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Review

Production of green surfactants: Market prospects ☆

Charles Bronzo B. Farias [a,b,c], Fabíola C.G. Almeida [a,c], Ivison A. Silva [a,b,c], Thais C. Souza [c], Hugo M. Meira [a,c], Rita de Cássia F. Soares da Silva [a,c], Juliana M. Luna [a,c], Valdemir A. Santos [a,c], Attilio Converti [c,d], Ibrahim M. Banat [c,e], Leonie A. Sarubbo [a,b,c,]*

[a] Universidade Católica de Pernambuco (UNICAP), Rua do Príncipe, n. 526, Boa Vista, Recife, Pernambuco CEP 50050-900, Brazil
[b] Rede Nordeste de Biotecnologia (RENORBIO), Universidade Federal Rural de Pernambuco (UFRPE), Rua Dom Manuel de Medeiros, s/n, Dois Irmãos, CEP: 52171-900 Recife, PE, Brazil
[c] Instituto Avançado de Tecnologia e Inovação (IATI), Rua Potyra, 31 - Prado, Recife, Pernambuco CEP: 50751-310, Brazil
[d] Università degli Studi di Genova (UNIGE), Dipartimento di Ingegneria Civile, Chimica e Ambientale (DICCA), Via Opera Pia, n. 15, 1-16145 Genova, Italy
[e] Faculty of Life and Health Sciences, School of Biomedical Sciences, University of Ulster, BT52 1SA Northern Ireland, UK

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ABSTRACT

Science has greatly contributed to the advancement of technology and to the innovation of production processes and their applications. Cleaning products have become indispensable in today's world, as personal and environmental hygiene is important to all societies worldwide. Such products are used in the home, in most work environments and in the industrial sectors. Most of the detergents on the market are synthesised from petrochemical products. However, the interest in reducing the use of products harmful to human health and the environment has led to the search for detergents formulated with natural, biodegradable surfactant components of biological (plant or microbiological) origin or chemically synthesised from natural raw materials usually referred to as green surfactants. This review addresses the different types, properties, and uses of surfactants, with a focus on green surfactants, and describes the current scenario as well as the projections for the future market economy related to the production of the different types of green surfactants marketed in the world.

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* Corresponding author.
E-mail address: leonie.sarubbo@unicap.br (L.A. Sarubbo).

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1. Introduction

The development of industrialisation in most economic markets has received considerable support from the advances achieved through the uninterrupted encouragement of science, with innovative research projects and the proper use of technology over time [1,2]. Investigations and explorations of natural resources, such as fossil fuels, and the use of hydrocarbons, such as crude oil, have had a positive impact on today's economy and society through the parallel advancement of science. However, pollutants produced by these exploration activities and their harmful by-products, such as heavy metals and inorganic substances or recalcitrant organic compounds that end up in ecosystems, soils, rivers, and oceans, are harmful to terrestrial and marine flora and fauna [3,4].

Petroleum is in demand in various industrial sectors and is part of the world energy matrix due to its high energy value and its importance for the chemical industry. The discovery of petroleum has led to huge changes in the economic development of international markets and the consequent improvement in technologies in the modern world of the past century [5,6,7,8,9]. The detergent industry deserves particular attention, as the raw materials of these products are often derived from petroleum. Cleaning products have become indispensable, as hygiene has become important to mankind worldwide and is used in homes, different work environments and most industrial sectors.

The detergent market includes products for different applications such as cleaning products for homes, personal hygiene and industrial cleaning of heavy oils. *MarketsandMarkets*™ data predicted that the global cleaning products industry will achieve a growth rate of $ 46.8 billion in 2019, with estimates of $ 58.3 billion by 2024 and an annual growth rate of 4.5% [10]. This perspective is based on factors such as the growing awareness of populations around the world on the issues of health, hygiene, and cleanliness [11,12]. The detergent industry has also shown a growing interest in developing environmentally friendly products, which each year account for a larger share of the market, particularly through the growth of biotech industries. This need for sustainability is causing a shift in the detergent industry that is potentially moving away from synthetic surfactants to replace them with more sustainable alternatives. One way to achieve this has been the potential utilization of green surfactants [5,8,9].

This paper offers a description of biotechnological advances involving natural surfactants of microbial or plant origin and the use of biodegradable synthetic surfactants, as well as a market analysis of the biosurfactant industry and the expected changes in the detergent market in the near future.

2. Detergents and soaps

Records of soaps and cleaning agents date back to ancient civilisations, with products made by Sumerians, Egyptians, Babylonians, Jews, and many other people. The first soaps and detergents, which were made with clay, animal fat, plants that contained saponin, and essential oils, were used for hygienic and medicinal purposes. Over time, products have been prepared for different uses, with the addition of specific materials suitable for each application, such as detergents for cleaning metal surfaces, degreasers, soap powder, dish detergent and soap for personal hygiene. All these products were born according to customer needs and have been adapted to the context of each era [13,14,15].

Detergents began to be industrially produced during the Second World War due to the scarcity of oils and fats for the manufacture of soaps, and in the United States the consumption of detergents surpassed that of soaps by 1953. Another example of product adaptation occurred in the mid Twentieth Century, when women were finding jobs in the labour market and needed less time-consuming practices and more efficient products to do household chores. Therefore, the focus of detergents has changed, with greater emphasis on practicality, efficiency, and shorter application time. As a result, detergents became a commercial success of chemistry in the Twentieth Century and, together with soaps, they currently account for 85% of the world's consumption of cleaning materials. Detergents clean in the same way as soaps (through fat solubilisation), but they can have both negative and positive charges [16].

Detergents are synthetic products derived from petroleum that are produced by chemical means and leave residues that can pollute rivers and other environments. Over the years, there has been an increase in the use of biodegradable detergents, which do not have these shortcomings and are made up of linear chain (unbranched) organic compounds that allow organisms to degrade them effectively. Therefore, the need to develop clean products and technologies has led to the use of different techniques to optimise production systems as well as the creation of tools aimed at sustainability. However, this implementation continues to be a challenge for the consumer goods industry [17].

