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Agro-Waste: A Potential Bio-Surfactant Source

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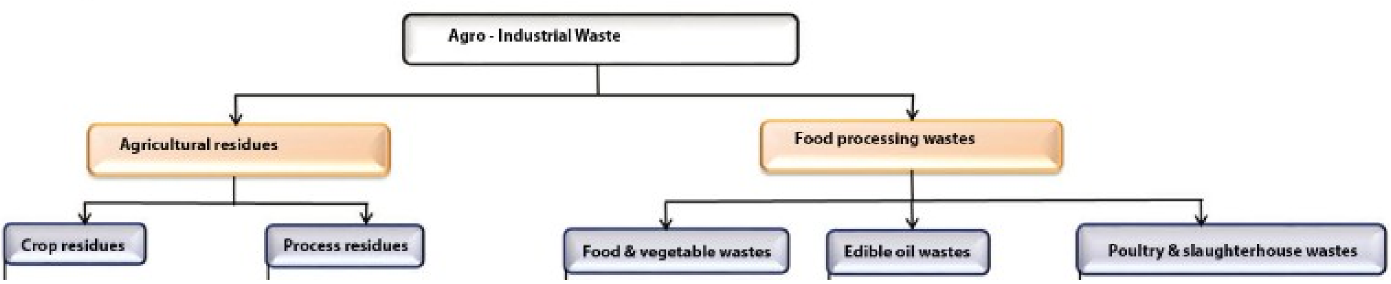
Abstract

The agroindustry, a significant contributor to global economic growth, generates substantial quantities of organic waste due to crop residues, biomass, and processing by-products. This chapter focuses on the potential of agroindustry-generated wastes as valuable sources for the production of bio-based and biosurfactants addressing environmental and economic concerns. Bio-based surfactants, derived from renewable resources, offer an eco-friendly alternative to traditional surfactants, presenting a sustainable solution with diverse applications spanning across agriculture, cosmetics, and industrial processes. The chapter delves into the types and composition of agroindustry wastes, extraction methods, and production processes for biosurfactants. The diverse chemical composition of agro-wastes provides a wide array of precursors for biosurfactant synthesis. Lipids, polysaccharides, and proteins found in these wastes can be selectively extracted and transformed into biosurfactants through various biochemical and chemical processes. Extraction techniques may include enzymatic hydrolysis, microbial fermentation, and chemical treatments, allowing for the efficient isolation of surfactant-active compounds from the complex matrices of agro-wastes. Additionally, the diverse applications of these biosurfactants in different sectors were assessed. By converting these residues into value-added products, the agroindustry not only minimizes environmental impacts associated with waste disposal but also contributes to the development of a more sustainable and eco-friendly industrial landscape. Different agro-wastes contribute distinct characteristics to the biosurfactants they yield. This diversity allows for the customization of biosurfactants meeting specific industrial needs. This chapter contributes to sustainable practices by transforming agroindustry wastes into high-value, green sustainable solutions for various industries and proposing future avenues for research to enhance the efficiency and applicability of bio-based surfactants. Thus, the utilization of agro-wastes for biosurfactant production aligns with the principles of circular economy and sustainable agriculture.

***Keywords*:** Agroindustry, bio-based surfactants, sustainable chemistry, agro-waste utilization, waste valorization, industrial sustainability

9.1 Introduction

Agricultural activities are vital for sustaining global food production and inevitably generate significant quantities of by-products and residues, collectively known as agro-wastes. This waste arises from agricultural sector residues and food processing wastes. These materials encompass a diverse range of organic matter originating from crop cultivation, processing, and post-harvest activities. Due to rapid growth of population and urbanization, a significant quantity of waste from agroindustrial waste is being generated every day. The importance of agro-waste lies not only in its sheer volume but also in its potential as a valuable resource. That, if effectively utilized, can contribute to sustainable practices and address environmental challenges. Figure 9.1 details the classification of agro-based industrial waste [120]. The agricultural sector annually produces substantial amounts of agro-wastes, including crop residues such as leaves, stems, seed pods, and straw, as well as process wastes such as husks, bagasse, seeds, and roots. Harnessing the potential of these materials can significantly impact the resource landscape. The food sector produces a sizable amount of waste from food processing, such as peels, seeds, and trimmings [63] besides the crop wastes generated during agricultural harvests [94]. Food processing waste includes fruit and vegetable waste, edible oil waste, kitchen waste, poultry farms, slaughterhouses, dairy and egg related processing waste. Also, wastes from fruit and vegetable peels, tops, skin, and shells are generated. Edible oil wastes include cooking oil or vegetable oil wastes, and oil cakes.



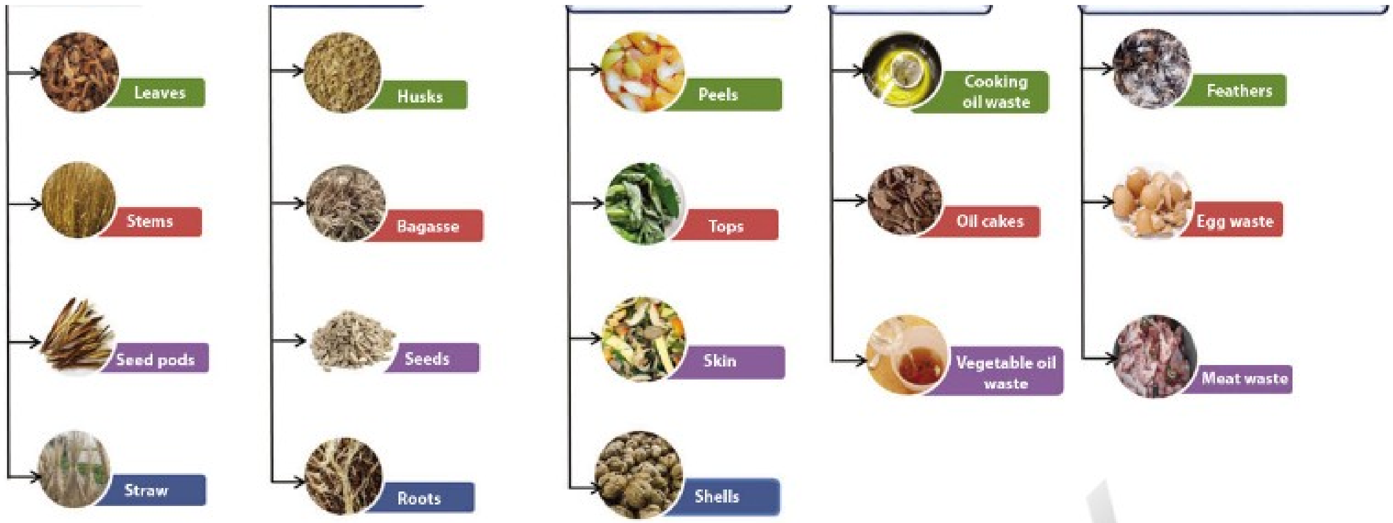


Figure 9.1 Classification of agroindustrial wastes [120].

