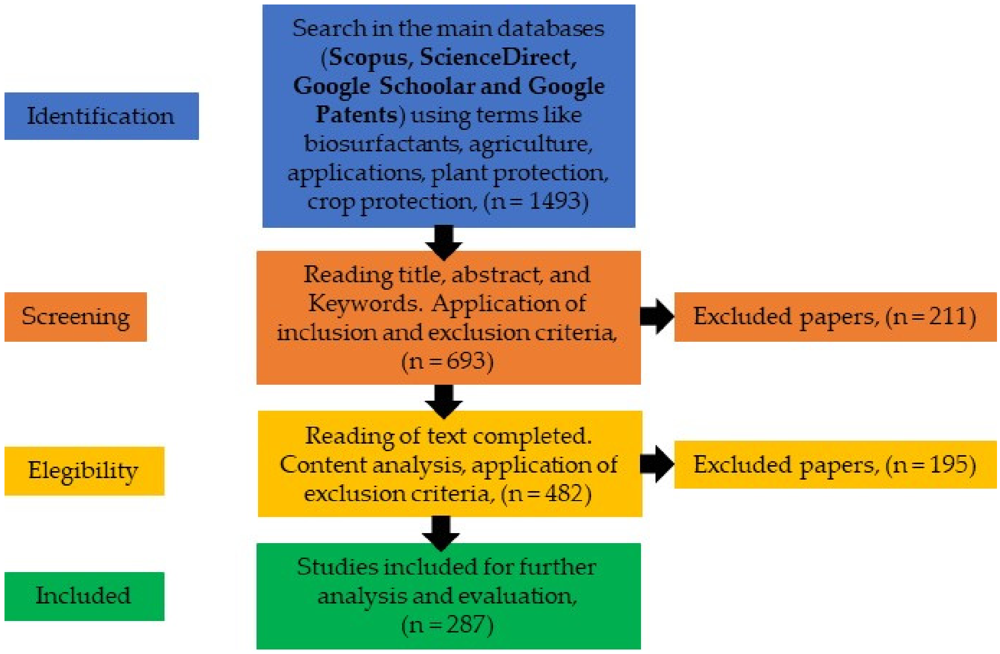

Figure 1. PRISMA flow diagram for the literature review.

2. General Aspects of Global Agricultural Activity

With the exponential growth of the world population starting from the 1900s (Figure 2), there was a need to increase food production due to the rising demand for food, as illustrated in Figure 3. As a result, it was necessary to boost production and/or minimize crop losses caused by fungi, pests, and weeds, for which pesticides, chemical substances designed for the biological control of microorganisms, macroorganisms, and competing plants, began to be used. At the same time, the development of genetically modified organisms (GMOs) and genetically modified foods, which aimed to enhance resistance against pathogens and/or increase productivity, was also intensified to reduce pesticide usage [12].

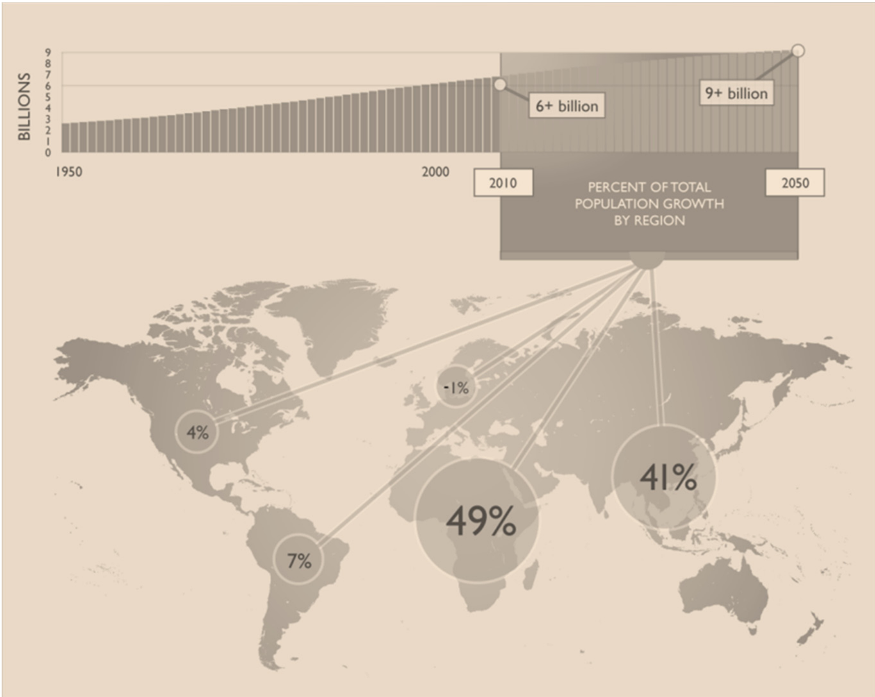

Figure 2. World population growth between 1950 and 2050 (source-https://www.canr.msu.edu/news/feeding-the-world-in-2050-and-beyond-part-1, accessed on 25 April 2023).

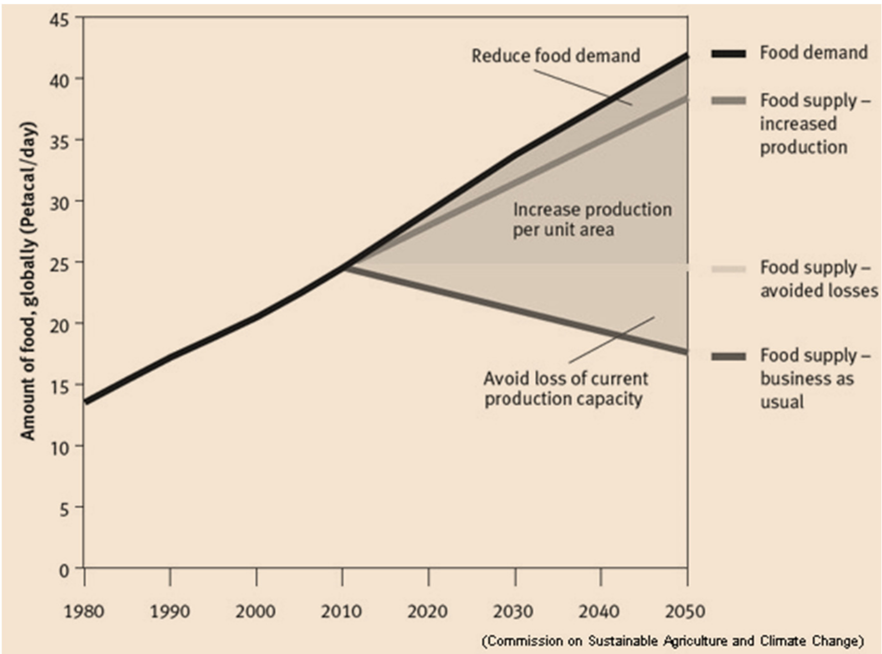

Figure 3. Global food demand until 2050 (source-https://earthbound.report/2012/04/12/feeding-the-world-in-2050/, accessed on 25 April 2023).

However, with the use of GMOs, the use of pesticides increased up to approximately 250 tons. This occurred because GMOs exhibited increased resistance against certain pathogens but became more susceptible to others, thereby not reducing this practice [25]. The adoption of herbicide-resistant crop technology in the United States resulted in a significant rise in herbicide usage, totaling 239 million kilograms (527 million pounds). Conversely, the implementation of *Bacillus thuringiensis* crops resulted in a 56-million-kilogram (123 million pounds) reduction in insecticide use. Consequently, the overall pesticide consumption in the country increased by approximately 183 million kilograms (404 million pounds), equivalent to a 7% increment [26].

3. Pesticides

3.1. Agricultural Defensives

Pesticides are chemical compounds used to control pests in a generalized way, most of which have a long degradation time and are highly toxic to humans and other animals [9]. Many of the problems caused by pesticides occur due to incorrect use and exceeding the allowed concentration, and some studies have already shown that this indirectly affects pollinating animals [10]. The low biodegradability of pesticides leads to their accumulation in riverbeds and an increase in their presence in a single food item. These factors contribute to the contamination of fishery resources, and humans can be indirectly affected by consuming these contaminated foods [5]. Pesticides include herbicides, fungicides, and insecticide products.

Herbicides are pesticides used to control competing or undesirable vegetation (weeds). Since it is not possible to target only one type of vegetation in crops, it is recommended to use herbicides with different actions against various types of vegetation. However, this strategy is environmentally harmful because the herbicide mixture can be carried into riverbeds, especially when applied near the roots. Furthermore, they are the type of pesticide that affects mammals the most [5,27].

Fungicides are pesticides used to combat fungi that attack plant species, thus being among the major pathogens of crops. They represent 30% of all pesticides in the current global market. The most common fungicide is Cu, a heavy metal that can contaminate water and is highly toxic to living beings [6]. Fungicides are the main cause of poisoning in pollinating insects [28].

Insecticides, the last category of pesticides, are used to control pests, mainly insects, which use crops as a food source, breeding ground, and development site. Due to their accumulation on the surface of foods, they have a large impact on humans, who can absorb them [7,29].

The increase in crop yield associated with the "green" revolution was partly made possible by using chemical products for pest control. Concerns regarding the harmful effects of pesticides on the environment and human health have prompted the creation of new pesticide registration procedures, such as the Food Quality Protection Act in the USA. The implementation of new regulations has resulted in a decrease in the availability of synthetic pesticides in the field of agriculture. New pesticides, both synthetic and natural, are being developed to compensate for lost compounds due to new registration requirements. [3].

3.2. Biological Control

In contrast to pesticides, biological control utilizes nature itself to achieve control. As a result, it does not impact the environment, although it may not have the same efficiency as a pesticide and requires certain special conditions for its application [9]. Biological control can be carried out with parasitoids, predators, and entomopathogens. Parasitoids are introduced by inoculating insect larvae into the eggs of a pest, where they feed, develop, and then emerge as adults. An example is *Trichogramma pretiosum*, which parasitizes moth eggs [30]. One of the oldest methods for pest control involves introducing a predator into the same environment as the pest so that it can use it as food. *Harmonia axyridis* (ladybug) is a good example, as it feeds on *Myzus persicae* (aphid) [31,32]. Entomopathogens, on the other hand, are fungi or bacteria that attack pests (insects or microorganisms). This method is not common but, in some cases, it proves to be the most efficient [33].