Detergents and soaps reach numerous markets for use in homes as well as commercial businesses and large companies. Different versions of detergents are used for household cleaning, the food industry and heavy cleaning in industrial settings [18].

3. Surfactants

Surfactants are tensioactive agents responsible for the cleaning property of detergents and can be of a synthetic or natural origin [8,19,20]. Surfactants are amphipathic compounds with hydrophilic and hydrophobic portions that preferably partition at the interface between liquid phases with different degrees of polarity, such as oil/water or air/water interfaces [19], as illustrated in Fig. 1. This characteristic reduces the surface tension of liquids through specific, preferential interactions at surfaces and interfaces due to the presence of hydrophilic and hydrophobic portions in the same molecule [21,22]. The non-polar portion of a surfactant is often a hydrocarbon chain, whereas the polar portion (hydrophilic head group) may be ionic (cationic or anionic), non-ionic, or amphoteric [9]. The dynamics of the surfactant market are determined at a fundamental level by the cost, variety, and availability of hydrophobes as well as the cost and complexity of attaching or creating hydrophilic head groups [16].

The efficiency of a surfactant is determined by its ability to reduce surface tension, which is the mechanical energy required to create a unit new area of a liquid surface. Surfactants increase the aqueous solubility of hydrophobic molecules, reducing the surface/interfacial tension of air/water and oil/water surfaces/interfaces. Good surfactants can reduce the surface tension of water from 72 mN/m to 35 mN/m and the interfacial tension (tension between polar and non-polar liquids) of water and n-hexadecane from 40 mN/m to 1 mN/m [23,24].

Surface tension decreases with the increase in surfactant concentration in the aqueous medium up to the formation of micelles, which are aggregated structures with the hydrophilic portion positioned towards outside of the molecule and the hydrophobic portion positioned towards the inside. The critical micelle concentration (CMC) is the concentration that corresponds to the point at which the surfactant achieves the lowest stable surface tension, i.e., the minimum concentration of surfactant necessary for the maximum reduction in the surface tension. Micelles are usually formed when the CMC is reached [25].

3.1. Synthetic surfactants

Most surfactants of synthetic origin can be obtained from five simple reactions, which are described in more detail below. Among

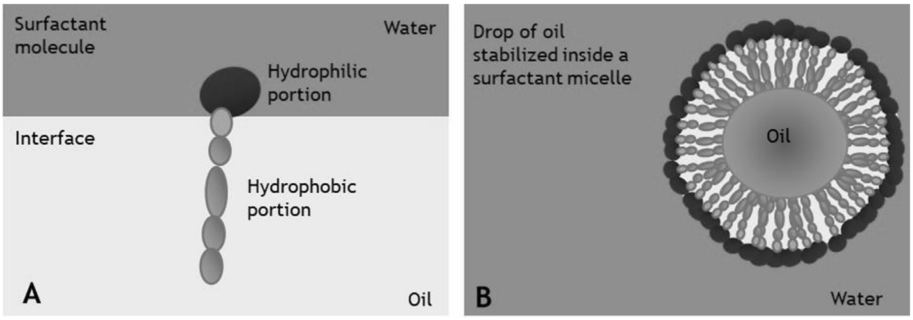


Fig. 1. Surfactant molecule at interface (A). When adsorbed, the surfactant is oriented at the oil/water interface so that its hydrophobic portion is directed towards the oil, while the hydrophilic portion is directed towards the water (B).

these processes, basically two types of reactions are responsible for more than half of the industrial production of surfactants, as most of the surfactants produced are either anionic (negatively charged) or non-ionic (neutral) [26]. The preference for these types of surfactants is due to their low toxicity and higher biodegradability compared to cationic and amphoteric surfactants [27].

The two major classes of inputs used in the production of surfactants are petrochemical and renewable sources [3,28]. The development of petrochemical processing, especially petroleum cracking, resulting in unsaturated, short-chain hydrocarbons, enabled the acquisition of hydrophobic structures of surfactant molecules through polymerization of these alkenes, such as ethylene or propylene, giving rise to surfactants with C9 to C18 carbon chains. Although ethylene has been employed as a carbon chain building block, its increased applicability in the industrial surfactant production has resulted from the production of an intermediate or precursor known as ethylene oxide, which is a key component of ethoxylation [29].

Surfactants of a natural origin are normally obtained from vegetable oils or animal fat, which appear in the form of triglycerides [16]. Prior to petrochemical processing, much of the surfactant industry was essentially directed to the saponification of oils and fats, yielding soluble salts of fatty acids, which can be subjected to the same reactions as their non-renewable counterparts. Such reactions allow modifying the chemical and physical properties of compounds to meet the needs of industrial segments working with product formulation and development [16,29].

3.1.1. Main reactions for producing synthetic surfactants

The most common sulfonation reaction employed in the surfactant industry occurs between an alkylbenzene and sulfur trioxide, forming alkylbenzene sulfonates, as illustrated in Fig. 2A. The main feature of this type of compounds is a direct bond between carbon and sulfur. Due to their acidic characteristics, these types of surfactants are normally neutralised as sodium salts as the final product. Although it appears similar, the sulfation reaction has crucial differences that lead to a less stable product, an ester of a mineral acid (generally sulfuric acid), which is susceptible to hydrolysis if not neutralized. The formation of these compounds occurs through a reaction between aliphatic or aromatic alcohols and sulfur trioxide through the carbon–oxygen bond (Fig. 2B). Although most reactions occur with the use of sulfuric acid or its anhydrous form (sulfur trioxide), it is possible to obtain similar compounds using phosphoric acid [16].

Ethoxylation is one of the most important reactions in industries that produce synthetic surfactants, given the possibility of creating numerous tensioactive molecules with different hydrophilic–lipophilic balances. This reaction consists in the creation of ether groups whose chain terminations normally have alcohol functions responsible for the hydrophilic portion of the molecule.