The agricultural, food processing, and related industries generate agro-based industrial wastes that can be harmful to human health and the environment and are a global concern [4]. Inefficient management and disposal of agro-wastes can lead to environmental issues, such as air and water pollution, greenhouse gas (GHG) emissions, and soil degradation. Recognizing the environmental impact highlights the importance of adopting sustainable practices in their utilization. Waste cooking oil is not appropriate for consumption by humans because of its higher levels of harmful compounds such as short-chain fatty acids, ketones, aldehydes, mono/di-glycerides, and other aromatic compounds [119]. Microbial lipid production can be achieved by co-fermenting food waste with industrial waste oils [52]. Kitchen waste residues are having a good amount of carbohydrates, lipids, proteins, organic acids, lignin, inorganic salts, and a few other bioactive constituents and hence can be potential substrates for the production of enzymes by microorganisms [117]. Slaughterhouses generate waste that includes organic materials such as feathers, hair, hooves, horns, skin, and residues of deboning. These wastes are high in protein and animal fat [8, 123]. These lipids-rich wastes can be potentially used as surfactants in mineral processing industries wherein fatty acids are being used. Lipids, polysaccharides, and proteins found in these agro-wastes can be selectively extracted and transformed into biosurfactants through various biochemical and chemical processes. Extraction techniques may include enzymatic hydrolysis, microbial fermentation, and chemical treatments, allowing for the efficient isolation of surfactant-active compounds from the complex matrices of agro-wastes.

9.2 Effective Utilization of Agroindustrial Wastes

Mismanagement and improper disposal of agroindustrial wastes can have negative effects on the environment and can cause damage to the ecosystem. However, with the right approach, this waste can be transformed into a valuable resource that benefits both the environment and society. It is crucial to devise innovative ways to manage this waste and minimize its negative impact on ecosystems and human health.

The agroindustrial wastes can be effectively used as fertilizers, soil improvers, animal fodder, and in several other processes [8, 138]. The agricultural and food processing industries' waste could be utilized as probable substrates for biofuel production, enzyme production, organic acid production, biosurfactant production, etc. Various research studies have shown that agroindustrial waste such as rice straw, corn stalks, sweet potato trash, sawdust, sugar beet waste, potato debris, and sugarcane bagasse can be exploited as effective feedstock in biofuel production [43, 74, 75]. Biofuels have high potential as biosurfactants in mineral processing.

The potential of *B. licheniformis* KC710973 to produce biosurfactants using different substrates, such as orange peel, banana peel, potato peel, and two commercial extracts, including citrus peel was studied. Their results showed that the most effective substrate for biosurfactant production was orange peel (4%), which yielded 1.8 g/L and exhibited a 75% emulsification index (EI) against diesel [75].

9.3 Bio-Based Surfactant

Surfactants, also known as surface-active agents, find extensive applications in various industries such as detergents, paints, paper products, pharmaceuticals, cosmetics, petroleum, food, and water treatment [44, 56, 58, 79, 85, 133]. At present, plants, animal fats, microorganisms, and petrochemicals are being used to produce surfactants for commercial use. However, research shows petrochemicals are the primary source for most production markets [36, commercial use. However, research shows petrochemicals are the primary source for most production markets [36, 46, 62, 109].

Bio-based surfactants helps to lower the surface tension between two different substances. These compounds are derived from renewable biological sources such as plants, microorganisms, or agricultural by-products. Unlike traditional surfactants that often rely on petrochemical feedstocks, bio-based surfactants offer a more sustainable and environmentally friendly alternative. Derived from renewable resources, bio-based surfactants reduce dependence on limited petrochemical sources, contributing to sustainable practices.

Surfactants that are commonly used consist of two parts—oleochemicals as the tail group and petrochemicals as the head group. Oleochemicals can be produced from renewable sources like coconut, palm, and palm kernel oil, while petrochemicals are derived from fossil fuel reserves and used in larger quantities [48, 103]. Mostly biosurfactants are produced from several substrates biologically. The residues from fruit processing, coffee, tropical crops and oil mills can be used to produce biosurfactants [76, 81, 83, 88, 127].

Bio-based surfactants are agents that occur naturally and have hydrophobic heads and hydrophilic tails. These properties make them particularly effective at accumulating at the interface between two phases, such as between water and oil. By doing so, they reduce surface tension and facilitate the stabilization of the interface, which is essential for many industrial and biological processes. Biosurfactants are highly versatile compounds and have gained significant attention due to their ability to decrease surface as well as interfacial tension even at lower critical micellar concentrations (CMC). This unique property makes them suitable for a vast array of uses [70]. Bio-based surfactants have a head group derived from a variety of compounds, such as peptides, amino acids, and carbohydrates [41]. Carbohydrates are frequently utilized in commercial applications due to their cost-effectiveness and widespread availability, which allows for flexible properties [19, 48]. Although these surfactants are biodegradable, they can persist in the environment, causing water and air pollution over extended periods. The use of surfactants that have been conventionally manufactured and used in various industries over the years has been found to have significant negative effects on both the environment and human health. These concerns stem from the fact that such surfactants are often made from non-renewable resources and can persist in the environment for prolonged periods, leading to pollution and degradation of natural resources. Additionally, exposure to these surfactants has been linked to various health issues, including respiratory problems, skin irritation, and even adverse health complications in some cases. Therefore, there is a growing need to explore and adopt alternative, sustainable surfactants that are safe for both living beings and the environment. These alternatives offer significant advantages, including enhanced safety, abundance, biodegradability, and performance.

9.3.1 Agro-Waste-Based Biosurfactant

Various agro-wastes serve as promising sources for the generation of biosurfactants, offering sustainable alternatives to traditional surfactants derived from petrochemicals. Researchers have taken a keen interest in utilizing agroindustrial waste as a substrate for the production of biosurfactants due to its low cost and abundance [86]. This innovative approach has the potential to substantially reduce the production expenses of biosurfactants and make them a more sustainable alternative to conventional surfactants. By using agroindustrial waste as a substrate, this method also addresses the issue of waste disposal and provides a practical solution for its management. The bioconversion of waste materials derived from renewable substrates presents a sustainable source of organic biomaterials. This process is important because it is economical, environmentally friendly, and easy to operate. This method is practical and affordable, since it requires less capital and energy costs. Biosurfactants also have the added benefit of reducing pollution levels, making this an eco-friendly approach to production [87]. The bio-based surfactants are promising, economical alternatives to synthetic options.

Many of the waste products are used in biosurfactant production, namely oily effluents, vegetable oils [16, 93, 114], vegetable fat [59], animal fat [38, 89], waste cooking oil [5, 30, 60, 89], starchy effluents [49, 132], soap stock [18, 89, 116], molasses [54, 69, 76, 88], dairy industry waste (whey) [127], oil distillery waste [81–83, 110] cassava flour wastewater [100], corn steep liquor [125], and glycerine [122]. By utilizing agroindustry wastes as a source of bio-based surfactants, there is a tangible reduction in the environmental impact associated with traditional surfactants derived from petrochemicals. This sustainable approach not only aligns with the principles of green chemistry but also addresses growing concerns related to waste management and resource utilization in the agroindustry.