3.3. Agricultural Biodefensives

Agricultural biodefensives include bioherbicides, biofungicides, and biopesticides. Bioherbicides use organic products, such as fungus extracts [16], oil extracts [21], fruit enzymes [15], and other biological materials. Biofungicides are a group of agricultural biodefensives based on competing fungi that do not affect the development of the agricultural product [22]. The use of seeds as biofungicides has also been described [23,34]. Finally, biopesticides are the most used agricultural biodefensives to replace pesticides. Similar to other agricultural biodefensives, they are derived from plant or microorganism extracts, fruits, crustaceans, seeds and tree saps, and cellular mass, among other natural substances. Their use has significantly increased in North America in recent years [14].

3.3.1. Formulation of Agricultural Biodefensives

Formulations of agricultural biodefensives can either be diluted in water or other solvents or can be applied as such. Formulations for dilution in water can be sold as an Emulsifiable Concentrate (EC), in the form of emulsions with small amounts of water, giving them a milky appearance [35,36]; as Suspension Concentrates (SCs), which are inert and stable and need to be shaken before application [37]; as Soluble Powder (SP) [38] or as Wettable Powder (WP), which is very similar to SP but does not dissolve in water when applied, requiring agitation during application [39]; or as Microencapsulated, which is a specific characteristic of WP as it is not in direct contact with water but encapsulated for continuous and controlled release over time during application [40]. Formulations for dilution in other solvents are marketed in high concentrations and need to be diluted in oils or organic solvents [41]. Formulations for direct application are provided in the form of Dry Powder (DP), which is essentially applied in a mixture with inert powders such as talc and clay when water spraying can damage the area or agricultural products [42], in the form of Granules (GRs), which are similar to Dry Powder but consist of larger granular solids (ranging from 0.3 to 0.6 mm) for slower and continuous release of the biodefensive [43], or in the form of Baits, which are composed of even larger granular solids than the GR formulations and are intended to be consumed by pests [44].

3.3.2. Agricultural Adjuvants as Activators or Enhancers of Agricultural Defensives

The market offers many solutions and products to ensure application quality, reduce losses, and increase the efficiency of phytosanitary management. Adjuvants encompass a wide range of chemical substances that are commonly included in spray tanks to enhance the efficacy and application efficiency of pesticides. Their primary function is to improve the pesticide's performance and mode of application [45].

Agricultural adjuvants have a long history dating back to the 18th and 19th centuries. During this time, various additives such as resins, molasses, flour, pitch, and sugar were combined with sulfur, arsenates, lime, and copper to enhance "adhesion" and improve biological performance by altering the chemical and physical features of the applied mixture [3,46]. Research indicates that adjuvants can influence various factors in pesticide applications. The main points are related to altering solution properties, increasing biological efficacy, and improving operational performance. Benefits such as increased wetting, better spreading on leaves, greater efficiency, and speed of active ingredient absorption on the target (crop, weeds, and insects) can be achieved using adjuvants [47].

It should be noted that there are many barriers involved in agricultural pesticide applications. Regarding plants, leaf surfaces have waxes that are difficult to wet and prevent liquid entry into the plant. These waxes are primary obstacles to the deposition, retention, spread, and penetration of agrochemical droplets. Adjuvants can overcome these impediments and increase the deposition, spread, absorption, and penetration of products into the plant [48–50].

As for climatic barriers, several factors can negatively affect applications. Deviation from the trajectory, preventing the droplets from reaching the target, is mainly related to droplet size and wind speed. Environmental conditions greatly influence the outcome of the operation, so it is necessary to understand the spectrum of sprayed droplets, adjusting not only their diameter but also seeking other tools. Adjuvants such as oils can be an alternative to achieve greater leaf penetration, while surfactants reduce evaporation, and nozzle selection helps produce more suitable droplets [51].

The portfolio of adjuvants available on the market is extensive and mainly includes mineral and/or vegetable oils, silicones, surfactants, emulsifiers, nitrogen, phosphorus, organic resins, EDTA, and essential oils, among others. Therefore, it is essential to classify them according to their benefits. Several authors define adjuvants as utility or activator-based [52,53].

3.3.3. Utility Adjuvants

Adjuvants for utilities can alter the spray solution's physical properties [54], improving the quality, viscosity, and surface tension of the droplets. Their main effects include reducing foam formation, cation sequestration, dispersing action, and pH reduction and buffering, among others.

3.3.4. Activator or Enhancer Adjuvants

Activator adjuvants enhance the biological and chemical efficacy of applied products, application quality, droplet size, and spreading, and may provide some resistance to rain [54]. The main products and their effects include surfactants, which ensure droplet spreading on leaves; emulsifiers, nitrogen fertilizers, and oils that increase the speed of product absorption; wetting agents, which reduce evaporation; and adhesives, which prevent runoff and ensure better adhesion to leaves. Activator adjuvants also modify the deposition of the spray on plant foliage and increase movement on the leaf surface for greater absorption in specific areas [52,54].

Three factors are important in the selection of adjuvants, namely, (i) plant (species, phenological stage, and location), (ii) application (method, timing, and environmental conditions), and (iii) biological target (weed, insect, and disease). The need for adjuvants is directly related to the pesticide used and the objectives of the application. In a study, Xu et al. [47] tested concentrated vegetable oil (CVO), methylated seed oil (MSO), a nonionic surfactant (NIS), and a surfactant and oil mixture (SOM). The addition of adjuvants to the spray solution led to a significant reduction in droplet contact angle, resulting in increased spreading and wet area. The authors noted that the quality of applications varied depending on the plant species and type of adjuvant used. Overall, the SOM and NIS enhanced droplet spreading and maintained the evaporation time of droplets on leaf surfaces, and after evaporation, chemical residues formed ring-shaped accumulations. Droplets with oil-based adjuvants exhibited a residual distribution with a more uniform deposition. According to Yu et al. [55], droplet size and relative humidity significantly affect droplet evaporation time and coverage area as well as evaporation and deposition dynamics. In an environment with 30% to 90% relative humidity, the addition of surfactants increased the evaporation time of droplets and their coverage area by 4.5 to 10.1 times on hairy leaves and by 3.4 to 4.1 times on waxy leaves.

4. Surfactants

Agrochemical formulations require surfactants for physical stability and biological efficiency [3].

Research suggests that less than 0.1% of pesticides utilized for weed and pest control hit their intended targets. Most of these chemicals are lost due to factors such as spray drift, off-target deposition, runoff, and photodegradation [56].

Agrochemical products use around 230,000 tons of surfactants annually, typically in formulations containing 1–10% of one or more surfactants. As a plasticizer, the surfactant softens the crystalline waxes on the cuticle, thereby increasing the mobility of agrochemicals through the cuticular membrane [3,57].

Surfactants of various types are being used in the pesticide production industry [58]. In particular, they are commonly used in pesticide formulations, which, however, leads to their accumulation in the soil, thus affecting texture, color, and plant growth. These hazardous chemicals are also leached from the soil into groundwater [59], persist in the soil for years, can spread through the air and water, and can even be found on the outer surfaces of fruits and vegetables. Synthetic surfactants are also considered powerful organic contaminants in the soil [60].

Given the negative effects of pesticides and surfactants used in pesticides, environmentally friendly biosurfactants should be used to replace the hazardous synthetic ones in the multibillion-dollar pesticide industry, thus reducing contamination [61].

Depending on the characteristics of their molecule, surfactants can reduce surface tension and solubilize water in oil or oil in water since these molecules have a hydrophilic part and a hydrophobic part, allowing water encapsulation within an oily substance or, vice versa, forming a structure known as amphiphilic [62].

The best method for characterizing a surfactant is to measure the attractive forces among liquid molecules, thereby assessing the surfactant's ability to influence surface and interfacial tensions. Effective surfactants reduce surface tensions, facilitating interactions between molecules with different polar features [63]. The critical micelle concentration (CMC) is defined as the minimum surfactant concentration required to reach the lowest surface tension. Upon reaching the CMC, the amphiphilic molecules aggregate with the hydrophilic portions positioned outward and the hydrophobic portions inward [64]. After reaching CMC, no further addition of surfactant will result in an additional reduction in surface tension. Thus, surfactants with a lower CMC are preferably used compared with those with higher CMC values [63].

Surfactants can be divided into two categories: chemical surfactants and green surfactants. Green surfactants are further divided into two subclasses: biosurfactants and biobased surfactants [19].

4.1. Chemical Surfactants

Chemical surfactants originate from petrochemicals and dominate the global surfactant market, accounting for 90% of it [64]. Due to their large-scale production, chemical surfactants are more competitively priced compared with natural surfactants. However, despite their high surface activity and lower cost, they pose various problems due to their high toxicity and long degradation time [65]. There are four types of surfactants categorized by the nature of their hydrophilic group: anionic, cationic, nonionic, and amphoteric [63].

According to Xu et al. [47], surfactants reduce the surface tension of droplets on leaf surfaces, ensuring greater coverage and foliar absorption. Their concentration greatly influences the efficacy of agrochemical applications. For instance, increasing surfactant concentration from 0.01% to 1% promoted better foliar absorption of products; however, for some surfactants, higher concentrations can have a negative effect on chemical absorption [51].

Anionic surfactants often include sulfonate, sulfate, or carboxylate groups, with counterions such as sodium or calcium. Among them, linear alkylbenzene sulfonates (LASs) are extensively produced worldwide as household cleaning detergents, and calcium LAS is used as an adjuvant in many agrochemical formulations [66].

In nonionic surfactants, the hydrophilic behavior is achieved through polymerized glycol ether or glucose units [67]. They are predominantly synthesized by adding ethylene oxide or propylene oxide to fatty alcohols, alkylphenols, amines, acids, or fatty acid amides. Nonionic surfactants find significant applications as emulsifiers, detergents, dispersants, and wetting agents, and a substantial portion of them are used as adjuvants in agrochemical formulations.

Cationic surfactants, which have hydrophilic portions formed by quaternary ammonium ions, have gained importance due to their bacteriostatic properties and are applied as disinfectants and antiseptics in personal care products. They are also used as textile softeners, flotation agents, and corrosion inhibitors due to their high adsorptive capacity [3].