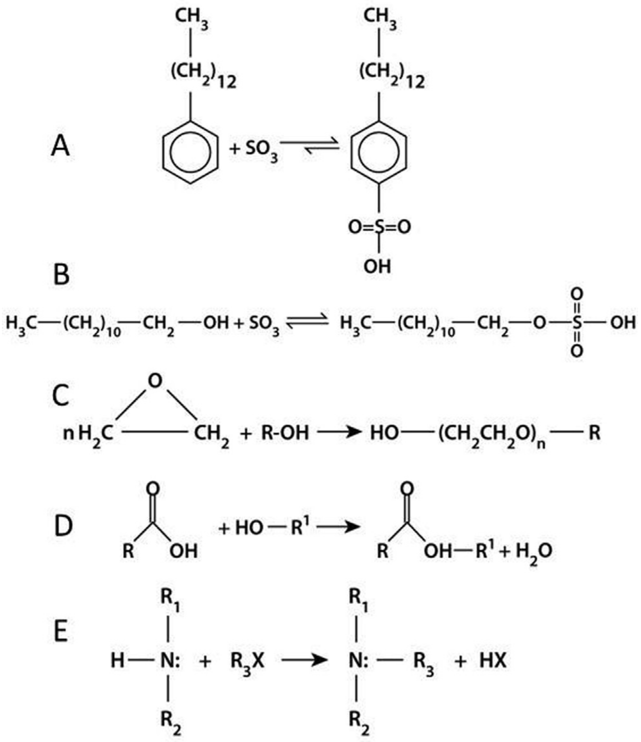


Fig. 2. Reaction between dodecyl benzene and sulfur trioxide to form anionic surfactant dodecylbenzenesulfonic acid (A). Reaction between dodecanol and sulfur trioxide forming the surfactant hydrogen dodecyl sulfate (B). Generic ethoxylation reaction between ethylene oxide and alcohol function (C). Generic esterification reaction between a carboxylic acid and alcohol, forming ester and water (D). Reaction of a secondary amine with halide, forming tertiary amine (E).

The creation of these chains occurs by reaction between ethylene oxide and an alcohol (Fig. 2C), which is generally a fatty alcohol in the case of surfactants [30]. The surfactants produced in this way, known as ethoxylated fatty alcohols, are very numerous, since the length of their chain (described by the subscript "*n*" in Fig. 2C) can vary from one to 10 carbon atoms. Ethoxylation reactions are generally combined with other reactions described in the production of synthetic surfactants [16].

Esterification is one of the simplest reactions employed in the production of surfactants, whose practicality also lies in the wide availability of reagents involved, such as fatty acids found in oils and fats and a compound with alcoholic functions like glycerol or one of the many types of sugars. In general, the esterification process consists of the reaction between an acid (generally carboxylic acid) and an alcohol, as illustrated in Fig. 2D. Monoglycerides are examples of surfactants produced by this type of reaction, which are widely used in the food industry as emulsifying agents. Many of these surfactants are classified as non-ionic and have low toxicity and high biodegradability, especially if derived from renewable sources. Therefore, the cosmetic and food industries often employ them in commercial formulations [31].

Alkylation, which consists of the transfer of an alkyl group from one structure of the molecule to another, can be performed in different ways. This reaction is mainly employed in the petroleum industry to increase the size of the carbon chains of the molecules, as mentioned above. However, some of these processes end up producing branched types of carbon chains, which later proved extremely harmful to the environment [16]; therefore, new types of alkylation have been developed to create linear chains that could be more easily degraded. The creation of longer carbon chains is only one of the possible applications of alkylation in the production of surfactants. Other classes of surfactants that benefit from this type of reaction are cationic and amphoteric surfactants, as an amine can react with a haloalkane to form a substituted alkylamine and the respective halogen acid (Fig. 2E) [32].

Although the hydrophilic head groups of surfactants usually fall into one of the four categories described above, there are a number of exotic hydrophobic "tail" groups, both synthetic and natural, which confer unique surface-active properties to all classes of surfactants, such as achieving extraordinarily low air/water and interfacial tensions and improving consumer and industrial product performance at surprisingly low usage levels [33]. Similarly, naturally derived surfactants extracted from fermentation broths or prepared by partial hydrolysis of natural extracts, the so-called biosurfactants, have unique structural features that cause them to deposit on chemically similar surfaces and modify the surface energy even at very low concentrations [19,20]. According to Zoller [16], the emergence of biotechnology in the 21st century will drive the development of new surfactants and improve the commercial feasibility of known surfactants from such processes, as we will discuss in the following sections.

3.2. Green surfactants (biosurfactants)

Advances in sustainable technologies have driven the search for natural, biodegradable compounds to remediate sites contaminated with hydrocarbons [5,34]. Environmental legislation and governmental restrictions related to the use of toxic detergents in products have also contributed to the development and use of biosurfactants as possible alternatives to synthetic surfactants [35]. Due to their compatibility with the environment and low toxicity as well as numerous other advantages, the replacement of chemical surfactants with these natural compounds has been studied [36]. Indeed, biosurfactants or "green surfactants" are considered the next generation of industrial surfactants, as these compounds meet most of the requirements for low environmental impact industrial projects [8,35,37].

Although for a long time the concept of biosurfactant was restricted only to microbial surfactants, the current classification divides biosurfactants, based on their origin, into first-generation and second-generation compounds [3,38]. First-generation biosurfactants are those extracted and purified from plant-based and animal-based raw materials or entirely produced from renewable resources through chemical synthesis, including, for example, saponins, sugar esters, alkyl polyglucosides and alkanolamines [39]. Main examples of second-generation biosurfactants, which are instead produced entirely from renewable resources or by a biological process (biocatalysis or fermentation), are microbial surfactants such as glycolipids and lipopeptides [35].

