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Effect of synthetic surfactants on the environment and the potential for substitution by biosurfactants

Phillip Johnson, Anna Trybala,* Victor Starov, and Valerie J. Pinfield

Department of Chemical Engineering Loughborough University, Loughborough, UK

*Correspondence: A.Trybala@lboro.ac.uk

Abstract

The environmental impacts of the use of synthetic surfactants are discussed in this work such as their high levels of toxicity and low biodegradability. These materials destroy aquatic microbial populations, damage fish and other aquatic life, and reduce photochemical energy conversion efficiency of plants as well as adversely affecting waste-water treatment processes. With global usage of surfactants being over 15 million tonnes annually, and an estimated 60% of surfactant ending up in the aquatic environment, there is an urgent need for alternatives with lower adverse environmental effects; this review explores biosurfactants as potential alternatives. The sources and natural function of biosurfactants are presented, together with their advantages compared with their synthetic counterparts, including their low toxicity and biodegradability. Their comparable effectiveness as surfactants has been demonstrated by surface tension reduction, achieved at much lower critical micelle concentrations than those of synthetic surfactants. The limitations and challenges for the use of biosurfactants are discussed, particularly low production yields; such limitations must be addressed before wide range industrial use of biosurfactants can be achieved. Although there has been focus on achieving greater production yields, a remaining issue is the lack of research into the use of biosurfactants in a greater range of industrial and consumer applications to demonstrate their efficacy and identify candidate biosurfactants for production. This review highlights such research as deserving of further investigation, alongside the ongoing work to optimize the production process.

1. Introduction

Surfactants are in widespread use in a range of applications, functioning as detergents, wetting agents, emulsifiers and foaming agents. They appear in consumer and industrial products from foods, healthcare products, to paints and coatings, as well as being a crucial component of many industrial processes such as oil recovery and printing. Global production of surfactants was reported to be 7 million tonnes annually 20 years ago (1), increasing to 12.5 million tonnes in 2006 (2) and to 14.1 million in 2017 with a forecast growth of 18% by 2022 (35). As of 2019 the market size for surfactants was 39,901million USD globally and is projected to grow to 52,417 million USD by 2025. This anticipated growth is now thought to be an underestimate due to the increasing demand for surfactant-containing products as a result of the Covid-19 pandemic (3). The vast majority of surfactants currently in use are synthetic, and these are used in great quantities in households and industry every day. The substantial volume of research and development on synthetic surfactants over many years has resulted in highly optimised use of these surfactants in processes and products in a wide range of industries. However, so ubiquitous are these components that their environmental impacts have too often been overlooked. Below, the current understanding of the adverse impacts of *synthetic* surfactants is presented, along with a discussion of the potential for *biosurfactants* to act as replacements, retaining functional properties but reducing the environmental impacts.

The utilisation of surfactants in numerous applications is due to their surface-active properties; the molecular structure of a hydrophilic head and hydrophobic tail (4–6) leads to the molecules gathering at a phase boundary (for example an air/water interface), thus reducing surface tension and stabilising the system (e.g. an emulsion or foam). Beyond a certain concentration, the critical micelle concentration (CMC) (7,8), further increases in concentration of surfactant lead to no further reduction in surface tension (9). Above the CMC, surfactant molecules aggregate in the bulk phase, a process known as micellization (10), forming micelles in spherical, rod, or disc shapes, or even more complex shapes; the shape of micelles influences the rheological and dynamic properties of the surfactant solution (11). In some applications, the presence of micelles is critical for the functional performance of the surfactant; for example, in a study for a household cleaning product, greater quantities of foam were produced at concentrations above the CMC (12). Antibacterial properties and solubilisation properties of surfactants are also characterised by the CMC point (11,13,14). The CMC provides a clear reference point for surfactant concentration, enabling direct comparison of performance by different surfactants through use of the concentration relative to the CMC.