Amphoteric surfactants are water-soluble and compatible with other surfactants, as they possess both cationic and anionic groups in their structure, which make them zwitterionic compounds. Their charge changes with pH, influencing detergency and foam formation, among other properties. They have properties that closely resemble those of nonionic surfactants and are commonly used in shampoos, but they are also starting to be used in agrochemical formulations [66].

4.2. Biobased Surfactants

The term biobased surfactant refers to green surfactants synthesized through chemical or enzymatic processes using renewable raw materials. The main resources used for their synthesis are vegetable oil triacylglycerides, methyl esters of fatty acids, fatty alcohols, fatty acids, glycerol, carbohydrates, and amino acids. Triglycerides form the hydrophobic moiety, while sugars or amino acids and peptides act as the hydrophilic ones [67]. Although biobased surfactants are still relatively new, they have already shown excellent results in various applications [17,18,68].

4.3. Biosurfactants

Biosurfactants constitute a subclass of green surfactants of biological origin, which can be obtained from plant extracts, roots, and fruits or through the metabolic transformation of microorganisms, especially bacteria, and yeasts [69]. Microbial biosurfactants are the most efficient and widely studied and possess the same specifications as chemical surfactants, but they exhibit biodegradability, reduced toxicity, and biocompatibility [20,70].

Biosurfactants have diverse industrial applications, ranging from petroleum and cleaning products to cosmetics, textiles, food, and agriculture. In the agricultural sector, biosurfactants can be used in the formulation of biopesticides, biofertilizers, and biostimulants [71].

At present, biosurfactants make up only 10% of the world's total surfactant production, which is around ten million tons annually. However, if synthetic surfactants were replaced with biosurfactants, it could reduce CO_2 emissions by 8% over the long term. This would prevent the release of roughly 1.5 million tons of CO_2 into the atmosphere [63,68]. The first studies in the field of microbial biosurfactant research occurred in the 1960s, and since then, research has led to the commercialization of numerous products containing them. In the last decade, studies focused on biosurfactant production have intensified due to their efficiency and biocompatibility [63].

Currently marketed biosurfactants have a higher production cost compared with their synthetic counterparts, despite their high efficiency [72]. On the other hand, this cost can be reduced through the selection of more suitable substrates during fermentation, that is, with lower cost, and the selection of microbial strains with greater capacity for biosurfactant production [73]. In most cases, strains produce a mixture of different biosurfactants. However, for certain applications in the food, medical, and pharmaceutical industries, a high level of purity is necessary, which can be a limiting factor for their use. Therefore, it is crucial to develop strategies that facilitate the production and large-scale application of biosurfactants [20]. The microbial source and molecular structure are the most important criteria for classifying biosurfactants, the main classes of which are glycolipids, lipopeptides, phospholipids, polymeric biosurfactants, particulate biosurfactants, and fatty acids. Biosurfactants are categorized into low and high molecular weights based on their average molecular weight, which ranges from 500 to 1500 Da. Low molecular weight biosurfactants have the ability to reduce surface tension efficiently, while higher molecular weight biosurfactants are commonly used for stabilizing oil–water emulsions [63]. Biosurfactants such as proteins, lipoproteins, polysaccharides, and lipopolysaccharides, which are of high molecular weight, are commonly referred to as emulsifiers [74], while the low-molecular-weight ones, which include glycolipids, lipopeptides, and phospholipids, are considered classic biosurfactants [62].

Glycolipids have been extensively studied among the different types of biosurfactants. The structure of glycolipids consists of a hydrophilic carbohydrate moiety connected to hydrophobic fatty acid chains of different lengths via an ester group [74]. These glycolipids are commonly characterized based on the structure of their carbohydrate fraction, with sophorolipids, rhamnolipids, mannosylerythritol lipids, and trehalose lipids being the most investigated subclasses.

Rhamnolipids consist of one or two fatty acids attached to one or two rhamnose sugar molecules. The primary source of rhamnolipids is the Gram-negative bacterium known as *Pseudomonas aeruginosa*, although subsequent research has shown that other bacterial species are actively producing rhamnolipid-type biosurfactants [75]. Rhamnolipids are a class of biosurfactants with unique characteristics that depend on the strain, carbon source, and cultivation conditions. Various renewable materials such as exhausted oils or waste from the food industry can be used as carbon sources for their production. Rhamnolipids can lower the air–water surface tension from 72 mN/m to around 30 mN/m, as well as the water–oil interfacial tension from 43 mN/m to around 1 mN/m. The CMC of pure rhamnolipids and their mixtures largely depends on the chemical composition of the constituents and ranges from 50 to 200 mg/L [71].

Sophorolipids consist of a sophorose head, in which two glucose units are connected by a β-1,2 bond, and a long-chain fatty acid (hydroxyl) tail connected by a glycosidic bond. These biosurfactants, which are generally synthesized by yeasts such as *Starmerella bombicola* [76], have a surface tension of around 33 mN/m and an interfacial tension of about 5 mN/m in n-hexadecane and water. *S. bombicola* is considered one of the most productive strains, being capable of producing about 300 g/L of sophorolipids [77,78].

Trehalose lipids, which contain the disaccharide trehalose linked to a fatty acid (mycolic acid), are mainly produced by species of the genera *Nocardia*, *Rhodococcus*, *Mycobacterium*, and *Corynebacterium* and have high structural diversity [76]. Trehalose lipids produced by *Rhodococcus erythropolis* and *Arthrobacter* spp. can decrease surface and interfacial tensions to 25–40 and 1–5 mN/m, respectively [71].

Pseudozyma antarctica yeast produces mannosylerythritol lipids (MELs) in large quantities from vegetable oils. MELs are made up of mannose and fatty acid and can be further classified based on the hydrophobic chain length, degree of saturation, and acetylation at positions C4 and C6 of the monosaccharide [71].

There are different types of low-molecular-weight biosurfactants, such as lipopeptides, phospholipids, and polymeric surfactants. One of these is surfactin, which is produced by the Gram-positive bacterium *Bacillus subtilis*. Surfactin is a cyclic lipopeptide that contains seven hydrophobic amino acids with a length of 13 to 15 carbon atoms. It also has a mixture of seven amino acids, which are L-asparagine (Asn), L-leucine (Leu), glutamic acid (Glu), L-leucine (Leu), L-valine (Val), and two D-leucines, connected through a lactone bond [79]. It is widely recognized that surfactin is among the most powerful biosurfactants on record, and due to its antibacterial, antiviral, and antifungal activities, it is widely used in various applications; it is also utilized as an efficient stabilizer, emulsifier, and surface modifier in the food industry [80]. Due to its ability to reduce surface tension to 27 mN/m at a concentration of less than 5% [81] and its low CMC, it is explored in different applications [82].

Phospholipidic biosurfactants are produced during the growth of yeasts and bacteria on n-alkanes, including *Acinetobacter* spp. and *Thiobacillus trioxidans*. Liposan and emulsan are examples of polymeric biosurfactants. These compounds are good emulsifiers and can be also synthesized by bacteria and yeasts of the *Candida* genus [76]. The literature describes the use of liposan as an emulsifier in the food and cosmetic industries [73].

Figure 4 shows examples of microbial surfactants.

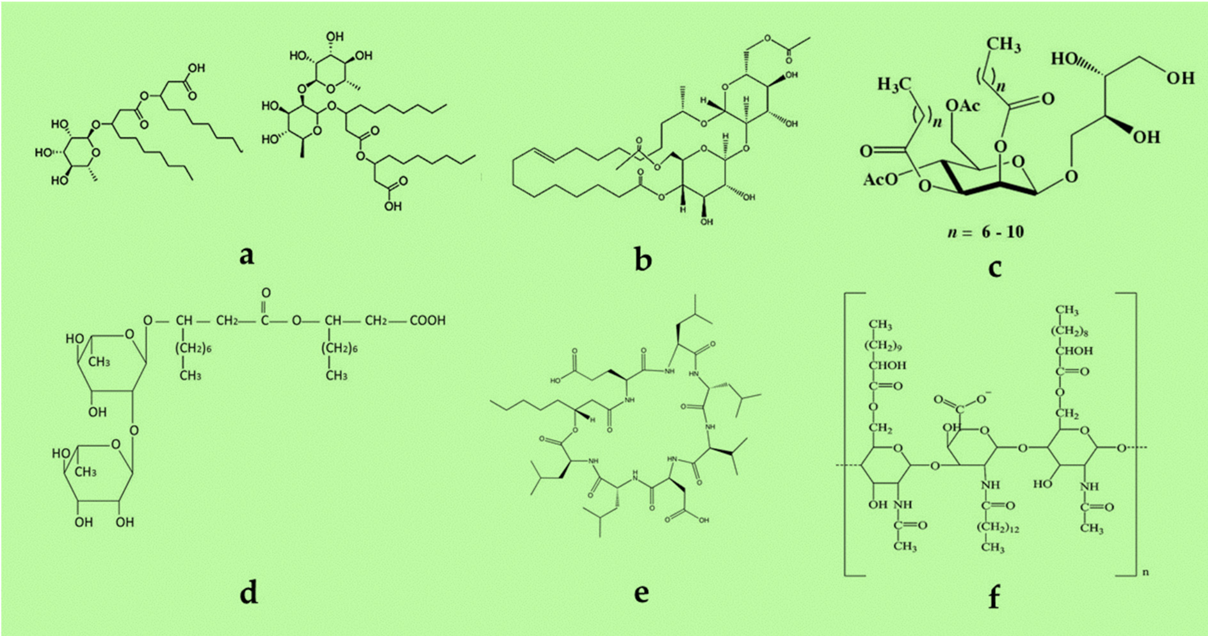

Figure 4. Chemical structure of most studied microbial surface-active compounds: (**a**) rhamnolipid, (**b**) sophorolipid, (**c**) mannosylerythritol lipids (MELs), (**d**) trehalose lipids, (**e**) surfactin, and (**f**) emulsan.