The physicochemical properties and classification of biosurfactants are based on their structural characteristics, with a hydrophobic portion consisting of a hydrocarbon chain or one or more fatty acids, which can be saturated, unsaturated, hydroxylated, or branched, linked to a hydrophilic portion, which can be an ester, hydroxyl group, phosphate, carboxylate, carbohydrate, amino acid, or peptide. Most biosurfactants have neutral or anionic polar groups ranging from small fatty acids to large polymers [40,41].

As mentioned above, biosurfactants are of paramount importance in the current scenario, as these compounds are considered ecologically sound products due to their low (or absent) toxicity and high biodegradability. Compared to their synthetic counterparts, biosurfactants are more efficient at reducing surface and interfacial tensions and are tolerant to high temperatures as well as extreme values of pH and ionic strength [34,42]. They are also considered versatile compounds thanks to their broad applicability in the petroleum, chemical, food, pharmaceutical, textile, and agricultural industries [43,44,45,46].

3.2.1. Biosurfactants of microbial origin

Microbial surfactants are a structurally diverse group of compounds ranging from simple molecules, such as phospholipids and fatty acids, to glycolipids, lipopeptides and high molecular weight polymers, such as lipopolysaccharides. The hydrophilic portion can be composed of a carbohydrate, amino acid, cyclic peptide, phosphate, carboxylic acid, or alcohol, while the hydrophobic one can be composed of long-chain fatty acids, hydroxylated fatty acids, or other structures [34,35]. Microbial surfactants are mainly classified into two categories: low molecular weight tensioactive agents (biosurfactants) and high molecular weight tensioactive agents (bioemulsifiers) [47,48].

A variety of microorganisms, such as bacteria, yeasts, and filamentous fungi, are capable of producing biosurfactants with different molecular structures. The main species investigated for this purpose are *Bacillus subtilis, Pseudomonas aeruginosa, Acinetobacter calcoaceticus*, *Candida lipolytica*, and *Starmerella (Candida) bombicola* [23,38,49].

Some microorganisms produce biosurfactants when grown on different substrates. The use of different carbon sources alters the structure of the biosurfactant produced and, consequently, its emulsifying properties. These changes can be beneficial when specific properties are desired for a given application [23,35].

Most biosurfactants are glycolipids, i.e. carbohydrates linked to aliphatic or hydro-aliphatic long-chain fatty acids via an ester bond, the best known of which are rhamnolipids and sophorolipids. Rhamnolipids are extracellular metabolites produced mainly by the opportunistic pathogenic bacterium *P. aeruginosa* on a variety of substrates, which allow to achieve surface tension values around 29 mN/m [50,51,52]. Sophorolipids are produced by yeasts and consist of a dimeric carbohydrate called sophorose linked to a long-chain hydroxylated fatty acid via a glycosidic bond [53]. Although *Starmerella (Candida) bombicola* stands out among the different types of yeast used to produce these biosurfactants [54], a survey of the literature also identified the potential of other species of the genus *Candida* as glycolipid producers, such as *Candida sphaerica* [55], *C. lipolytica* [56,57,58], *Candida utilis* [59,60], and *Candida tropicalis* [61,62,63]. These biomolecules achieve surface tension values of about 30 mN/m.

Among the lipopeptides, surfactin, which is mainly produced by the bacterium *B. subtilis* is considered one of the most powerful biosurfactants ever reported in literature, as it is capable of reducing the surface tension of water from 72 mN/m to 27 mN/m [64]. Table 1 displays the main classes of biosurfactants and their respective microbial sources, while Fig. 3 illustrates the structure of some of the main types of biosurfactants produced.

Table 1
Main classes/subclasses of microbial biosurfactants.

Class	Subclass	Microbial source	Reference
Glycolipids	Rhamnolipids	*Pseudomonas aeruginosa*	[65,66]
		Pseudomonas cepacia	[52]
		Lysinibacillus sphaerica	[67]
	Trehalose lipids	*Rhodococcus sp.*	[68]
		Nocardia farcinica	[69]
	Sophorolipids	*Candida bombicola*	[70,71]
		Starmerella bombicola	[72]
		Candida sphaerica	[55,73]
		Candida magnolia	[74]
		Torulopsis petrophilum	[74]
		Torulopsis apicola	[74]
Lipopeptides	Surfactin	*Bacillus subtilis*	[75]
		Kocuria marina	[76]
	Lichenysin	*Bacillus licheniformis*	[77]
Phospholipids		*Pseudomonas putida*	[78]
		Thiobacillus thiooxidans	[79]
Polymeric biosurfactants	Rufisan	*Candida lipolytica*	[80,79]
	Liposan		
	Emulsan	*Acinetobacter calcoceticus*	[79]
	Biodispersan		
	Alasan		

Table 2
Use and functions of phospholipids (adapted from Dorsa [89]).

Industry	Products	Functions
Food	Baked goods	Modification of baking properties, emulsifier, antioxidant
	Chocolate	Reduction in viscosity, antioxidant
	Margarine	Emulsifier, waterproofing, antioxidant
	Dietetic products	Nutritive supplement
	Solubles	Humectant, dispersant, emulsifier
	Substitute in milk	Emulsifier, humectant, dispersant
Chemistry	Insecticides	Emulsifier, dispersant
	Paints	Dispersant, stabiliser
Textiles	Fabrics	Softener, lubricant
	Leather	Softening agent, penetrating oil
Cosmetics	Hair	Foam stabiliser, emollient
	Skin	Emulsifier, emollient, humectant
Pharmaceuticals	Parental nutrition	Emulsifier
	Suppositories	Attenuating agent
	Creams, lotions	Emulsifier

3.2.2. Biosurfactants of plant origin

Plant-based surfactants are widely distributed throughout the planet, being present in different parts of plants, such as the roots, stems, seeds, fruit, and leaves. They are amphiphilic compounds (hydrophobic and hydrophilic) that constitute a diverse group of compounds characterized by a structure of phospholipids, proteins or protein hydrolysates and saponins [81].