The availability of sources for bio-based surfactants from agroindustry wastes highlights the rich potential of renewable resources for sustainable and eco-friendly alternatives. Agro-wastes are abundant and diverse, offering various organic materials that can be harnessed for the production of bio-based surfactants.

Agroindustry generates vast quantities of waste, including crop residues, biomass, and processing by-products. These wastes are often underutilized or treated as environmental burdens, presenting an opportunity for their effective valorization.

valorization.

Crop residues from fruits, vegetables, cereals, and oilseeds provide a diverse range of materials for surfactant production. Processing by-products, such as peels, pomace, and leftover biomass, contributes to the availability of feedstock.

9.3.1.1 Oilseed and Vegetable Oil Residues

Seeds from oil crops, including soybeans, sunflowers, and rapeseed, offer oil-rich residues suitable for biosurfactant production. Waste oils and used cooking oils, often discarded, can be repurposed as lipid-rich sources for surfactant synthesis.

9.3.1.2 Forestry and Biomass Residues

Lignocellulosic materials from forestry and agricultural processes, including wood residues and plant biomass, can be sources for lignin-derived biosurfactants. Agricultural residues, such as stalks and husks, are rich in cellulose and other organic compounds.

9.3.1.3 Fruit and Vegetable Processing Waste

By-products from fruit and vegetable processing industries, such as peels and pomace, are potential sources for pectin-derived surfactants. The diversity of waste streams from these industries contributes to the availability of different surfactant precursors.

9.3.1.4 Whey and Dairy Industry By-Products

By-products from the dairy industry, particularly whey, contain proteins and lipids that can be utilized for biosurfactant production. Whey, earlier treated as waste, serves as an abundant source for sustainable surfactant materials.

9.3.1.5 Oil Wastes

Suitable substrates for producing biosurfactants include waste oil generated from food processing and vegetable oil-based refineries. These substrates are rich in fatty acids and triglycerides, which can be converted into biosurfactants through microbial fermentation. The production of biosurfactant from waste oil not only offers an effective way to manage this waste stream but also provides a sustainable alternative to chemical surfactants that are derived from non-renewable resources. The cheap oil waste [101] and oil refinery waste from soybean, cottonseed, babassu, palm, and corn oil [96] could be utilised in producing rhamnolipids. The cost involved in the industrial-scale manufacturing of biosurfactant could be curtailed by effectively utilizing these cheap oil wastes as the main source.

9.3.1.6 Dairy Whey

Around 6 litres of dairy whey are produced from about 1 kg of cheese and it also serves as cheap, sustainable, and durable substrate for the fermentation of biosurfactants. One effective utilization of these dairy wastes as substrates is their use in producing sophorolipids of higher concentrations for *Cryptococcus curvatus* ATCC 20509 yeast by a cultivation process involving two stages [31].

9.3.1.7 Starchy Waste

Starchy waste can be utilized as a valuable and cost-effective resource for producing biosurfactants. Potato and tapioca ball processing industries are the primary sources of starchy waste. Potato processing results in the generation of waste that is rich in starch, such as water, peels, and inedible potatoes, ideal for microbial growth. It is worth noting that only 59% of the potato crop is utilized for consumption, leaving behind difficult-todispose wastes with high starch content [87]. These wastes are rich in carbon, sulfur, nitrogen, trace elements, and contain a significant amount of sugars, starch, minerals, and vitamins. Surfactin can be produced from the potato processing effluents as substrates [132]. The efficiency of *B. subtilis* ATCC 21332 in producing biosurfactants using potato as a carbon source has been assessed [49]. Two strains of Bacillus subtilis were effective in producing biosurfactants using powdered potato peels as a substrate in two different fermentation systems [33]. Through solid-state fermentation, biosurfactants have been synthesized by the *Bacillus subtilis* strain (B6-1), from residues of sweet potato and soybean [137].

9.3.1.8 Molasses

During the production of sugar from either sugarcane or sugar beet, a by-product called molasses is generated. Molasses is primarily composed of sugars, with sucrose making up 48-56% of its composition. Additionally, it

Molasses is primarily composed of sugars, with sucrose making up 40-50% of its composition. Additionally, it contains 50-55% fermentable sugar along with inorganic matter, organic components (non-sugar), vitamins, and proteins. Molasses is considered to be a carbon-rich source. *P. aeruginosa* GS3 is used with corn-steep liquor and treated molasses as main sources of nitrogen and carbon to produce rhamnolipid biosurfactant [104]. When using molasses at 2%, 4%, 6%, 8% and 10%, the specific rate of production of rhamnolipid was reported as 0.003, 0.009, 0.053, 0.041 and 0.213 respectively [89]. In a study, *Bacillus subtilis* was employed as the microbial strain to produce surfactin involving the use of a culture medium containing molasses (16%) and $NaNO_3$ (5g/L) along with other trace elements. The concentration of surfactin obtained from the fermentation broth was found to be 1.12 g/L [1].

9.3.1.9 Animal Fat

When meat is processed, animal fat and tallow is generated as a by-product. However, instead of being discarded, these waste materials can be utilized to manufacture biosurfactants. This could be achieved by treating the animal fat and tallow with *C. bombicola* yeast, which results in the production of sophorolipids, a type of biosurfactant with excellent emulsifying, foaming, and cleaning properties [38].

9.3.1.10 Soap Stock

Another by-product, soap stock generated during processing of oil-seeds at industry levels could also be utilised for producing biosurfactant. Surfaceactive rhamnolipids (RLLBI) can be produced using *P. aeruginosa* LB1, which is isolated from petroleum-contaminated soil. The production can be achieved in a mineral salt medium through a batch fermentation process that uses soap stock as the sole source of carbon [18].

9.3.1.11 Cassava Wastewater

Cassava wastewater refers to the liquid by-product produced during the processing of cassava and typically contains a significant amount of dissolved starch, sugars, and mineral salts making it the perfect substrate for a wide range of biotechnological processes. In fact, it is commonly utilized to produce cassava flour and is a highly sought-after alternative substrate for fermentation processes [111]. Biosurfactant production from cassava effluent has been studied using two *Bacillus subtilis* strains, ATCC 21332 and LB5a [99]. These two strains were tested for their surface activity and surfactin production efficacy, both of which were found to be effective and produced similar amounts of surfactin. *B. subtilis* was also used for producing surfactin from cassava wastewater [98]. Similarly, Siddhartha *et al.* [121] used *Pseudomonas aeruginosa* and cassava wastewater to produce rhamnolipids and polyhydroxyalkanoates together [121].