Biosurfactants and synthetic surfactants share several properties such as reducing surface tension, foam-forming capacity, emulsification, stabilization ability, solubility, and detergent activity. However, biosurfactants possess some properties listed below that make them more appealing than their synthetic counterparts [71]:

- Surface activity: Surfactant efficiency is measured with the CMC, which ranges from 1 to 2000 mg/L based on molecular structure, as discussed earlier [63]. An optimal biosurfactant can reduce the surface tension of water from 72 to 30–35 mN/m and the interfacial tension of oil and water from 40 to 1 mN/m [83]. Compared with synthetic surfactants, most microbial surfactants have lower surface and interfacial tensions and CMC values, making them more effective.
- Foam capacity: Biosurfactants are compounds that can reduce the surface tension of liquids, making it easier to create foam, or improve their colloidal stability by preventing bubbles from merging. They are particularly effective at the gas–liquid interface, where they form bubbles that move through the liquid, creating foam. In short, biosurfactants are substances that promote the production of foam [84].
- Emulsification and demulsification: Biosurfactants have emulsifying and demulsifying properties. Emulsions are a colloidal system of two immiscible liquids, wherein a liquid phase is dispersed and suspended in the form of small droplets, the dimensions of which range from 1 nm to 1 μm, in a second liquid (continuous phase). The two types of emulsions are water-in-oil (W/O) and oil-in-water (O/W). Biosurfactants signify the solubilization of large particles with micellar structures by assisting the dispersion of one liquid into another and making it easier for two immiscible liquids to be mixed. Demulsification is a process that occurs in two steps. Firstly, flocculation takes place when droplets come together to form flocs. Then, coalescence occurs when water droplets combine to form larger droplets. This reduction in the quantity of water droplets leads to demulsification. During the demulsification process, the stable interface between the internal and bulk levels is disturbed, causing the emulsions to split. Biosurfactants help to make the demulsification process easier [83].
- Solubilization: When the concentration of biosurfactants in a liquid surpasses a certain point known as the CMC, they spontaneously group together and form small nano-sized aggregates. These aggregates have a hydrophobic core and a hydrophilic

surface that is exposed to water. This unique structure enhances the bioavailability of water-insoluble substances, such as chemical agents or molecules, by enabling their transportation and confinement within the aqueous phase [63,84].

- Wetting: Wetting capability refers to a liquid's ability to connect with another surface and spread evenly over it. When a liquid with a high wetting capacity comes in contact with a surface, it creates a thin and continuous film. Biosurfactants are effective wetting agents because they can lower liquid surface tension by reducing attractive forces, which increases their affinity toward different surfaces. Instead of being connected to surface tension, they penetrate through the pores [84].
- Dispersion: Dispersion occurs when the cohesive attraction between similar particles decreases. A small amount of dispersing agent (such as BS) is added to a suspension to prevent insoluble particles from aggregating. For example, BS can remove hydrophobic molecules from rock surfaces, making them more mobile and easier to recover during oil extraction. Dispersion also plays a role in reducing or completely preventing the formation of biofilms by unwanted microbes [63,71].
- Temperature, pH, and ionic strength tolerance: Several biosurfactants remain effective in adverse conditions, such as high temperatures, a pH range of 3–12, and up to a 10% saline concentration, while synthetic surfactants are inactivated by $\geq$2% NaCl [71].
- Specificity: The high diversity of molecules, each with its own complexity and specific functional groups, confers particular/specific activities to biosurfactants. Similar to synthetic surfactants, biosurfactants show the ability to self-aggregate and form micelles, which increase their specificity and allow them to have different morphological structures. In addition, their ability to create spherical, rod-shaped, and vesicle-like structures has caught the attention of various industries like food, cosmetics, and pharmaceuticals. They also have the potential to detoxify pollutants and demulsify industrial emulsions [71].
- Biocompatibility and digestibility: The composition of biosurfactants makes them more biodegradable and biocompatible than their chemical counterparts under variations in temperature, pH, and degradation time [85].

Biosurfactants, by solubilizing pollutants, also enhance biodegradability. Studies conducted on seawater samples simulated a bioremediation process, demonstrating oil degradation rates greater than 90% in the presence of a biosurfactant together with its producing species [86]. The literature also discusses the role of biosurfactants in supporting the biodegradation of heavy oil in contaminated soils [71]. Regarding digestibility, the chemical structure of microbial surfactants, which mainly includes glycolipids and lipopeptides, makes them important compounds for use in the food, pharmaceutical, and cosmetic industries [87].

Synthetic surfactants are used in remediation and wastewater treatment; therefore, they can be released into industrial wastewater. When this industrial effluent is intentionally or accidentally discharged into a natural body of water, its presence can pose a threat to marine and freshwater ecosystems. When the concentrations of surfactants released into the environment reach high levels, they will accumulate in animals up to toxic levels through the food chain, eventually affecting humans through food consumption [88]. In contrast, biosurfactants are less toxic to aquatic fauna and flora, since they are products of microbial fermentation, in addition to being more easily degraded by microorganisms in soil and aquatic environments [89]. The biocompatibility of these compounds has increasingly attracted industries seeking to replace synthetic surfactants with green surfactants.

Biosurfactants are produced by excretion or cell adhesion. The primary function of biosurfactants is to reduce surface tension between phases, making insoluble substrates more available for absorption and metabolism by microorganisms. Different mechanisms of substrate absorption are described, namely, direct absorption of hydrocarbons dissolved in the aqueous phase, interaction with emulsified droplets, and direct contact between cells and large hydrocarbon droplets. In addition to emulsifying the carbon source, biosurfactants are also involved in microbial cell adhesion to hydrocarbons, i.e., biosurfactant excretion after adsorption of microbial cells onto insoluble substrates allows them to grow on these carbon sources [19].

Achieving the highest possible production of biosurfactants is difficult due to various factors that affect microbial growth and metabolism during fermentation. Numerous studies have attempted to identify the ideal combination of substrates for a specific culture medium, which can enhance intracellular diffusion and the synthesis of desired compounds [71]. To optimize biosurfactant production with the selected microorganism, defining culture conditions is crucial. Factors to be considered include carbon and nitrogen sources, the concentration of the lipophilic substrate, inoculum size, micronutrients, temperature, aeration rate, pH, and agitation [83]. While most biosurfactant-producing microorganisms produce these compounds under restrictive conditions, e.g., after depletion of an important nutrient, the phase in which the highest yield is achieved (exponential or stationary growth phase) should also be investigated. Statistical methods can optimize the physicochemical parameters of the fermentation process. This allows for the study of how different variables interact and helps find the most cost-effective conditions for maximum biosurfactant production [90].

Therefore, to cheaply produce biosurfactants, production needs to be associated with downstream processing and explore alternatives to improve production using genetically modified microbial strains, innovative statistical approaches (e.g., surface methodology), and techniques based on Artificial Intelligence (AI) such as Artificial Neural Intelligence coupled with Genetic Algorithm (ANN-GA). Genetically modified microbial strains, cheap substrates, optimized media, enhanced fermentation process, and downstream processing and purification of final products using well-developed static models can be biological and engineering solutions from the commercial point of view to achieve economically sustainable large-scale industrial production of biosurfactants [91].

The generation of agro-industrial by-products is rapidly increasing. In 2019, the industrial activities linked to bioethanol production, animal slaughter, cassava, palm oil, and milk processing resulted in over four billion liters of wastewater [92]. Therefore, it is urgent to reduce the impacts caused by these and other effluents by utilizing them in processes capable of generating other products. The food industry should be explored by utilizing its waste, effluents, and by-products [71,92]. Microbial fermentation can be utilized to produce biosurfactants from various industrial wastes. Studies have shown that biosurfactants can be obtained from different substrates, including solvents, hydrophobic mixtures, hydrocarbons, dairy products, and vegetable oils. The literature describes various residual products used in biosurfactant production, including vegetable oils, oily effluents, animal fat, starchy effluents, vegetable cooking oil waste, vegetable fat, laundry detergent, corn steep liquor (corncob), dairy industry waste (whey), molasses, cassava, flour mill effluents, petroleum distillery waste, and glycerol [71].

The increasing production costs associated with microbial surfactants compared with synthetic surfactants can be overcome by using raw materials obtained from other industrial processes [93]. The implementation of biosurfactant production on an industrial scale can become economically viable with the use of agro-industrial by-products [71]. The use of low-cost raw materials obtained from other industrial processes, however, needs to be evaluated to provide the necessary amounts and types of nutrients to microorganisms, maintaining a balance of carbohydrates and lipids so that microbial metabolism occurs appropriately for the production of the target surfactant. These raw materials also need to provide substantial amounts of micronutrients, including iron, magnesium, phosphorus, manganese, and sulfur, which can further reduce the cost associated with the production process.

In selecting components for production, considerations such as nutritional content, waste availability, transportation and storage costs, pretreatment requirements, and waste purity should be considered. Each type of raw material has unique characteristics that affect how microorganisms interact with it. This is why some microorganisms may be able to produce effective biosurfactants from a certain raw material while others cannot [93].

The reuse of industrial waste to produce valuable compounds is essential for both economic benefits and waste management. On the other hand, the utilization of industrial waste cannot solely rely on the low cost of these raw materials, i.e., the availability, stability, and variability in each component should be also considered. Variability is an important limit to industrial use since the structures and properties of biomolecules must remain well-defined and constant, requirements that cannot always be guaranteed when using these substrates.

4.3.1. Application of Biosurfactants in the Agricultural Industry and Trends

Biosurfactants have diverse uses in agriculture, including improving soil quality and promoting plant growth. They can also enhance the biodegradation of pollutants to their antimicrobial properties [63,94,95]. Biosurfactants can replace the aggressive synthetic surfactants currently used in pesticide industries, as they can act as carbon sources for microbes inhabiting the soil, which also helps to remove them from the soil [14,15,21,23,46]. Figure 5 shows the possible applications of biosurfactants in the agricultural sector.