Surfactants can be separated into different groups depending on the charge of the hydrophilic head of the molecule, these are anionic (negative charge), cationic (positive charge), amphoteric (both negative and positive ions) and non-ionic (no charge) (7,9). Their character often determines the applications to which they are best suited. Anionics are the oldest and most widely used surfactants in detergents; examples include sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS) (which are used in laundry detergents, household and personal cleaning products) (15,16). There are also examples of anionics in the cosmetics industry (17), pharmaceutical industry (13,14) and hydrocarbon removal from soils (7,18). Cationics are used in detergents, fabric softeners and hair conditioners though they are not as effective as anionics for detergency. This is due to the fact that surfaces of fabric and hair are mostly negatively charged, leading to the surfactant being readily adsorbed onto the surface but subsequently difficult to remove (19). However, this strong surface interaction lends cationic surfactants to applications such as hair conditioners and fabric softeners where the adsorbed molecules alter the surface texture, making it feel softer (20). Cationic surfactants also display bacteriostatic properties i.e. preventing the reproduction of bacteria, so they can be used to improve cleaning and antibiotic products (21). Amphoterics (for example lauryl betaine) have charge that is switchable with pH from cationic to anionic, allowing them to be used in different applications depending on the environment (7). Non-ionics are widely used as emulsifiers, wetting agents and foam stabilisation agents (7) though they are often mixed with another ionic surfactant to enhance the ability to remove dirt from the surface; the non-ionic component provides reduced sensitivity to water hardness. Mixtures of non-ionic and anionic surfactants can also achieve a much lower CMC point than individual anionic surfactants, thus reducing the overall quantity of surfactant required to achieve the same detergency effect (22). Many other products exist in which surfactants are used, including firefighting foams, household cleaning materials, and pharmaceutical products and processes (23–31). They are also vital components in processing, such as enhanced oil recovery (EOR) (32,33) and mineral flotation (34,35).

To illustrate the ubiquitous applications of surfactants, let us consider a day in the life of a typical person in a consumer society. The morning shower involves both shampoo and conditioner, typically comprising (respectively) sodium dodecyl sulfate (SDS), an anionic surfactant used for oil removal and lather production, and a cationic surfactant such as Polyquaternium-10, which prevents rapid redeposition of oils. The drive to work is along a road comprising asphalt, laid at a lower temperature than many, due to use of a surfactant, Evotherm (Ingevity, USA), to lubricate the oil/rock interfaces. In the workplace, the carpeted floor has been dye-jet-printed, necessitating use of a cationic surfactant Albafix to enhance wettability and dye fixing. At the end of the working day,

the evening meal comprises many food products that benefit from surfactants, whether natural or synthetic, to enhance their texture and stability. A complex product such as ice-cream includes mono- and di-glycerides, lactic acid esters and propylene glycol esters (36) acting as surfactants. The washing up and cleaning of food surfaces also involves products containing surfactants.

Just from this simple example of a person's daily life it is possible to appreciate the wide range of surfactant usage. An understanding of the effects such chemicals have on the environment and public health are therefore of paramount importance. In this review, the environmental impacts of synthetic surfactants are explored, as well as applications where biosurfactants have been used as replacements including their comparative advantages and disadvantages. Areas are highlighted where further work is needed to address the challenges to industrial-scale adoption of biosurfactants.

2. The Environmental Impact of Synthetic Surfactants

2.1. Release into aquatic environment

Most surfactant ends up released into the environment since the vast majority of consumer products that incorporate them are marketed as down-the-drain disposable (37). Studies have shown that about 60% (by weight) of the total surfactant produced enters the aquatic environment (38); that is equivalent to around 7 million tonnes globally at current levels. Surfactants released into the aquatic environment have been listed as organic pollutants by the British Geological Survey (39), having been detected in surface water. Figure 1 shows the main pathways for contaminants to reach groundwater, as highlighted in that study (39). These pathways include "direct" routes such as through landfill leaching, emergency spills and industrial leaks as well as "indirect" paths through the discharge from a water treatment system.