9.3.1.12 Palm Oil Mill Effluent

Palm oil mill effluent is a type of high-strength organic waste slurry that contains a significant amount of fat, oil and grease [66]. Its nutritional value is utilized by microorganisms as a source of energy for their growth and production of useful metabolites such as biosurfactants [95]. Biosurfactants has been produced from palm oil contaminated sites [112]. Biosurfactants produced from palm oil mill effluent using *Nevskia ramose* NA3 [25] were found to reduce the surface tension of water from 72mN/m to 27mN/m.

9.3.1.13 Olive Oil Mill Effluent

Olive oil mill effluent is a waste generated during olive oil extraction, a high-strength organic effluent. The improper disposal of olive oil mill effluent can lead to the degradation of soil and water quality, which can have a detrimental effect on both aquatic and terrestrial ecosystems. *P. aeruginosa* 47T2 could produce rhamnolipids using olive oil mill effluent as the sole carbon source [93]. *Penicillium citrinum* was subjected to cultivation on a mineral medium that was supplemented with 1% olive oil as the primary source of carbon to study the production of a particular type of glycolipid that has emulsifier properties [23].

9.3.1.14 Peanut Oil Cake

The solid residue left over from refining peanut oil is rich in protein, carbohydrate and lipids. In a study conducted by Sobrinho *et al.* [125], it was observed that *Candida sphaerica* can be utilized for the production of biosurfactant from groundnut oil refinery residue (5%) and cornsteep liquor (2.5%) as substrates. The resulting biosurfactant had a surface tension reducing activity of approximately 26 mN/m, with 0.08% CMC. That suggested a high potential for its application in various industries. Several studies have been conducted to investigate the potential of using peanut oil cake as a substrate for the production of biosurfactants. It has been found that *Azotobacter chroococcum*, *Bacillus megaterium*, and *Corynebacterium kutscheri* are capable of producing biosurfactants with higher yields using peanut oil cake as a substrate [131]. The use of this low-cost and readily available substrate could offer a sustainable alternative to the traditional methods of producing biosurfactants, which often rely on synthetic cassava wastewater to produce rhamnolipids and polyhydroxyalkanoates together [121].

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9.3.1.15 Soybean Waste

Soy molasses is a by-product obtained from the processing of soybean oil, which is rich in fermentable carbohydrates accounting for 30% of its weight by volume. Moreover, it consists of approximately 60% solid carbohydrates, which makes it an excellent source for the production of biosurfactants, as it is a cost-effective option [87]. Sophorolipids, a type of biosurfactant, can be synthesized using soy molasses by Candida bombicola, a yeast-like fungus, with a high yield of 55 g/l [126]. Sophorolipids are widely used in various industries including food, pharmaceutical, and cosmetic industries due to their excellent surface-active properties and low toxicity.

9.3.1.16 Orange Peel

Citrus fruits, such as oranges, play a vital role in the global market as they are used for various purposes, including consumption as a fruit, production of juices, and for their essential oils. However, the production and processing of citrus fruits generate a considerable amount of waste, including peels, seeds, and pulp. The amount of waste generated from the citrus industry is a significant environmental concern that needs to be addressed [2]. Orange peel is a valuable source of carbon for rhamnolipid production by *P. aeruginosa* MTCC 2297, with a yield of 9.18g/l and surface tension of 31.3mN/m [53]. It is also the best substrate for biosurfactant production, with a yield of 1.796g/l and an emulsification activity of 75.17% against diesel [75].

Hence, the diverse array of agro-wastes as sources for bio-based surfactants offers a promising avenue towards sustainable and environmentally conscious alternatives. From crop residues to processing by-products, these agro-wastes present an ample supply of organic materials that can be effectively repurposed for the production of eco-friendly surfactants. This not only addresses the challenges of waste management in the agroindustry but also contributes to the development of greener alternatives in various sectors.

9.4 Microorganisms and Enzymatic Processes

Biosurfactants are microbial amphipathic substances obtained from various carbon sources, and are similar to synthetic surfactants [20]. Agroindustrial waste is a promising source of carbohydrates for the production of synthetic surfactants [20]. Agroindustrial waste is a promising source of carbohydrates for the production of biosurfactants in microbial media. They are a great substrate for fermentation by microorganisms due to their nutrient-rich environment. Microorganisms, such as bacteria, fungi, yeasts, algae, and enzymatic processes, offer versatile approaches for biosurfactant production from agroindustrial wastes as shown in Figure 9.2. Many microorganisms have been identified and isolated for their potential use in waste management [13]. Enzymatic hydrolysis of agro-waste components provides a controlled and sustainable method for obtaining surfactant precursors.