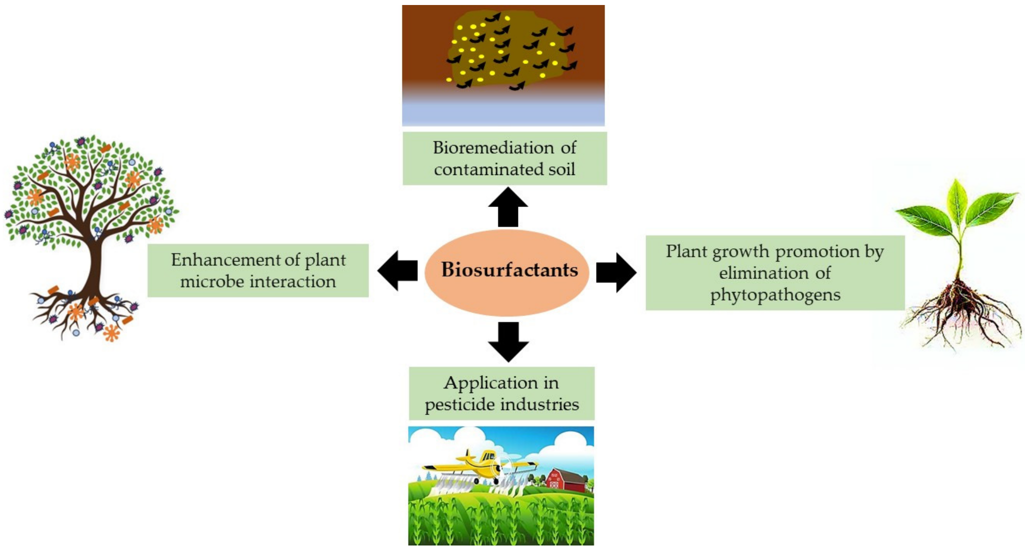

Figure 5. Possible applications of biosurfactants in the agricultural sector.

Biosurfactants have shown great potential in the agricultural area, and trends in the application of biosurfactants are constantly involved. Some of the most recent trends are shown in Table 1.

Table 1. Trends in the application of biosurfactants in agriculture and other promising applications in related fields.

Trends in Biosurfactant Application in Agriculture	Other Promising Applications of Biosurfactants in Agriculture
Development of more effective and affordable biopesticides and biofertilizers [96].	Utilization of biosurfactants in irrigation systems [97,98].
Biocontrol of plant pathogens [99].	Use of biosurfactants to enhance biofuel production [100].
Stimulation of plant growth [101].	Removal of biofilms in irrigation systems [102].
Stabilization of pesticide and fertilizer emulsions [103].	Application of biosurfactants for remediation of contaminated soils [104].
Enhancement of herbicide and foliar nutrient absorption [96].	

Soil Quality Enhancement with Soil Amendments

Organic and inorganic pollutants affect soil productivity and cause abiotic stress in cultivated plants. Bioremediation processes are recommended to improve the quality of soils contaminated with hydrocarbons and heavy metals. Microorganisms producing biosurfactants and/or biosurfactants themselves can be used to remove hydrocarbons and heavy metals [105]. Biosurfactants enhance the bioavailability and biodegradation of hydrophobic compounds, and soil washing and combined cleaning technologies using biosurfactants have been used for the effective removal of hydrocarbons and metals, respectively [46,60].

Soil washing has become an appealing technology with the use of surfactant agents, especially for hydrophobic contaminants that adhere to soil particles' surfaces and typically have low solubility in water. Surfactants can be added to solubilize soil contaminants. Anionic, cationic, zwitterionic, and nonionic surfactants have been applied for soil remediation [106].

To successfully implement enhanced remediation of surfactant-contaminated soils, several factors must be considered, including surfactant adsorption behavior in soil, their capacity to solubilize/elute target contaminants, and their toxicity and biodegradability. Economic factors such as surfactant cost and the extent of contaminated soil should also be considered. Ideally, in addition to strong contaminant desorption capacity, an ideal surfactant should be efficient and effective. It should have a low CMC and function at a low dose for washing solutions to reduce remediation costs and further ensure process economy [106].

Soil washing using surfactants can be carried out ex situ and in situ. Soil washing carried out outside its original location can effectively treat a wide range of contaminant concentrations and allow clean soil fractions to be returned to the site at a relatively low cost [107]. In the ex situ washing process, the contaminated excavated soil is pretreated, mixed with surfactants, and agitated. After washing, the clay particles are deposited, and the washing solutions can be separated and regenerated for use in the next round [105].

In the in situ remediation method, surfactant-containing washing solutions are injected into the contaminated area through injection wells. This process mobilizes soil contaminants by dissolving them through the formation of micelles with the help of washing solutions or chemical reactions. The contaminated fluid is then collected and can be either disposed of, recirculated, treated, or reinjected back into the area [105].

When surfactants are introduced into a water–soil system, the soil particles tend to adsorb a certain amount of surfactants. The amount of adsorbed surfactants increases with the increase in their concentration, which leads to a reduction in their ability to solubilize pollutants. Moreover, the hydrophobicity of the soil also increases as a result of surfactant absorption, leading to the reabsorption of solubilized organic contaminants on the soil surface [71,105]. Consequently, surfactants in low concentrations accumulate mostly at the solid–liquid or liquid–liquid interface in the form of individual molecules. As the concentration increases, surfactant molecules gradually replace the interfacial solvent, such as water, leading to a lower polarity of the aqueous phase and a decrease in surface tension. Accelerated dissolution of contaminants, such as liquid non-aqueous phase contaminants, can be achieved while increasing the surfactant concentration. When the concentration of surfactants is further increased, micelles are formed. The concentration of surfactants at which micelles start to form is referred to as the critical micelle concentration (CMC) [71]. Micelles with hydrophilic surfaces and lipophilic nuclei are effective in dispersing contaminants, such as liquid non-aqueous phase contaminants. These micelles improve the solubility of contaminants in the aqueous phase, which in turn promotes the desorption of contaminants from the soil. When contaminants are dissolved in the aqueous phase, they become more mobile, making it easier to remove them through biotic routes (such as plant uptake and microbial degradation) or abiotic pathways (such as soil washing and subsequent separation) (Figure 6) [106].

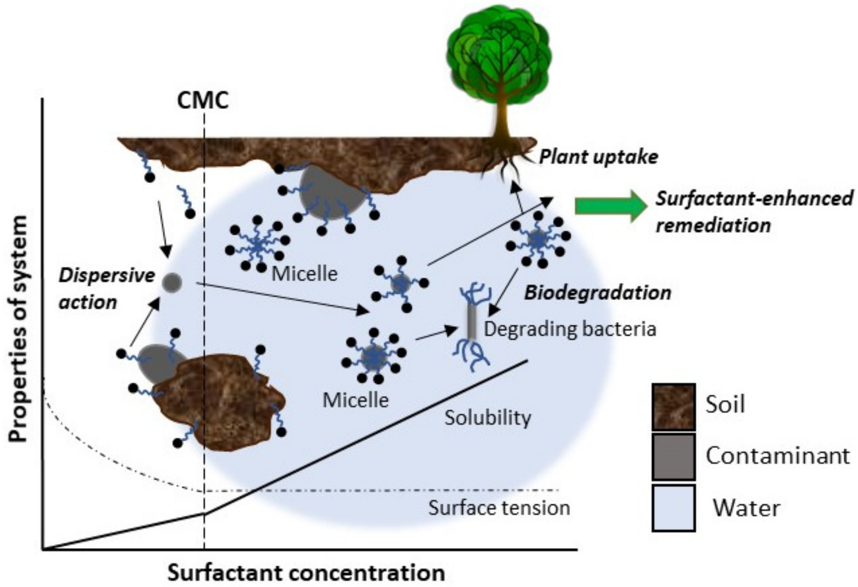

Figure 6. Schematic of surfactant-enhanced remediation of contaminated soils [105].

The process of washing soil with biosurfactants to remove hydrophobic organic pollutants can occur through two mechanisms. The first mechanism, called displacement, occurs below the CMC. The second mechanism, called solubilization, occurs above the CMC (Figure 7). Surfactant monomers below the CMC cause the soil to roll. They accumulate at the interfaces between the soil contaminant and soil water, changing the wettability of the system by increasing the contact angle between the soil and hydrophobic contaminants. When biosurfactant molecules are adsorbed on the contaminant surface, they cause repulsion between the main groups of surfactant molecules and soil particles. This further promotes the separation of contaminants from soil particles [107,108]. When the concentration is above the CMC, the biosurfactant can increase the solubilization of hydrophobic organic pollutants in the micelles and the partition of pollutants in the aqueous phase increases notably. Contaminants that are found in the micellar phase during the soil washing process can be further separated and treated using methods such as adsorption with activated carbon, electrochemical treatment, and demulsification. The washing solution or surfactant can be recycled or disposed of finally. It is desirable to recycle surfactants to reduce the cost of the remediation process.

Biosurfactants can improve the degradation of chemical insecticides in agricultural soils [47]. Reports suggest the role of biosurfactants in improving the health of agricultural soil through soil remediation processes. Examples include surfactin-supported pesticide biodegradation [109] and hydrocarbon degradation supported by glycolipids [110]. *Burkholderia* species isolated from oil-contaminated soil produce biosurfactants that could potentially remediate pesticide contamination [111]. Thus, biosurfactants have the potential to enhance soil quality, making them a valuable addition to agriculture. Soil pollution caused by metal salt-based fungicides, sewage, and sludge reduction techniques in agricultural fields can lead to the presence of heavy metals. While these metals are essential micronutrients for plant growth and physiological processes, high concentrations can cause harm to plants, damaging their roots and foliage. In contrast to organic contaminants in soil, heavy metals are mainly removed from the soil through complexation associated with surfactants and ion exchange [107]. The usefulness of surfactants in remediating heavy metal-contaminated soils is primarily based on their ability to form complexes with metals. Anionic surfactants, through ionic bonds, form complexes that are usually stronger than the metal's bonds with soil complexes, leading to the desorption of the metal–surfactant complex from the soil matrix into the solution due to reduced interfacial tension. Cationic surfactants, on the other hand, can compete with charged ions on negatively charged surfaces through ion exchange. Metallic ions can also be removed from the soil surface by surfactant micelles [105,112].