Phospholipids, such as phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol, are surfactants with structures comprising a molecule of phosphoric acid bound to nitrogenous bases (primary or secondary amines) and alcohols. Lecithin is a commercial blend containing various compounds of this class, whose hydrophilic/hydrophobic nature causes it to be classified as a natural emulsifier that also offers stabilizing, thickening, and lubricating properties, with applications in the food, pharmaceutical, detergent, paint, and cosmetic industries [82,83,84,85,86].

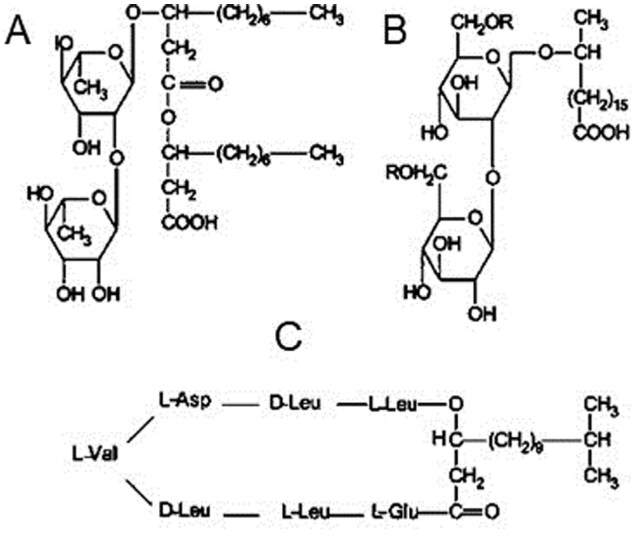


Fig. 3. Chemical structure of most studied microbiological surfactants: (A) rhamnolipid; (B) sophorolipid, and (C) surfactin.

Lecithin is currently one of the most widely used phospholipids in the world market thanks to its surfactant properties and wide availability, as it is produced through the degumming of soybean, rice, canola, cottonseed, palm, corn, and sunflower oils. It is estimated that 95% of commercially available lecithin is produced from soy [84,87].

The technological bases used in processes for the production of lecithin are diverse and normally involve extraction and purification with solvents or a membrane. Production methods have been continually adapted over the past decades to meet the demands of internal and external markets and it has become necessary to find new low-cost sources of lecithin with a high degree of purity. Thus, industries are employing used soybean oil, formerly previously considered a waste product, as a rich, low-cost substrate to increase production [88]. A detailed description of the industrial use of different types of phospholipids and their qualitative characteristics is shown in Table 2.

Proteins have larger molar masses and contain various quantities of hydrophilic and hydrophobic groups randomly distributed throughout the structure. Proteins are emulsifiers that generate more stable emulsions and foams and do not reduce surface tension as much. However, in protein hydrolysates their structure is modified by chemical, thermal, or enzymatic treatments that alter their composition and size and improve their functional properties, such as emulsification and foaming. The main applications of proteins and protein hydrolysates are in the food and cosmetic industries [86].

Saponins are part of a group of tensioactive compounds synthesised through the acetate mevalonate pathway, which lead to a significant reduction in surface tension and abundant foaming [23,90,91]. Foam is one of the consequences of the amphiphilic structure of saponins that ensures their surfactant property. They are stable even in the presence of diluted mineral acids, unlike common soaps [39,84,92]. These biosurfactants are classified, based on the type of aglycone structure, as steroids or triterpenes, which have a high molecular mass (known as sapogenins) bound to long glycidic chains. Steroidal aglycones are less common than triterpene aglycones, but both types may be present in the same plant, as occurs in *Avena* sp. and *Lysimachia paridiformis* (Fig. 4) [93,94,95,96].

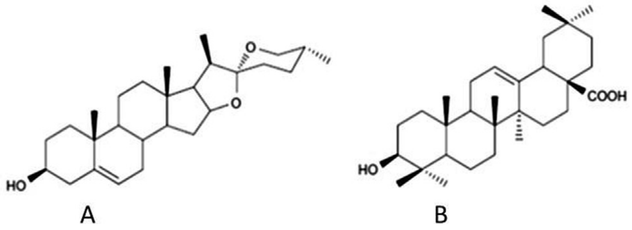


Fig. 4. Representative structure of steroidal (A) and triterpenic (B) saponins.

Saponins are found nearly exclusively in plants, although there are reports of these compounds in some marine animals such as starfish and sea cucumbers [82,97]. A variety of raw materials can be used to obtain saponins, which are widely reported in the literature. The main sources of steroidal saponins are distributed among the families Agavaceae, Alliaceae, Asparagaceae, Costaceae, Dioscoreaceae, Liliaceae, Ruscaceae, and Solanaceae as well as the species *Aspilia montevidensis* (Asteraceae), *Balanites aegyptiaca* (Balanitaceae), *Trigonella foenum-graecum* (Leguminosae), and *Tribulus terrestris* (Zygophyllaceae). Triterpene saponins are found in a number of dicotyledons [98,99].

Saponins have been widely studied and are available commercially as natural surfactants [39,84]. Studies have shown that the surfactant power of saponins from the genus *Quillaja* is similar to that of the commercial tensioactive agent Tween 80, suggesting that these compounds have the potential to replace commercial surfactants in food and beverage formulations [97]. Other biological effects have been attributed to saponins such as immunostimulating, anticarcinogenic, antimicrobial, antifungal, anti-inflammatory, antiviral, antiallergic, and antioxidant properties [100,101]. Therefore, these compounds are widely used in the food, pharmaceutical, cosmetic, agricultural, and environmental sectors, mainly as foaming agents and to reduce surface tension [23]. Table 3 provides examples of plant species from which saponins are obtained.

Other studies report the effect of saponins on the biodegradation of hydrocarbons, the removal of organic compounds, and the hydrophobicity of cells resulting from the use of these plant-based surfactants [102,103]. Zhou et al. [104], comparing the ability of saponin from the pericarp of *Sapindus mukorossi* to mobilize phenanthrene from contaminated soil compared to the synthetic surfactant Tween 80, demonstrated that the plant-based surfactant promoted a linear increase in the solubilisation of the pollutant.