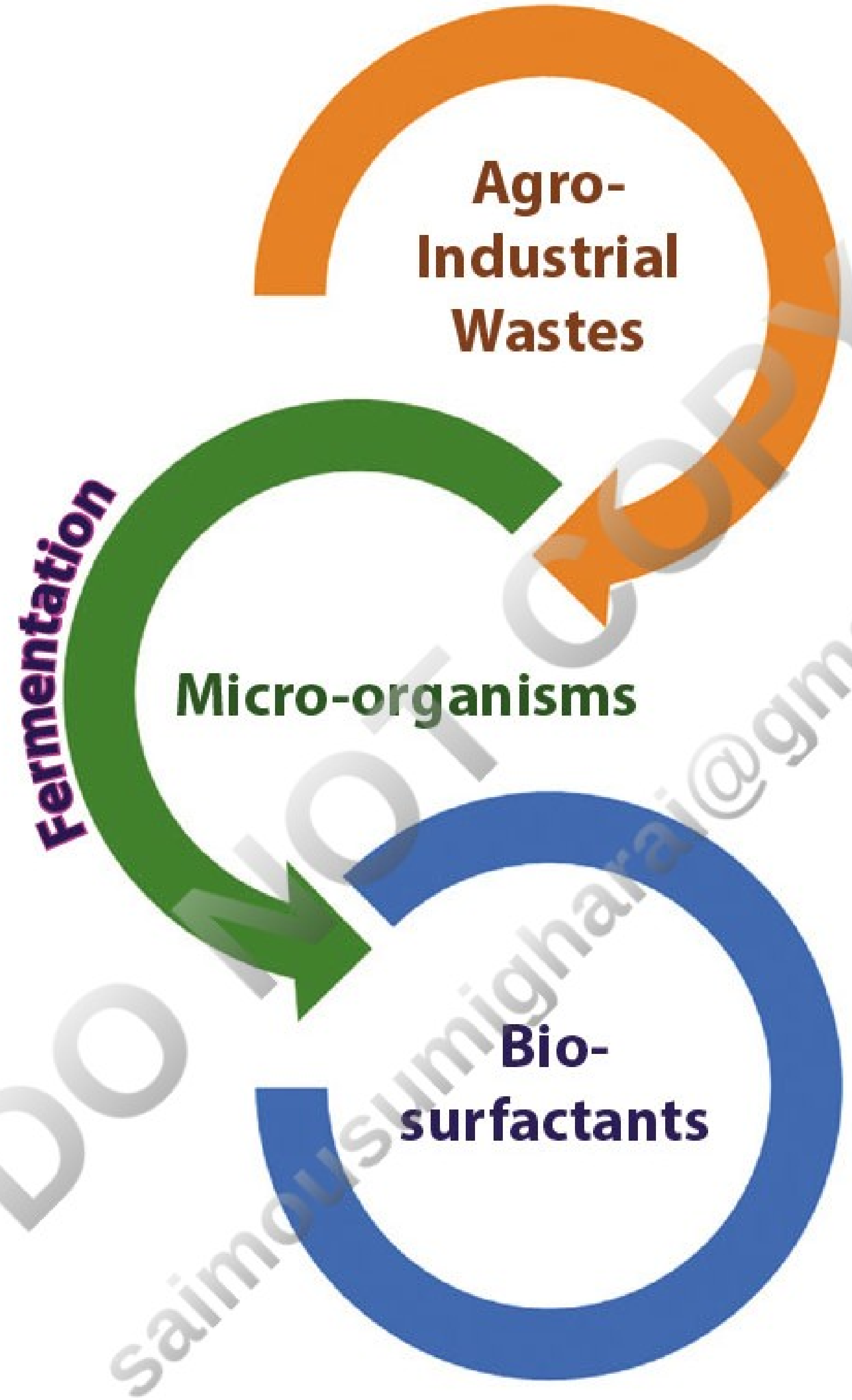

Figure 9.2 Bio-surfactant production by microorganisms using agro-industrial wastes.

The abundance and diversity of agro-wastes emphasize their potential as sustainable sources for bio-based surfactants. Efforts to harness these resources contribute to the development of environmentally friendly alternatives and some of the agro-waste sources are discussed in detail.

9.5 Types of Biosurfactant

Several types of biosurfactant exist, categorized based on their chemical composition and microbial origin. The wide range of biosurfactant types reflects the adaptability of various microorganisms in different environments and holds range of biosurfactant types reflects the adaptability of various microorganisms in different environments and holds promise for applications in industries ranging from bioremediation to pharmaceuticals and food production.

Biosurfactants are classified into two categories based on their molecular mass [107]. The first category is surfactants with low-molecular weight. They exhibit low surface and interfacial tension and are efficient in their function. Glycolipids, lipopeptides, phospholipids, lipoproteins, fatty acids and neutral lipids fall under this category. High-molecular weight surfactants belong to the second category of surfactants. They are known for their effectiveness as emulsion-stabilizing agents. This category comprises two main classes of surfactants, namely polymeric and particulate surfactants.

9.5.1 Low-Molecular Weight Biosurfactant

9.5.1.1 Glycolipids

Many types of biosurfactants produce glycolipids, which consist of sugars bonded to long-chain aliphatic or hydroxyaliphatic acids through either ether or ester linkage. The most well-known glycolipids include rhamnolipids, sophorolipids, and trehalolipids. Food waste can be used as fermentation feedstock to produce valuable glycolipid biosurfactants through bioconversion [9]. *Pseudomonas aeruginosa* ATCC 10145 microbial strains use soy molasses as carbon source for glycolipids biosurfactant production.

9.5.1.2 Lipopeptides and Lipoproteins

Lipopeptides, such as surfactin, are cyclic lipopeptides consisting of a polypeptide chain and a lipid moiety. This class includes gramicidins (decapeptide anti-toxins) and polymyxins (lipopeptide anti-toxins). *Bacillus* spp. can produce lipopeptides using whey waste as a substrate [37, 55, 68] whereas *Bacillus* sp. *HIP3* microbes can utilize used–cooking oil as substrates to produce lipopeptides [92]. *Bacillus subtilis* strains DM-03 and DM-04, *Bacillus pumilus* DSVP18, *Bacillus mojavensis* A21 and *Bacillus licheniformis* strain J1 microbes use starchy substrates such as potato peel, potato waste and potato peel powder as carbon sources for lipopeptide biosurfactant production [10, 32, 33, 118].

9.5.1.3 Fatty Acids, Phospholipids, and Neutral Lipids

Bio-based surfactants are largely composed of fatty acyl groups derived from oilseeds, such as palm, coconut, etc., animal fats and their derivatives, such as fatty alcohols and amines [61]. These components are essential to produce high-quality surfactants that are not only effective but also environmentally friendly. In food-related applications, high-oleic oils like corn, olive, cottonseed, palm, or soybean oils are the most used feedstocks of lipophilic building blocks to produce bio-based surfactants. *Microorganism Acinetobacter* sp. can produce phospholipids from carbon sources by fermentation process [17]. Phospholipids are derived from soapstock and degumming of seed oils.

9.5.1.4 Rhamnolipids

Rhamnolipids are glycolipids consisting of rhamnose and hydroxydecanoic acid. These compounds have been extensively studied due to their unique properties as biosurfactants. They are known to be the primary glycolipids produced by *P. aeruginosa*, a bacterium commonly found in soil and water environments. Soap-stock [18], cheap oil waste [101], Cassava wastewater [121], olive oil mill effluent [93], oil refinery waste from soybean, cottonseed, babassu, palm, and corn oil [96] could be utilized in producing rhamnolipids surfactants.

9.5.1.5 Sophorolipids

Sophorolipids are complex molecules that are synthesized by yeasts. They consist of two components: sophorose, a carbohydrate, and a long-chain hydroxy fatty acid that is linked to sophorose *via* a glycosidic linkage. These compounds are known for their hydrophobic properties and typically consist of a mixture of at least six to nine different hydrophobic compounds. The lactone form of sophorolipids is particularly useful for a wide range of applications. Sophorolipids are a promising area of research due to their potential use in a variety of industries, including pharmaceuticals, cosmetics, and bioremediation. Dairy wastes [31], animal fat [38], soy molasses [126], etc., can be used as substrates to produce sophorolipids. Sophorolipids biosurfactants are produced by the *Candida bombicola* ATCC 22214 using dairy wastewater from the dairy industry [31]. Several researches have been reported on production of rhamnolipid by *Pseudomonas aeruginosa* strains using whey waste as substrate [28, 35, 42, 105].

9.5.1.6 Trehalolipids

This is a type of glycolipid found in most types of *Mycobacterium*, *Corynebacterium*, and *Nocardia*. The molecule is composed of trehalose disaccharide that is linked at both C-6 and C-6' to a long chain of mycolic acid, which is a βhydroxy, α-branched fatty acid. *Rhodococcus erythropolis*, *Arthrobacter* sp., *Rhodococcus qingshengii*, *Nocardia erythropolis*, *Nocardia farcinica*, *Corynebacterium* sp., and *Mycobacterium* sp. microorganisms are useful in the production of Trehalolipid biosurfactants from agro-waste– based carbon sources by fermentation process [17].