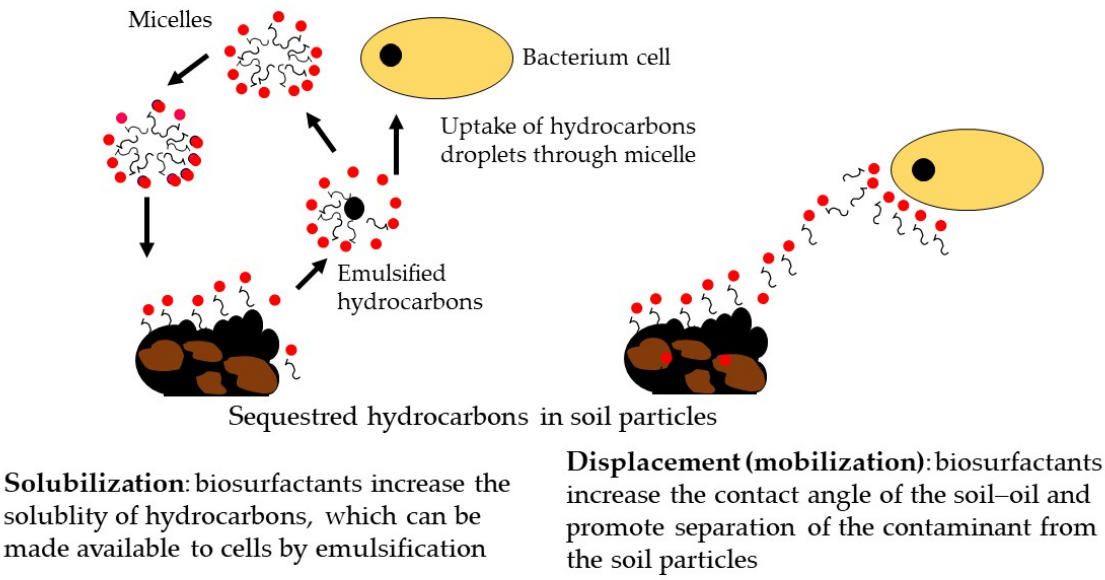

Figure 7. Solubilization (above the CMC) and displacement (below the CMC) mechanisms of biosurfactants during the washing of soils contaminated with hydrocarbons [108].

In more detail, ionic surfactants remove heavy metal by the following sequence: (1) biosurfactant complexation with the metal through sorption of the biosurfactant to the soil surface, (2) desorption of the metal from the soil into the solution, and (3) association of the heavy metal with surfactant micelles, i.e., heavy metals are trapped in the micelles through electrostatic interactions and can be recovered with membrane separation techniques [107] (Figure 8). Several studies have highlighted the abilities of biosurfactants produced by *Bacillus* sp., *Pseudomonas* sp., and *Acinetobacter* sp. in removing heavy metals from soil and accelerating pesticide biodegradation [112]. Rhamnolipids and surfactin can remove metals such as Mg, Ca, Cd, Ni, Mn, Ba, Cu, Li, and Zn from the soil [113]. Synthetic surfactants are also used to remove nonpolar organic compounds from the soil. However, these surfactants are required in high concentrations and can affect microbial biodegradation [114].

Micronutrients present in the soil are essential for plant physiological processes, contributing to hormonal metabolism, protein synthesis, improvement in plant defense mechanisms, and maintenance of biological membranes, among others [115–117]. Many chemical fertilizers have been administered to maintain nutrient supply for plant growth, but they often become unavailable due to complexation with soil particles. Nevertheless, these chemical fertilizers can damage the physical structure, chemical balance, and biological activities of soils, and their activities are influenced by soil ionic charge and pH [18,118].

Therefore, biosurfactants can enhance the availability of metals to plants grown in soil by reducing interfacial tension and increasing the solubility and mobility of ionic nutrients, leading to increased uptake by plants [19,105]. When anionic biosurfactants form stabilizing forces with complexes, they become stronger than metal complexes with soil particles. This results in the desorption of metals from the soil matrix, allowing mixing at the soil–water interface and making them more available to soil microflora and plant roots. In contrast, cationic biosurfactants follow the ion exchange mechanism and replace charged metal ions that are bound to soil particles due to their higher affinity for them. [71].

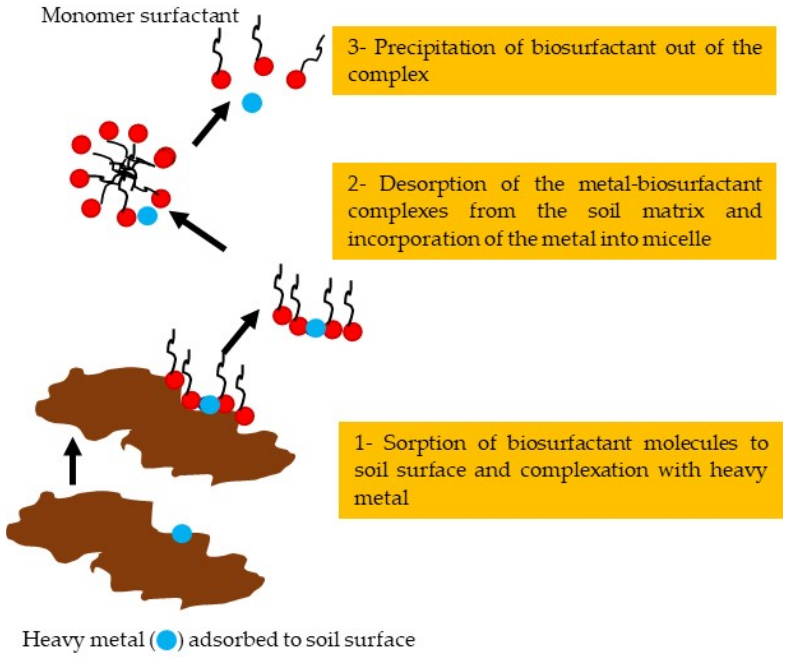

Figure 8. Mechanism of heavy metal removal by biosurfactants [107].

Glycolipids, particularly sophorolipids, rhamnolipids, trehalose lipids, and MELs, are the most studied surfactants in metal complex formation [71,107]. Surfactin, for example, enhances nutrient acquisition through emulsification and supports surface colonization through biofilm formation. These biosurfactants have been reported to increase the capacity of colonizing plant roots by *Bacillus amyloliquefaciens* in *Arabidopsis thaliana* [119] and wheat by *B. subtilis* strains [120].

Adjuvants for Plant Pathogen Elimination

Microbial surfactants often have antimicrobial properties, measured with the minimum inhibitory concentration (MIC), which is the lowest concentration needed to prevent pathogen growth [18]. Several biosurfactants show antimicrobial activity against plant pathogens, including Gram-positive and Gram-negative bacteria and yeasts, making them promising biomolecules for sustainable agriculture [71]. The nature of the biosurfactant defines its antimicrobial activity. In a comparative study among some biosurfactants, the biosurfactant from *P. aeruginosa* UCP 0992 was the most efficient in inhibiting *Staphylococcus aureus* and *Escherichia coli* (MIC: 20 μg/mL), while the biosurfactants from *P. aeruginosa* UCP 0992 and *Candida bombicola* URM 3718 showed similar effects on *Streptococcus mutans* (MIC: 20 μg/mL). The biosurfactants from *P. aeruginosa* UCP 0992, *Bacillus cereus* UCP 1615, and *C. bombicola* URM 3718 exhibited the same effect against *Candida albicans* (MIC: 40 μg/mL) [71]. In another study, the biosurfactant from *Candida sphaerica* UCP 0995 did not show antimicrobial activity against other *Candida* species or bacteria (*E. coli*, *P. aeruginosa*, and *B. subtilis)*. Still, it exhibited bacteriostatic activity against *S. aureus* and *Klebsiella pneumoniae* [121]. Luna et al. [122] investigated the antimicrobial activity of the same biosurfactant against different fungal and bacterial species and obtained positive results. Rufisan, a microbial surfactant obtained from *C. lipolytica* UCP 0988 in a refinery waste-supplemented medium, demonstrated excellent antimicrobial potential against various *Streptococcus* species at concentrations above its critical micelle concentration as well as anti-adhesive activity against most tested microorganisms [123].

The use of chemical surfactants and biosurfactants in agriculture helps control microbes that affect plant growth through various methods, including parasitism, antibiosis, competition, induced systemic resistance, and hypovirulence. This enhances the activities of beneficial microbes and their products [124]. The insecticidal activities of surfactants have been shown in multiple in vitro and in situ studies [46]. The combination of surfactants with the fungus *Myrothecium verrucaria* has been used to prevent the spread of and eradicate weed species that affect land productivity and negatively affect biodiversity [125]. They have also been used to inhibit the production of aflatoxins by *Aspergillus* sp. that infect cotton, peanut, and maize crops during storage [126]. Thus, both synthetic and biological surfactants play diverse roles in the elimination of phytopathogens, directly or indirectly, and in different processes related to agriculture.

Isolates of biosurfactant-producing *Pseudomonas* and *Bacillus* strains exhibited biocontrol capacity against phytopathogens [127]. It has been demonstrated that rhamnolipids can inhibit plant pathogens that have developed resistance to chemical pesticides [128], as well as insecticidal potential. For instance, Kim et al. [129] isolated a biosurfactant from a *Pseudomonas* strain that showed insecticidal activity against green peach aphids (*Myzus persicae*). *Pseudomonas putida*, a plant growth promoter, produces biosurfactants that cause lysis of cucumber pathogen zoospores [130]. The *Bacillus* strains produced a lipopeptide biosurfactant that inhibited the growth of phytopathogenic fungi from the *Fusarium* and *Aspergillus* genera [131]. The *Brevibacillus brevis* HOB1 strain produced a surfactin with strong antibacterial and antifungal properties that can be explored for phytopathogen control [132]. The antifungal properties of biosurfactants obtained from *Pseudomonas fluorescens* strains are well-described in the literature [133]. The pathogen *Colletotrichum gloeosporioides*, which attacks papaya leaves, was successfully controlled with the biosurfactant from *Bacillus subtilis* isolated from soil [134]. The above examples demonstrate that green biosurfactants are well-documented in the literature for promoting plant growth due to their effects on various pathogens. Microbial surfactants have the potential to replace chemical pesticides and insecticides in agriculture. In addition to these anti-phytopathogenic properties, biosurfactants can accelerate the composting process by providing favorable conditions for microbial growth, offering an additional advantage of using these green surfactants [135]. Biosurfactants have been shown to reduce the surface tension between liquids and solids and increase the bioremediation of organic matter, as stated by De Giani et al. [136]. Additionally, the presence of biosurfactants boosts bacterial growth, which in turn enhances organic matter decomposition. Rhamnolipids have been found to increase microbial growth in composting. The combined action of *Bacillus* sp. and *Streptomyces* sp. during composting leads to a more efficient breakdown of organic materials. The use of a consortium of bacteria that generate biosurfactants, along with a cell suspension containing biosurfactants, has been proven to increase bacterial communities in composting, indicating that biosurfactants do not hinder the development of bacteria in composting and may even have a minor stimulatory effect on their growth, as noted by Shi et al. [137].