Saponins are quite effective in the biodegradation of hydrocarbons, although their concentration does not have significant influence on cellular hydrophobicity [105]. Smułek et al. [106] reported that the addition of *S. mukorossi* extract can be a useful tool to enhance the microbial degradation of hydrocarbons by strains present in contaminated soil environments. Davin et al. [103], who investigated the potential of saponins as intensifiers of the bioremediation of soils contaminated by polycyclic aromatic hydrocarbons, observed that the saponin solution (4 $g.L^{-1}$) led to an increase in the removal of acenaphthylene, fluorene, phenanthrene, anthracene, and pyrene compared to the control (water) after 28 d.

3.2.3. Economy and global market of green surfactants

The growing interest of consumers in eco-friendly products is a factor that has increasingly influenced the cleaning products market. This demand has prompted the search for natural or derived biodegradable raw materials with fewer preservatives and petrochemicals. Biosurfactants and plant-based compounds are examples of materials that have been gaining more prominence in attempts to create or transform products, making them more ecologically sustainable [8].

Recent studies have shown that the global market believes in new initiatives and is looking for biological replacements for synthetic surfactants, whose sales reached approximately $ 1.74 billion in 2011. In 2013, the world production of biosurfactants was estimated at approximately 344 thousand tonnes, and in 2016 biosurfactant sales surpassed $ 1.8 billion. Estimates for 2018 were $ 2.21 billion and approximately 442 thousand tonnes, with projections for 2020 of $ 2.31 billion and annual production of about 462 thousand tonnes. The expected annual growth rate for this market was 4.3% between 2014 and 2020 [5,127,128]. Sales of biosurfactants are likely to reach 2.6 billion in 2023, with sophorolipids

Table 3
Distribution of saponins in some plant species and applications.

Industry	Family	Surfactant	Applications	Reference
Pharmaceutical	*Quillaja* (Family Quillajaceae)	Triterpenic Saponin	Adjuvants in oral and injectable vaccines	[91]
	Hedera (Family Araliaceae) *Aesculus* (Family Sapindaceae) *Calendula officinalis* (Family Asteraceae)	Triterpenic Saponin	Phytotherapy	[107,108,109]
	Camellia sinensis, *Camellia oleifera* (Family Theaceae)	Triterpenic Saponin	Anti-protozoan	[97,110]
Cosmetics	*Calendula officinalis* (Family Asteraceae) *Camellia japonica* (Family Theaceae) Argania spinosa (Family Sapotaceae)	Triterpenic Saponin	Lipstick and shampoos	[98,111,112]
	Camellia oleifera, *Camellia sasanqua* (Family Theaceae)	Triterpenic Saponin	Antioxidant	[113,114,115]
Agricultural	*Tribulus terrestris* (Zygophyllaceae)	Steroidal Saponin	Additives in animal feed (pet, bird and swine lines)	[116,117]
	Clematis tangutica	Triterpenic Saponin	Antifungal	[92,118,119]
	Camellia Oleifera (Family Theaceae)	Triterpenic Saponin	Insecticide	[120,121,122,123]
Food	*Quillaja saponaria* (Family Quillajaceae)	Triterpenic Saponin	Dentifrices and beverages (sodas, beer, sauces)	[99,124]
	Solanum melongena (Family Solanaceae)	Steroidal Saponin	Fermented vegetables and sauces	[94,125]
	Avena (Family Poaceae)	Triterpenic Saponin and Steroidal Saponin	Sauces and beverages	[126]

and rhamnolipids expected to achieve 8% in sales growth. Another market research predicted that the global biosurfactant market will exceed $ 5.52 billion by 2022, with a Compound Annual Growth Rate (CAGR) of 5.6% from 2017 to 2022 [129].

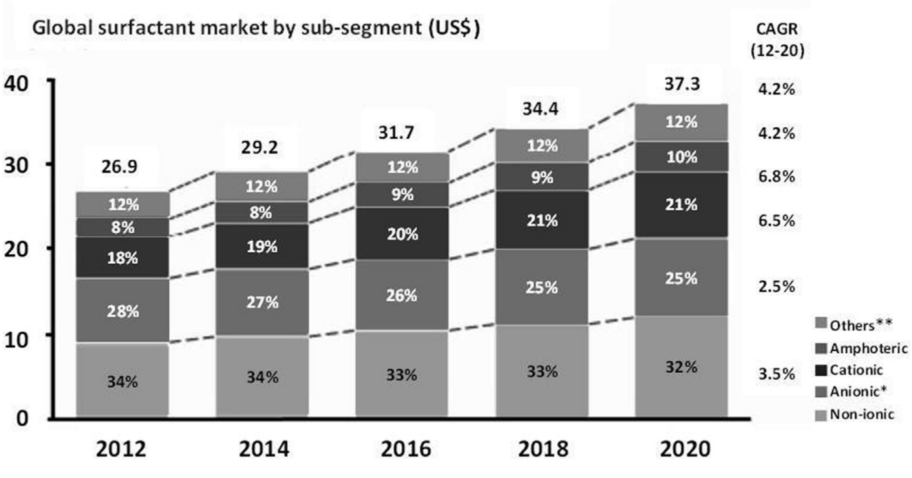
However, one of the biggest obstacles to the widespread use of biosurfactants in industries is their high cost. While the average price of synthetic surfactants, such as sodium dodecyl sulfate and plant-based amino acid surfactants, is one to four dollars per kilogram, the average price of sophorolipids, which are the most viable microbial biosurfactants, is $ 34 per kilogram. The higher price of a biosurfactant is due to production factors, such as lower yields, longer times, higher downstream processing costs, energy requirements for sterilisation, and maintenance of biological culture, among others [130]. Studies, however, have been seeking to reduce costs using agro-industrial waste products as substrate for fermentation processes, increasing yields and reducing downstream processing costs [41,131,132]. Indeed, the choice of a low-cost substrate is important for the economy of the process, as the substrate represents for up to 50% of the final manufacturing cost. The argument of using industrial wastes, however, cannot be limited to the cost of the raw materials alone, since the availability, stability and variability of each component are also critical factors to consider. Moreover, the amount to be used, form (solid or liquid), particle size, texture, packaging, transportation, storage, stability and purity all play a fundamental role in final selection and formulation of any substrate for biosurfactant production [41].