9.5.1.7 Surfactin

Bacillus subtilis is responsible for producing one of the most powerful biosurfactants. Seven amino acids are arranged in a ring structure. This unique arrangement of amino acids is linked to an unsaturated fatty acid chain through a lactone bond. It possesses the impressive ability to significantly lower the surface tension from 72 to 27.9 mN/m, even at extremely low concentrations of just 0.005. Surfactin can be produced from cassava waste [98], molasses [1], and potato processing effluents [132] as substrates. Microorganism *B. subtilis* KB1 can produce surfactin from by-products and waste generated during vegetable oil processing, while *B. subtilis* LAMI008 and B. subtilis LAMI005 are known to synthesize surfactin from cashew apple juice. Another microorganism, *B. subtilis* LB5a, uses wastewater generated (as by-product during the pressing process) in the manufacture of cassava flour as a substrate to synthesize surfactin biosurfactant [40]. Subtilis MTCC 2423 generated surfactin using waste frying oil, yeast extract, and mineral salts in a submerged cultivation [135].

9.5.1.8 Lichenysin

Several biosurfactants are produced by *Bacillus licheniformis* that work together and remain stable in various conditions of temperature, salt, and pH. Surfactants produced by *B. licheniformis* can significantly reduce the surface tension of water to 27 mN/m and the interfacial tension between water and n-hexadecane to 0.36 mN/m. The microorganisms *Bacillus subtilis* 20B, R1, and HS3 have the ability to produce a biosurfactant called lichenysin, which possesses similar structural and physicochemical properties to the well-known surfactin. These microorganisms use molasses and whey diary waste as their carbon sources for the production of lichenysin biosurfactant [68].

9.5.2 Other Types of Biosurfactant

9.5.2.1 Polymeric Biosurfactant

Alasan, Liposan, Lipomanan and several other polysaccharide-protein compounds are well-studied polymeric biosurfactants. *Acinetobacter calcoaceticus* RAG-1 is capable of producing a highly potent extracellular bio-emulsifier composed of a polyanionic, amphipathic and heteropolysaccharide compound. Emulsan can effectively emulsify hydrocarbons in water at concentrations as low as 0.001% to 0.01%.

9.5.2.2 Particulate Biosurfactant

Microbial cells uptake hydrocarbons through extracellular vesicles. In this process, hydrocarbons are segmented to create a microemulsion which is crucial for the process to occur. These vesicles are 20-50 nm in diameter and composed of protein, phospholipids, and lipopolysaccharide with a thickness of 1.158 cg/cm^3. *Acinetobacter* sp. is an example of a bacterium that produces such vesicles [108].

Different types of biosurfactants possess unique properties that cater to specific needs. Their unique properties make them increasingly important in the development of innovative and eco-friendly technologies. Some are highly effective at emulsification, while others excel at foaming or solubilization. These diverse types of biosurfactants offer a range of solutions across different industries, contributing to sustainable practices, environmental protection, and advancements in fields such as agriculture, pharmaceuticals, and biotechnology.

9.6 Industrial Applications of Agro-Waste-Based Biosurfactants

The need for biosurfactants is increasing due to rising consumer concern for eco-friendly and biodegradable products. This has led to growth in the biosurfactant market and high demand in many industries for a greener approach. The global biosurfactant market was worth USD 4.20 billion in 2017 and recent data indicates that the market grew to 4.39 billion USD in 2023 at a rate of 7.8%. According to the "Biosurfactants Global Market Report" [21] report, it is predicted that the market will continue to grow and reach USD 6 billion by 2027 at a rate of 8.1% per year.

Table 9.1 Application of biosurfactants in various industries.

Industry	References
Agriculture	[22, 143, 145]

Food industry	[22, 97, 145]
Pharmaceutical/Cosmetic	[22, 26, 134]
Petroleum	[22, 45]
Textile	[22]
Wastewater Treatment	[50, 106, 143]

Various industries, including petroleum, food, cosmetics, and medicine, can benefit from using biosurfactants produced utilizing agro-wastes. The applications of biosurfactants are rapidly expanding, with huge potential in areas such as environmental and soil remediation, wastewater and sludge treatment, microbial-enhanced oil recovery, heavy metal remediation, pharmaceuticals, and the petroleum industry. Table 9.1 summarizes the various industrial processes where biosurfactants have application.

Agro-waste-based biosurfactants contribute to the valorization of agricultural residues and by-products, transforming them from waste into valuable and eco-friendly products. Industrial applications of agro-waste-based biosurfactants represent a significant stride towards sustainable and eco-friendly practices across diverse sectors, namely agriculture, cosmetics and personal care industry, mineral processing. This diversified range of applications underscores the versatility and importance of agro-waste-based biosurfactants in fostering a more sustainable and responsible industrial application, and some of the major industrial applications are discussed.

9.6.1 Contaminated Soils

Lately, biosurfactants have been the subject of many studies, with a particular focus on their potential environmental applications. These compounds have superior physicochemical properties and environmentally friendly characteristics, making them versatile. They can efficiently remove hydrophobic organic compounds (HOCs) and heavy metals from contaminated soil. The presence of heavy metals in contaminated soil poses a significant environmental threat. Common heavy metals found in such soil include lead, mercury, arsenic, cadmium, chromium, zinc, copper and nickel. These metals are inorganic chemical hazards that can cause a wide range of health issues for plants, animals, and humans [3, 6, 64, 71, 77, 78, 84, 102, 129, 139]. Biosurfactants from plants and microorganisms outperform chemical surfactants in removing heavy metals from contaminated soil [27, 80, 128, 136].

9.6.2 Oil Recovery

In the petroleum industry, enhanced oil recovery (EOR) techniques play a crucial role in extracting the maximum amount of oil from reservoirs. These techniques consist of various thermal, physical, and chemical processes that help in recovering the trapped oil reserves that cannot be extracted through conventional methods. The thermal methods include steam injection and *in-situ* combustion, physical methods include water flooding, while chemical methods involve the use of surfactants, polymers, and other substances to change the properties of the reservoir rock and improve oil recovery. The traditional approach involves injecting air/gas or water into oil reservoirs. Petroleum industries rely heavily on chemical-based surfactants for EOR. However, the use of these methods has high financial and environmental costs and can result in reduced yields [7]. However, the low rate of oil recovery in EOR can be attributed to several factors. Firstly, hydrocarbons can become trapped in the porous matrix of the reservoir, making it difficult to extract. Secondly, the high viscosity of the oil can make it harder to move through the reservoir. Lastly, the high interfacial tension between the injected water and oil can also hinder the recovery process [47, 142]. An eco-friendly approach can be adopted by refraining from the use of chemical surfactants to oil reservoirs. This will help preserve the environment and promote the well-being of all living beings by preventing contamination of groundwater and soil [67].

Utilizing microorganisms that produce biosurfactants for EOR, known as microbial-enhanced oil recovery (MEOR), has been shown to be an efficient method in various studies [11, 12, 15]. In the MEOR technique, multiple microbial species are utilized to produce biosurfactants that increase oil recovery. Some of these species include *Bacillus amyloliquefaciens*, *Bacillus megaterium*, *Bacillus subtilis*, and *Pseudomonas aeruginosa* [7, 39, 47, 140, 141].