Biosurfactants with antagonistic properties against phytopathogens can also affect other flora in the system. Therefore, to obtain an attractive green surfactant with specificity against phytopathogens, the chemical structure of the biosurfactant can be varied by altering production strategies [46].

The ability of the *Lactobacillus rhamnosus* cell-bound-derived glycolipid surfactant to inhibit bacterial adhesion and antibiofilm activities was recently observed [138]. Studies have shown that iturin, a cyclic lipopeptide produced by *B. subtilis* and related bacteria, has the ability to activate a plant's natural defense mechanisms. These substances can promote the production of defense-related compounds, enhance plant immunity against infections, and improve overall plant health. Additionally, they offer an environmentally friendly alternative to chemical fungicides [139]. The lipopeptides produced by the marine bacterium *B. subtilis* subsp. *spizizenii* MC6B-22 showed broad-spectrum activity against ten phytopathogens of tropical crops at a minimum inhibitory concentration of 400 to 25 μg/mL and with a fungicidal mode of action, demonstrating the potential of the MC6B-22 strain as a biocontrol agent for agriculture [140]. The efficacy of *Bacillus* species associated with plant roots as antifungal biocontrol agents was evaluated. The production of lipopeptide biosurfactants was analyzed to determine their ability to control fungal infections. The results showed that the lipopeptide biosurfactant produced by *B. velezensis* PW192 is stable and possesses strong antifungal properties. Therefore, it can be used as a biocontrol agent in agriculture [141]. An extract of the biosurfactant derived from corn steep water, which is a residual stream of the corn wet milling industry, is fermented by probiotic lactic acid bacteria (*L. casei*). This extract was tested for its effectiveness as a bactericide. The results showed that at concentrations of 1 mg/mL, the biosurfactant extract was effective against *P. aeruginosa* and *Escherichia coli*. This opens up the possibility of using the biosurfactant extract in agrifood formulations to reduce the need for chemical pesticides and preservatives [142].

Adjuvants for Seed Germination and Plant Growth

Plants sensitive to hazardous substances can be used as bioindicators to measure seed germination, root growth, and seedling growth. Seed germination testing is widely used to assess the phytotoxicity of any substance. In general, in agricultural practices, biosurfactants have been shown to effectively promote seed germination [71]. Although most biosurfactants have stimulated plant growth, some studies also highlighted inhibitory actions [143].

The biosurfactant derived from *C. sphaerica* UCP0995 did not exhibit toxicity toward the seeds of *Solanum gilo*, *Brassica oleracea*, *Lactuca sativa* L., or *B. oleracea* L. Except for *B. Oleracea* L., the other species also exhibited increased root elongation and seed germination in the presence of increasing biosurfactant concentrations [144]. On the other hand, the isolated biosurfactant inhibited the germination of *Cichorium intybus* seeds with increasing concentration, while root growth was not affected. According to a study, *Solanum gilo* seeds had 100% germination when treated with biosurfactant extracts at 200 mg/L, whereas no germination occurred at the 400 or 600 mg/L concentrations. This indicates an inhibitory effect at higher concentrations [119]. Silva et al. [145], who conducted phytotoxicity experiments on *B. oleracea* at 175, 350, 520, and 700 mg/L of a biosurfactant from *P. aeruginosa* UCP 0992 cultivated on glycerol as a substrate, observed no inhibitory effect on seed germination, indicating safety regarding this plant species. A study on the influence of rhamnolipids (0.25–1.00 g/L) on the germination of sunflower, lettuce, soybean, and corn seeds demonstrated an increase of up to 75.50% in the germination rate of lettuce seeds and a stimulation of corn and sunflower seed germination at a concentration of 0.25 g/L but no influence on that of soybean [146]. Finally, the germination index was used by Santos et al. [147] to evaluate the phytotoxicity of the lipopeptide biosurfactant produced by *Streptomyces* sp. DPUA1566 on *L. sativa* L. and *B. oleracea*. Under all tested conditions, seed germination was stimulated, and the growth of leaves and elongation of secondary roots were observed.

The influence of MELs on the seed germination of lettuce seeds (*Lactuca sativa* L.) was recently investigated for the first time. The biosurfactant at 158 mg/L showed promising results in the biostimulation of cultivated seeds. However, the responses observed in the physiological and biochemical behavior indicated that MELs at 316 and 632 mg/L influenced oxidative stress and inhibited the germination and development of the seeds [148].

Soybean plant growth promotion mechanisms were observed in bacteria cells, as well as the role of bacterial metabolites, especially lipopeptides, in the biological control of diseases and the modulation of the plant's immune response. The treatments containing only bacterial cells were not efficient in reducing Asian rust severity, with losses of leaf area reaching 15%, while the addition of biosurfactants led to a result that was similar to the biofungicide, based on *B. subtilis* (Serenade®) [149].

Bioformulations were developed using *Pseudomonas putida* BSP9 and its biosurfactant to evaluate their impact on promoting the growth of *Brassica juncea* plants. The study found that bioformulations amended with biosurfactant, either alone or in conjunction with BSP9, resulted in a significant increase in the growth parameters of *B. juncea* compared with the untreated control. The greatest enhancement was observed in plants inoculated with the bioformulation containing both BSP9 and biosurfactant. Furthermore, the study suggested that growth promotion peaked at a certain level of biosurfactant concentration, beyond which increasing the concentration did not result in any further enhancement in the plant's growth parameters. These findings demonstrate that novel bioformulations that integrate plant growth-promoting rhizobacteria and their biosurfactants can be developed, and effectively utilized to increase agricultural productivity while reducing our dependence on agrochemicals [150].

Adjuvants for Beneficial Microbe Interactions

For rhizobacteria to provide beneficial effects to plants, their interaction with plant surfaces is crucial. Microbial factors such as biofilm formation on the root surface, motility, and release of quorum-sensing signal molecules are necessary to establish an association with a plant. Rhizobacteria rely on quorum-sensing molecules such as N-acyl-homoserine lactone (AHL) to produce antifungal compounds. Research indicates that these molecules are more abundant in the rhizosphere, the area surrounding plant roots, emphasizing their importance in the establishment of beneficial microorganisms on the root surface. Dusane et al. [151] found that *Pseudomonas* spp. rhamnolipids regulate quorum sensing. Biosurfactants are also known to influence the motility of microorganisms as well as biofilm formation [152]; therefore, they play an important role for microbes to establish a beneficial association with plant roots and enhance plant growth. Moreover, these biosurfactants produced by soil microorganisms enhance the bioavailability of hydrophobic molecules that serve as nutrients, ensure soil wetting, and support the appropriate dispersal of chemical fertilizers in the soil, thereby aiding in promoting plant growth [46].

In a recent study, Chopra et al. [153] discovered a strain of plant growth-promoting rhizobacteria identified as *P. aeruginosa* RTE4 in the tea rhizosphere. They found that its biosurfactant has biocontrol properties against tea pathogens *Corticium invisium*, *Xanthomonas campestris*, and *Fusarium solani*. The researchers also found that the biofungicide properties of the rhamnolipid biosurfactant are similar to the commercial fungicide carbendazim. In another study, Khare and Arora [154] designed a bioformulation that improved the yield of sunflowers by 80.80% under laboratory and field conditions. The bioformulation contains biosurfactants that enhance the biocontrol activity of the LE3 culture by 75% against *M. phaseolina*. The authors found that a formulation containing LE3 cells and biosurfactants enhances the yield and biocontrol activity of sunflowers by 75.45%.

The presence of biosurfactants in the formulation helps plant–bacterial interactions, improves soil properties, and controls plant diseases. Overall, biosurfactant-based formulations are very beneficial for the health and growth of plants, seedlings, and crops.

4.3.2. Producing Biosurfactant-Based Biopesticides for the Agricultural Industry

The process of obtaining biopesticides using biosurfactants involves several steps, which may vary according to the source of biosurfactants and the type of biopesticide to be produced [155]. Some of the most common steps are: (i) selection of the best biosurfactant source, with microorganisms that are able to sporulate being usually the most suitable; (ii) biosurfactant isolation from the selected source and its purification for further use, which involves growing the source under conditions suitable for biosurfactant production and separating it from cells and other cellular components; (iii) biopesticide formulation, which may involve the mixing of the isolated biosurfactant with other components such as preservatives and adjuvants to enhance the effectiveness of the product; (iv) efficacy tests using the formulated biopesticide against pests or diseases to be controlled, which are usually performed both at the lab scale and in the field to assess its effectiveness under actual growing conditions; (v) large-scale production, in case the efficacy tests were successful, of both the biosurfactant and biopesticide formulation; and (vi) biopesticide registration and regulation by the competent authorities, which implies providing product safety and efficacy data, as well as compliance with environmental and food safety regulations [3,58,96,103,156].

There are only a few patents that pertain to the direct use of biosurfactants for producing agro-products, as shown in Table 2. This is largely because of the difficulty in creating a viable bioformulation and the need for ample financial resources, qualified personnel, and extensive testing before launching the product on the market [157]. Additionally, the high production cost of formulations containing biosurfactants must be taken into consideration.

Table 2. Patents that mention biosurfactants and/or biosurfactant-producing microorganisms as ingredients for the formulation of agrochemicals used in various applications.