In recent years, various strategies have been used to establish biosurfactants as economical commercial compounds [41]. Response Surface Methodology (RSM) and statistical methods have been applied to optimize the composition of culture media for biosurfactant production. The use of nanoparticles (NPs) is another upcoming approach for enhanced biosurfactant production. Biosurfactant production is significantly affected by many metal salts, especially of Fe. Hence, an upcoming potential strategy for enhanced biosurfactant production is the use of low concentrations of Fe-NPs. Coproduction of biosurfactants with another economically important product in a single bioprocess would allow the entire production chain to become more profitable. One such compound used extensively in various industries is the enzyme lipase. Another strategy that could play an important role in studying and enhancing the large-scale yield of biosurfactants is the use of microbioreactors for optimization studies [133]. Biosurfactants have a variety of applications, which differ in the different purity required as well as the specific structure of the compound used. Hence, utilization of raw product without expensive purification processes would greatly contribute to lowering the overall production cost. This would be particularly profitable in case of environmental applications, where the use of the crude product would be equally effective [41].

Other compounds, such as chemical surfactants derived from vegetable oils and glycerol, are also sustainable alternatives considered by industries when creating formulations and products to satisfy consumers concerned with environmental sustainability [134,135,136]. Once a product is established in the market, it is possible to focus on strategies to increase profit through marketing strategies, improving consumer contact with the product, or through the appeal of safety and innovation with the proposal of a sustainable detergent. The success of a new environmentally friendly product is linked to market planning and the recognition that natural resources are renewable.

Fig. 5 illustrates the representativeness of the expected consumption of some types of synthetic and natural surfactants between 2012 and 2020. Some regions, such as China, Africa, and Latin America, contribute to this estimate. Analysing Brazil, the estimated sales were $ 2.1 billion for the year 2018 [137]. However, the European market was the largest consumer of biosurfactants, reaching 178.9 thousand tonnes in 2013, which represented more than 50% of global consumption. North America was the second largest consumer of biosurfactants in the same year, accounting for more than a quarter of the global market. The Asia-Pacific block had a relatively small consumer market in 2013, although significant projections were indicated for this market up to the end of 2019 due to the presence of large industries in the region [5]. The main biosurfactant-producing companies in the world market are Jeneil Biotechnology, Ecover, Soliance, Saraya, MG Intobio, and AGAE Technologies (Table 5), which together share the target markets of North America, Europe, and Asia-Pacific [138].

The study of the production costs of a biotechnological product is fundamental for the development of an economically sustainable fermentation process, which allows the estimation of global profit margins and ensures the continuity of the product in the market. Initial cost analyses are critical to optimizing production operations and minimizing expenses [9].



* Does not include tensioactive agents for soaps.

** "Others" includes tensoactive agents of silicone, fluorosurfactants, polymeric tensioactive agents and biosurfactants (produced by microorganisms).

Fig. 5. Global positioning in production of synthetic surfactants over time [137].

Table 4
Industrial applications of biosurfactants.

Industries	Properties									References
	Detergents	Emulsifiers	Demulsifiers	Wetting agents	Dispersants	Foaming agents	Corrosion inhibition agents	Antistatic, Antiadhesive agents	Antimicrobial agents	
Petroleum	•	•	•	•	•	•	•			[3,8,9,141]
Industrial cleaning	•	•		•	•	•	•			[8,142]
Food		•		•		•		•	•	[25]
Cosmetic	•	•		•		•		•	•	[23,143,144]
Pharmaceutical	•				•			•	•	[145,146]
Medical		•						•	•	[147]
Agriculture	•			•	•				•	[35,148]
Mining (metals), construction				•		•	•			[20,142]
Nanotechnology		•		•				•	•	[3]

Table 5
Green surfactant-producing companies with different industrial applications.