9.6.3 Cosmetic and Pharmaceutical Industries

In the cosmetics industry, bio-based surfactants derived from agroindustry wastes are utilized for their emulsifying and foaming properties, enabling the formulation of eco-friendly and natural cosmetic products. Also, biosurfactants have attracted interest in the cosmetic and pharmaceutical industries due to their versatility as wetting agents, foaming agents, detergents, emulsifiers, solubilizers, etc. [90]. Biosurfactants are commonly used in the cosmetic and healthcare industries as essential ingredients in various products, such as shampoo, soap, toothpaste, and skin care items, due to their useful properties [115].

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9.6.4 Commercial Laundry Detergents

Chemically synthesized surfactants, which are an essential component of modern detergents, pose a threat to aquatic life in fresh water. With increasing environmental consciousness, the potential hazards posed by chemical surfactants are becoming more evident. Therefore, there is a pressing need for the development of eco-friendly and natural alternatives to mitigate these risks. Biosurfactants, such as cyclic lipopeptide (CLP), have the ability to remain stable across a wide range of pH values, specifically from 7 to 12. Under no circumstances do these substances lose their surface-active property, even when subjected to high temperatures. These biosurfactants exhibit excellent emulsion-forming ability with vegetable oils and have significant compatibility and stability with commercially available laundry detergents, making them a suitable choice for eco-friendly detergent formulations [108].

9.6.5 Agriculture

Biosurfactants are essential in agriculture to promote biocontrol mechanisms of microorganisms like parasitism, antibiosis, induced systemic resistance, competition, and decreased toxicity. Bio-based surfactants from agro-wastes find applications in agriculture for improving pesticide efficacy, soil conditioning, and water retention. These sustainable alternatives contribute to environmentally conscious farming practices. Surfactants are necessary to increase the solubility of bio-hazardous compounds, such as polycyclic aromatic hydrocarbons (PAHs), which also enhances the solubility of hydrophobic organic contaminants. Microorganisms' adsorption to

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9.6.6 Reduction in CO_2 Emissions

Atmospheric gases such as carbon dioxide, water vapour, and methane have the ability to absorb long-wave radiation, specifically infrared, which is released from the earth's surface. This leads to the greenhouse effect. According to studies, biosurfactants can help reduce CO_2 emissions. In 1998, EU production of oleochemical surfactants prevented CO_2 emissions of 1.5 million tons [146].

9.6.7 Mineral Processing Industry

Surfactants are in high demand in the market, especially in the mining and mineral processing industries, but currently, most of them are synthetic and derived from petroleum. These chemical surfactants are harmful to the environment and not easily biodegradable. They can accumulate in biological systems and their production processes and by-products can also be environmentally hazardous. Due to increasing awareness of the need to protect ecosystems and rigorous environmental regulations, there is growing interest in the use of biosurfactants as a potential alternative to chemical surfactants [15].

Surfactants have the remarkable ability to significantly reduce surface and interfacial tension at the interfaces between liquids, solids, and gases. These surface-active compounds have the ability to adsorb at interfaces and create aggregates in solution. This unique property gives rise to separation methods that share common basic principles. Some major surfactant-based separations are ultrafiltration, extraction, froth flotation, surfactant adsorption, surfactant precipitation, etc. The flotation process is currently the most attractive area in mineral processing where the use of surfactant is supported on commercial and environmental grounds. The flotation process separates valuable minerals from impurities based on their surface properties. In flotation, surfactants adsorbed on particle surfaces can significantly enhance adhesion to rising air bubbles by reducing the surface tension. The adsorption of surfactant on a solid surface can be controlled by altering surfactant concentration, pH, counter ions, and surfactant type. Biosurfactants are a superior choice for flotation processes due to their significant degradability when compared to traditional reagents [113]. The use of glycolipids to dissolve toxic metals such as cadmium, chromium, copper, nickel, lead, and zinc has also been studied [14]. Iron sorbents and biosurfactants, surfactin-105 and Lichenysin-A as collectors have been used to remove heavy metal ions from laboratory samples, including floating metal-laden particles [144]. The study found that surfactin and lychenysin biosurfactants are better at removing goethite and collecting metal-laden solid particles than dodecylamine and sodium dodecyl sulfate in the pH range of 4-7. Surfactin was also found effective in removing 50 mg/l of zinc sorbed onto *in situ* generated hydrous ferric hydroxides at pH 6. The biosurfactant rhamnolipid produced by *Pseudomonas aeruginosa* MA01 strain was investigated as a frother in copper ore flotation, exhibiting significant frothing ability [72]. Cassava waste has been utilized for production of rhamnolipids using *Pseudomonas aeruginosa* [121]. Several researches have been reported on production of rhamnolipid by *Pseudomonas aeruginosa* strains using whey waste as substrate [28, 35, 42, 105]. The effectiveness of two sophorolipids - acetylated acidic sophorolipid (ac-ASL) and acetylated lactonic sophorolipid (ac-LSL) was tested as collectors of hematite $\alpha\text{-}Fe_2O_3$ and malachite $CuCO_3{\cdot}Cu(OH)_2$ in synthetic two-mineral systems with quartz. The results showed that both ac-LSL and ac-ASL had good collecting properties and could handle ultrafine particle sizes, making them promising alternatives for further research on natural metal oxide ores [124].

The flotation process is sometimes criticized for its use of potentially toxic collectors during pollution control or water treatment. However, the development and implementation of biodegradable biosurfactants may address these concerns and increase the acceptability of this separation technology. Hence, agroindustry waste-derived bio-based surfactants could also serve as flotation reagents in mineral processing, offering a sustainable alternative to traditional chemical reagents.

Hence, the applications of bio-based surfactants derived from agroindustry wastes span across multiple industries, showcasing their versatility and eco-friendly nature. In agriculture, these surfactants prove beneficial for crop protection, enhancement, and soil conditioning, promoting sustainable farming practices. Additionally, in the realm of cosmetics and personal care, these bio-based surfactants find applications as environmentally conscious emulsifiers and foaming agents. The industrial cleaning sector also stands to benefit, as these surfactants offer green alternatives for the formulation of eco-friendly cleaning products. Moreover, a novel and intriguing application arises in mineral processing, where these bio-based surfactants exhibit potential as flotation reagents, providing an environmentally sustainable alternative to conventional options.

9.7 Advantages of Agro-Waste-Based Biosurfactants

The advantages of agro-waste-based biosurfactants are multifold, presenting a compelling case for their adoption in various industries. Biosurfactants derived from agro-waste are a superior choice for various industries due to their exceptional properties. Firstly, these biosurfactants offer a sustainable alternative, derived from renewable agroindustry resources, reducing reliance on limited petrochemical feedstocks. Their production contributes to waste valorization, transforming agricultural residues and byproducts into valuable assets, aligning with circular economy principles. Additionally, agro-waste-based biosurfactants typically exhibit lower toxicity and improved biodegradability, reducing their environmental impact compared to conventional surfactants minimizing environmental impact. This aspect not only addresses environmental concerns but also promotes cleaner waterways and ecosystems.