Product	Specifications	Country	Patent ID/Year
Biopesticide	Biopesticide compositions and/or biopesticide formulations obtained from *Eucalyptus* species. The addition of rhamnolipid biosurfactant was cited in the composition of one of the formulations.	Australia	WO2011/013133A3/2011
Biocontrol agent	Application of microorganisms as biological control agents, more specifically, the *Serratia plymuthica* strain A30, BCCM Deposit N°. LMG P-26170, which is capable of degrading acyl-homoserine lactones and producing biosurfactants.	The Netherlands	EP2663659B1/2013
Biopesticides	The invention relates to methods for pest (nematodes) control with a microbial rhamnolipid biosurfactant, implying providing the microbial biosurfactant to pests in such an amount that pests are controlled.	United States	EP1750738B1/2007
Insecticide	Obtaining an insecticide that contains biosurfactant in its formulation. Preferably, the biosurfactant is a glycolipid, a glycoside, or their derivatives.	France	EP3122186B1/2017
Additive	A method of producing surfactin, a lipopeptide produced by *Bacillus subtilis*, and its application in aquafeeds to reduce the occurrence of mold contamination.	Taiwan	EP3039968B1/2016
Additive	A rhamnolipid is implemented to replace a chemical surfactant to be used as the additive of the pesticide, the fertilizer, and the feed additive to ensure significant effects.	China	CN103070167B/2010
Biofertilizers, biostimulants, bio dispersants, and other applications	Formulations comprising microbes and/or their growth by-products to be used to improve fertility, salinity, water retention, and other soil characteristics, as well as to control pests and stimulate plant growth. In some of them, growth by-products are biosurfactants.	United States	WO2021030385A1/2020
Bioremediators of soil	The invention reveals a type of method in which the surfactant repairs the soil contaminated with organochlorine pesticides, removing more than 85% of the pesticides and making the soil reach the environmental safety standard. The operation is simple, economical, and efficient and can be applied on a large scale in the repair of soils contaminated with organic pollutants.	China	CN104923558B/2015

Table 2. *Cont.*

Product	Specifications	Country	Patent ID/Year
Enhancers of fertility and health of soil, pesticides, plant immune modulators, and/or plant growth stimulants	Microbe-based formulations for restoring soil health and controlling pests. They can comprise one or more biosurfactants (glycolipids and/or lipopeptides).	United States	WO2021030385A1/2021
Fruit preservative	The invention belongs to the technical field of food preservation and relates to a sophorolipid fruit preservative and a method for prolonging the preservation life of fruits. Using microbiological fermentation technology, a sophorolipid was obtained, which was used in the preparation of a solution (3 mg/mL) sprayed evenly on the fruits to prevent fruit corrosion, maintain freshness, and extend the shelf life of fruits at room temperature.	China	CN101886047B/2010
Biofertilizers, biostimulants	Use of sophorolipids to increase the yield of crops.	Germany	DE102014209346A1/2014
Biopesticide	Sophorolipid agricultural antibiotic and its application to control fungal diseases of crops.	China	CN104178537A/2014

4.3.3. Nanotechnology for Delivering Pesticides

Nanotechnology is being explored as an innovative approach for delivering pesticides in a safer and more efficient way. This approach aims to reduce the indiscriminate use of pesticides and protect crops from pests while minimizing direct exposure to humans and animals. The use of the nanoencapsulation process and the nano-encapsulated pesticide formulation can improve the properties of pesticides, such as permeability, solubility, stability, and specificity. By protecting the active components of pesticides from degradation and enhancing their long-term efficacy against pests, nanoencapsulation can also reduce the actual dose of pesticides needed [103]. However, further research is needed to understand the synthesis of nano-encapsulated pesticide formulations and their behavior in plant systems and the environment. This will facilitate the establishment of guidelines and a regulatory framework for their commercialization. Agro-research has been focused on designing and developing organic NP-based formulations, and nanotechnology has substantially contributed to sustainable agriculture developments [158].

4.3.4. Metagenomics of Biosurfactants Applied in the Agricultural Industry

Metagenomics analysis is a powerful tool for uncovering information about the microbial community, including their sequence and function in different ecological niches. This approach has been used successfully in several studies [159,160]. For example, it has helped to identify novel microorganisms or gene clusters that express biosurfactants. Metagenomics is a scientific method that allows researchers to study the microorganisms in a particular environment, including those that cannot be cultured. It involves analyzing the taxonomic and functional composition of microbial populations using targeted or shotgun sequencing of 16S rRNA regions [161]. In the case of pesticide-contaminated materials like soil and water, metagenomics has been particularly useful in creating DNA libraries that can be tested for biosurfactant-producing clones. Additionally, the function-based approach has the potential to discover genes capable of forming entirely new bioactive compounds that have never been identified before [162].

Metagenomics plays a vital role in exploring distinctive biosurfactant-producing genes from bacteria in various surroundings and adopting different approaches for improved biosurfactant production. With the abundance and variety of biosurfactant-producing microbes present in cultured isolates, it is believed that utilizing metagenomics to investigate the even larger uncultured microbial community will lead to significant and novel discoveries of biosurfactants [161,163].

Metagenomics delivers an adequate metagenomic database that will give a substantial stock of genes to develop novel microbial strains for targeted application in biosurfactant production [161,164,165]. Metagenomics coupled with bioinformatics removes all the obstacles faced in the process of genomic studies such as phylogenetic analysis, taxonomic profiling, molecular phylogeny, the functional characterization of metagenomes, and enzyme and system biology studies, including genetic engineering using CRISPR (clustered regularly interspaced short palindromic repeats) [163].

According to Raj et al. [165], to date, only a few research studies using genetic modification methods for biosurfactant production have been published, and one such research method is the genetic modification of a wild *Bacillus* strain for surfactin production [166]. However, genetic engineering methods only resulted in a few or single-gene alterations, and commercial manufacturing of biosurfactants has yet to be achieved. As a result, experimentation-based optimizations to synthesize biosurfactants are still ongoing, new regulatory aspects need to be investigated, and methods should be used to transfer biosurfactant-producing genes to indigenous microbes residing in contaminated sites.

5. Concluding Remarks and Future Perspectives

Surfactants are necessary as adjuvants for fungicides, insecticides, and herbicides, as discussed earlier. The synthetic surfactants currently used in agricultural pesticides act as emulsifiers, dispersants, and wetting agents, enhancing their efficiency. Additionally, they are also used in the formulation of insecticides in modern agriculture as they possess defensive properties. Various types of surfactants, including anionic, cationic, amphoteric, and nonionic, are currently being used in various pesticide manufacturing industries. However, it is important to note that the surfactants present in pesticide formulations accumulate in the soil and affect the texture, color, and growth of plants. These harmful pesticides are also leached from the soil into groundwater. Pesticide residues can persist in soil for years and spread through air and water. Additionally, they can remain on the surface of vegetables and fruits.

Given the harmful effects of pesticides and their associated surfactants, it is crucial to utilize environmentally safe surfactants as alternatives in pesticide industries, thereby mitigating environmental pollution. The use of soil bacteria that can utilize chemical surfactants in agricultural soil as a carbon source could be another alternative to solve such an environmental problem [167]. Moreover, effective formulation technologies are needed in agrochemical industries to widely use green surfactant-based products in agriculture. Many corporations are now prioritizing microbial surfactants due to their sustainability initiatives and green agendas. Despite the advantages of biosurfactants, the use of these biocompatible adjuvants in the agricultural and agrochemical industries is still limited. The exact function of surfactants as facilitators of biocontrol is not yet well understood and requires further investigation. It is crucial to evaluate the environmental impact of biosurfactants to determine their overall sustainability [168]. The production, distribution, and end-use of biosurfactants should be carefully planned before establishing their viability as sustainable products. However, the literature on these issues is currently limited, and the use of biosurfactants as sustainable products within societal, commercial, and environmental frameworks requires focused attention [103].

Several researchers have studied the creation and utilization of biosurfactants in a way that is environmentally sustainable. According to Karamchandani et al. [103], life cycle assessment (LCA) and life cycle sustainability analysis (LCSA) have been used as tools to quantify the impact of human activities from social, economic, and environmental perspectives. These models are well-connected and accepted by the United Nations (UN) as a foundation for proposing sustainable development goals (SDGs) [169]. The SDGs support the transition from non-renewable resources to renewable resources, in order to improve all contributions including the value of products.

LCA protocols evaluate the processing of a product, from its initial stages (raw materials, production, distribution, etc.) to its final stages (application, recycling, and ultimate environmental fate), including its end-of-life and disposal [170]. Few other modes of assessment similar to LCA take into account certain inputs such as capital cost, infrastructure, energy, or gains throughout the process. Using this information, the net impact of the process is quantified. The LCA framework includes a well-defined goal and scope, as well as an analysis of the inventories' impact and interpretation [168].

Biosurfactants have been used at different stages in agricultural activities, and LCA and LCSA would be beneficial in assessing their impact at each stage to establish their sustainability. A study by Rebello et al. [171] revealed that the LCA of biosurfactants presented a lower environmental impact than other synthetic detergents. Therefore, synthetic surfactants should be avoided, and further investigation on the production of biosurfactant-based formulations should be encouraged as a first step toward environmental sustainability.

Such studies will help replace synthetic surfactants and aggressive chemicals with green surfactants. Investments to reduce the production costs of biosurfactants and enable market application of these biomolecules are essential not only in agriculture but also in other industrial sectors. The use of agricultural waste for the overproduction of biosurfactants also requires further in-depth studies. The chemical composition of biocontrol potential biosurfactants can also be altered with changes in the production process (medium, cultivation conditions, etc.). This approach can lead to the biosynthesis of highly specific surfactants for a particular application. The presence of biosurfactants and/or their producing bacteria in the rhizosphere indicates the potential of these biomolecules in sustainable agriculture. However, few genera of microorganisms have been explored in the literature as producers of biosurfactants for agricultural applications. Extending our understanding of biosurfactant-producing strains requires consideration of morphology, genetics, and biochemistry. Screening for virulent strains and improving process technology can help reduce production costs. It is crucial to conduct more genetic and bioengineering studies to identify genes that play a role in biosurfactant production. In addition, the implementation of advanced CRISPR (clustered regularly interspaced short palindromic repeats) technology can enhance the production of biosurfactants. By identifying biosurfactant genes and incorporating them into microbial species commonly found in contaminated sites using the CRISPR tool, we can improve the process of pesticide remediation.

Biosurfactants have various applications including treating polluted soils and water, heavy metals, enhancing oil restoration, treating skin conditions, preserving food, and eliminating plant diseases. Recent research indicates that utilizing biosurfactants in the aerobic composting process of municipal waste, yard waste, and crop residues can lead to improved composting efficiency and product quality. Combining BSs with nanotechnology is a promising approach for crop improvement. Therefore, research on green surfactants should be seen not only as an alternative but mainly as a priority in preventing the negative effects caused by synthetic surfactants used in many commercial sectors, including the agrochemical industries. Joint knowledge in several areas, such as microbiology, molecular biology, biochemistry, environmental science, and engineering, is essential for technological advances in including these green molecules in the global market.

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