Company	site	Tensioactive	Application	Reference
Fraunhofer IGB – Germany	https://www.igb.fraunhofer.de/	Glycolipid and cellobiose lipid biosurfactants	Cleaning products, dishwashing liquids, pharmaceutical products (bioactive properties)	[3,150]
AGAE Technologies – USA	https://www.agaetech.com/	Rhamnolipid biosurfactants	Pharmaceuticals, cosmetics, personal care products, bioremediation (*in situ* and *ex situ*), enhanced oil recovery (EOR)	[3,150]
TeeGene Biotech – UK	http://www.teegene.co.uk/	Rhamnolipids and lipopeptides	Pharmaceutical products, cosmetics, antimicrobials and anticarcinogen ingredients	[3,150]
Jeneil Biosurfactant – USA	http://www.jeneilbiotech.com/	Rhamnolipid biosurfactants	Cleaning and oil recovery from storage tanks, EOR	[3,150]
Allied Carbon Solutions (ACS) Ltd – Japan	https://www.allied-c-s.co.jp/english-site	Sophorolipids	Agricultural products, ecological research	[150]
Rhamnolipid Companies – USA	http://rhamnolipid.com/	Rhamnolipid biosurfactants	Agricultura, cosmetics, EOR, bioremediation, food products, pharmaceutical products	[3,150]
Saraya Co. Ltd. – Japan	http://worldwide.saraya.com/	Sophorolipid biosurfactants	Cleaning products, hygiene products	[3,150]
BioFuture – Ireland	https://biofuture.ie/	Rhamnolipid biosurfactants	Washing of fuel tanks	[3,150]
TensioGreen – USA	http://www.tensiogreen.com/index.php	Rhamnolipid biosurfactants	Petroleum industry, cleaning, and oil recovery from storage tanks, EOR	[150]
EcoChem Organics Company – Canada	http://www.biochemica.co.uk/	Rhamnolipid biosurfactants	Dispersant of insoluble hydrocarbons in water	[150]
Logos Technologies – USA	https://www.natsurfact.com/	Rhamnolipid biosurfactants	Petroleum industry, cleaning, and oil recovery from storage tanks, EOR	[3,150]
Synthezyme – USA	http://www.synthezyme.com/index.html	Sophorolipid biosurfactants	Emulsification of crude oil, petroleum, and gas	[3,150]
EnzymeTechnologies – USA		Bacterial biosurfactant (unknown)	Oil removal; oil recovery and processing, EOR	[3,150]
Ecover Eco-Surfactant – Belgium	https://www.ecover.com/	ACS-Sophor/Sophorolipid	Oil recovery and processing, EOR; biofilm removing agent, biofilm growth inhibitor; detergent action	[3,8]
Cognis (BASF) – Germany, USA	http://saifuusa.com/portfolio-item/mildsurfactants/	Green surfactant alkyl polyglucoside (APG) – 0810-65	Shampoo, body wash; facial wash; liquid hand soap; moistened towelettes, laundry, hard surface cleaning	[3]
Cognis (BASF) – Germany, USA	http://saifuusa.com/portfolio-item/mildsurfactants/	Green surfactant alkyl polyglucoside (APG) – 0810H-70N	Industrial and institutional surface cleaning	[3]
Cognis (BASF) – Germany, USA	http://saifuusa.com/portfolio-item/mildsurfactants/	Green surfactant alkyl polyglucoside (APG) – 0810-70DK	Hard surface cleaning	[3]
Paradigm Biomedical Inc – USA	http://www.akama.com/company/Paradigm_Biomedical_Inc_a7bcb2680775.html	Rhamnolipid biosurfactant	Pharmaceutical products	[3]
Kaneka Corporation – Japan	https://www.kaneka.co.jp/en/business/qualityoflife/nbd_002.html	Sodium surfactin	Cosmetics	–
Sabo S.p.A. – Italy	www.sabo.com/sabo/home.php.	Sodium surfactin	Cosmetics	–
Groupe Soliance – France	http://www.soliance.com/dtproduit.php?id = 42	Sopholiance S (Sophorolipid)	Cosmetics and pharmaceuticals	[3]

The vast structural diversity that characterizes biosurfactants and the wide range of properties exhibited by this group of molecules have increasingly attracted the scientific interest of researchers and companies, which has led to an increase in the number of patent applications [138]. Most of the patents relating to biosurfactants concern acquisition processes involving microorganisms, mainly belonging to the genera *Pseudomonas*, *Bacillus*, *Acinetobacter*, and *Candida*, which include an infinity of industrial applications [139,140]. These appear to be effective strategies for overcoming the competitiveness of synthetic products. Therefore, efforts towards the development of biosurfactant production technologies will enable access to innovative products in a field that has been little explored in one country [5].

The market for biosurfactants in Brazil is quite promising, given the existence of companies specialized in the production of these products. Although the biosurfactant industry has shown notable growth in recent decades, the large-scale production of these biomolecules continues to pose an economic challenge mainly due to the huge differences between the necessary financial investment and industrial production. Therefore, for biosurfactant production to become truly viable, the main criteria that should be considered are the type of raw materials, type of microorganisms, proper design of industrial bioreactors, target market, purification processes, properties of the biosurfactant, production conditions, and time required for adequate fermentation and achievable production yields, as discussed above [19].

The target market is also of fundamental importance for the installation of an industrial biosurfactant production project. For cosmetic, medicinal and food products, production is more viable on a small scale, as the methods required to separate the compounds are not cheap on a large scale. Thus, the use of raw fermentation broths could be a viable solution, especially if the application is in an environmental context, as biosurfactants in such cases do not have to be pure and can be synthesized using a blend of inexpensive carbon sources, which would enable the creation of an economically and environmentally sustainable technology for bioremediation processes [19].

3.2.4. Green surfactants manufacturing industries

Biosurfactants, besides being biodegradable, offer the advantages of a low environmental impact and the possibility of *in situ* production using renewable and cheap substrates. These biomolecules have many interesting properties that make them suitable for application in various industrial processes, such as emulsification and de-emulsification activities and dispersion, wetting and foaming capacities. They have also been found to possess several properties of therapeutic and biomedical importance [19,20,23,25]. Various applications for biosurfactants in industry are shown in Table 4.

Manufacturing industries are staking money on biosurfactants due to their potential and prospective characteristics and properties. With the use of microorganisms with high production capacities and inexpensive renewable substrates as raw material, production has been improved on an industrial scale. Regardless of the different composition and applications that biosurfactants have shown, the large-scale industrial synthesis of these compounds is the main goal today [3,149]. In this scenario, the biosurfactant market is expected to overtake the synthetic surfactant market in the future [5,9]. Table 5 lists some of the manufacturers of several types of biodegradable surfactants in different parts of the world and their products with potential use in different sectors.

The production of biotech products has currently become very attractive and promising in Brazil. According to data from *Associação Brasileira das Empresas de Biotecnologia* (ABRABI, Brazilian Association of Biotechnology Companies), the annual revenue of the biotechnology sector in the country is estimated to be between R$ 5.4 and R$ 9 billion, with a percentage of the gross domestic product of about 2.8% [151].

4. Conclusions

Global concern with sustainability has become a competitive edge for industries applying these concepts in their production processes, as the concern with the planet's environmental future has become an emerging trend among companies and consumers. One of the notable advantages of companies in the biotech sector over competitors is the biodegradable, non-toxic nature of these products and the potential for using industrial waste products or sustainably produced substrate as part of their manufacturing process. Another important point that needs to be considered is that the long-term global supply of fossil fuel-derived resources is expected to decline, and price of petroleum to increase, as will short-term market volatility. Furthermore, fossil fuel supply depends upon stability in the socio-political scenario, which is never guaranteed. In this scenario, the interest in green surfactants will increase in the years to come, and the biosurfactant market is expected to overtake the synthetic surfactant market in the long term.

Conflict of interest

The authors declare no competing interests.

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