In addition to being environmentally friendly, agro-waste-based biosurfactants are more efficient than their synthetic counterparts, especially in extreme conditions such as high temperature, pH, and salinity. They also exhibit better foaming properties, making them an excellent choice for producing foaming agents. Furthermore, these surfactants are specific in their action, which means they can be tailored to perform a particular function, making them highly versatile. Lastly, these surfactants have lesser toxicity, which means they are safer to handle and use. Therefore, they are an ideal choice for various applications, including agriculture, food processing, and pharmaceuticals, among others. For example, biosurfactants, such as sophorolipids from *Candida bombicola*, demonstrate lower toxicity profiles compared to chemical-derived surfactants, making them useful in food industries [51].

Although biosurfactants have a diverse range of chemical composition and properties, they share several characteristics that make them advantageous over traditional surfactants [97] in terms of the characteristics described below.

9.7.1 Environmental Factors

Many types of biosurfactants exhibit remarkable resistance to physical factors such as temperature, pH, and ionic strength. For instance, lichenysin, which is produced by the *Bacillus licheniformis* strain, can tolerate up to 50°C, a strength. For instance, lichenysin, which is produced by the *Bacillus licheniformis* strain, can tolerate up to 50°C, a pH range of 4.5 to 9.0, and high NaCl (50g/l) and Ca (25g/l) concentrations without any noticeable impact [91]. *Arthrobacter protophormiae* produces a robust biosurfactant that can withstand extreme temperatures (30-100°C) and pH levels (2-12). It is a promising candidate for industrial applications where such conditions are often encountered [34].

9.7.2 Surface and Interface Activity

Surfactants are substances that can help to decrease the surface tension and the interfacial tension between two phases. Surfactin, produced by *B. subtilis*, lowers water surface tension to 25 mN m^{-1} and interfacial tension with hexadecane to <1 mN/m [24]. P. aeruginosa produces rhamnolipids which significantly reduce surface tension to 26 mN/m and interfacial tension to <1 mN/m. Biosurfactants are more effective due to a lower Critical Micelle Concentration compared to chemical surfactants [29].

9.7.3 Biodegradability

Biodegradable biosurfactants are being assessed as a potential alternative for synthetic surfactants to remove phenanthrene from aquatic surfaces. Sophorolipid, a biodegradable biosurfactant, has enabled *Cochlodinium* algae to remove 90% of phenanthrene in 30 minutes [57].

9.7.4 Emulsion Framing and Emulsion Breaking

Emulsions are mixtures of two immiscible fluids, with two types: oil-in-water and water-in-oil. Additives such as biosurfactants can balance their low stability, making stable emulsions last from a few to several years [65].

9.7.5 Antiadhesive Agents

Biosurfactants change surface hydrophobicity and microbe adhesion. S*treptococcus thermophilus* and *Pseudomonas fluorescens* produce surfactants that slow colonization of other strains and inhibit microbe attachment to steel surfaces, respectively [73].

9.7.6 Antimicrobial Action

Biosurfactants have unique structures that can influence cell membranes. Some types possess strong antibacterial, antifungal, and antiviral properties, helping prevent pathogen adherence. They have potential uses in treating diseases and as therapeutic and probiotic agents. For example, *marine B. circulans'* biosurfactant exhibits potent antimicrobial activity against pathogens and semi-pathogenic strains, including MDR strains [16].

9.7.7 Anticancer Activity

Microbial glycolipids induce cell separation in human leukemia and PC12 cells. They improve acetylcholine esterase movement, increase neurite formation and disrupt the cell cycle, suggesting they could be used to treat cancer cells [49].

Versatility in applications, spanning agriculture, cosmetics, industrial cleaning, and mineral processing, showcases the broad spectrum of industries that can benefit from these biosurfactants. In essence, the advantages of agro-waste-based biosurfactants extend beyond their functional properties, embodying a sustainable, environmentally friendly, and economically viable solution for diverse industrial needs.

9.8 Conclusion

Agroindustrial wastes have the potential to be transformed into highly effective biosurfactants that possess numerous benefits over traditional petrochemical-based surfactants. Biosurfactants are a new generation of surfactants that are derived from natural sources like plant and animal fats, oils, and carbohydrates. The raw materials used in the production of biosurfactants are biodegradable, renewable, and environmentally friendly, making them an attractive alternative to conventional surfactants. Despite the potential of agro-waste–based biosurfactants, their production process has some challenges. One of the most significant obstacles is the low productivity of the production process, which can result in high downstream production costs. Furthermore, there is limited knowledge regarding the production of biosurfactants in bioreactor systems for commercial use. However, despite these challenges, there is an increasing market demand for biosurfactants/bio-based surfactants. This is primarily due to increasing awareness among consumers of environmental issues and the strict regulations enforced by governments worldwide on the use of chemicals in detergents. In response to the environmental challenges posed by traditional surfactants, researchers of chemicals in detergents. In response to the environmental challenges posed by traditional surfactants, researchers are striving to develop new, more sustainable alternatives. These surfactants are designed to be biodegradable and utilize renewable resources. Bio-catalysis or fermentation processes are carried out to produce these biosurfactants. Cost of the biosurfactant production can be significantly reduced by using inexpensive carbohydrate sources as substrates. To further reduce the production cost, it is essential to optimize fermentation strategies, consider different factors of the microbial culture broth, and streamline downstream processing. Another way to save costs is by using agroindustrial waste as a culture medium. The use of agro-waste–based biosurfactants has the potential to significantly reduce the environmental impact of chemical surfactants, contributing to a more sustainable future. The future of agro- waste-based biosurfactants is promising. In order to advance the field of biosurfactant production, there is a need for further research in several key areas. Firstly, screen for high-yield producers, enabling the identification of the most efficient agro-wastebased substrate. Secondly, a greater understanding of the waste composition and complementary needs of biosurfactant producers is required to optimize production. This understanding can be used to develop appropriate waste pretreatment and biosurfactant purification strategies, minimizing the environmental impact of the process. Finally, to further reduce the environmental impact of biosurfactant production, the entire life cycle of the process should be optimized, taking into consideration all aspects of production. Agro-wastes embody the principles of a circular economy, where waste is considered a resource. Effective utilization of agro-wastes closes the loop, transforming them into valuable products, thereby reducing dependency on non-renewable resources and minimizing waste disposal challenges. Recognizing the importance of agro-wastes and their effective utilization is essential for achieving sustainable agricultural and industrial practices. Through innovative and environmentally conscious approaches, agro-wastes can be transformed from potential environmental burdens into valuable assets, contributing to a more circular and resource-efficient future.

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Note

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