Surfactants in wastewater (including industrial, domestic and medical -see Figure 1) present challenges for wastewater treatment plants. Surfactants are difficult to remove from water (40,41) due to their molecular properties, so that a residual surfactant content remains after treatment and is discharged. This is not only true for surfactants but other materials that are highly soluble in water (42). In addition, due to their antimicrobial properties, surfactants can reduce the effectiveness of the microbes used to remove pollutants and break down sewage sludge, resulting in greater levels environmental pollution (7,43).

Figure 1: Pathways for contamination to reach groundwater in the urban environment (based on (39)).

Further impacts on the aquatic ecosystem in relation to plant life and microbial activity are explored in more detail below. This includes the effect of synthetic surfactant toxicity on living organisms and how these molecules disrupt biological processes. The lack biodegradability of synthetic surfactants leads to persistence in the environment, although in some cases the partial degradation products have been shown to be more toxic than the parent surfactant molecule. Surfactants also enhance the spreading of other pollutants such as heavy metals which cause additional problems to the ecosystem.

2.2. Effect on micro-organisms

A major concern relating to the environmental impact of synthetic surfactants is the toxicity of some of these molecules to living organisms (5,7,38,44–51) and their effect on biological activity. A study by Effendi et al. (5) observed the effect of detergents on heterotrophic bacteria populations in a river estuary; aquatic bacterial populations were substantially reduced as the concentration of surfactant increased, illustrated in Figure 2. The mechanism for the surfactant effects on micro-organisms depends on the nature of the surfactant. Cationic surfactants interact with the cytoplasmic membrane of bacteria (52) whereas anionic surfactants bind to enzymes and DNA (51); both effects may change the biological function and have detrimental effects on organisms (7,17). Non-ionic surfactants display antimicrobial activity by binding to various proteins which causes cell damage to the bacteria; alkylphenol ethoxylates (APEOs) which make up 7% of global surfactant usage were the subject of this study (53). These molecules are environmentally persistent organic pollutants, due to their very slow biodegradation (54).

Figure 2: Correlation between concentration of surfactant with bacterial cell population in sea water (originally published in “Detergent Disposal into Our Environment and Its Impact on Marine Microbes” by IOP Publishing Ltd) (5).

The release of surfactants into aquatic environments leads to foam formation in rivers (55–57) causing a reduction in the water oxygen level (5), resulting in the deterioration of aquatic ecosystems and potential disruption to the water cycle (51) by hindering evaporation. The long-term exposure of bacteria in the environment to surfactants, which are typically at low concentrations (below the lethal dose), can also lead to bacterial resistance (58,59) in a similar way to that observed for antibiotics. Thus, surfactants may become less effective as anti-bacterial products in the future (60,61).

2.3. Effect on other fauna

In aquatic systems, both fish and shellfish are adversely affected by synthetic surfactants. In fish, the external mucus layers, providing protection against attack by bacteria and parasites, are destroyed by detergents; gills also suffer severe damage (5). The authors stated that fish mortality rate was above 50% at detergent concentrations around 15 ppm; fish eggs were killed at concentrations of only 5 ppm (5).

Further, it has been shown by Ostroumov (62) that synthetic surfactants inhibit the filtering activity of oysters and mussels. Adverse effects on behaviour and development of zebrafish, and deformation of their larvae were demonstrated by Wang et al (47) Karrman et al. (48) reported the effects of surfactants from firefighting agents on algae, bacteria, water flea and fish, using zebrafish as an animal model and applying fish embryo toxicity tests to demonstrate mortality rate as a function of surfactant concentration. They observed acute toxicity for all firefighting foams tested.

Beyond the aquatic environment, cationic surfactants (e.g. cetylpyridinium bromide) have been demonstrated to be toxic to mammalian cells (63), damaging human lymphocytes (a sub type of white blood cells) (64) and rabbit corneal epithelial cells (protective barrier for the cornea) (65). Surfactants, such as the organosilicon category used in agrochemicals, have also been shown to have a negative effect on bees. The study of Chen et al. (50) demonstrated the oral toxicity of three common organosilicon surfactants on honeybees, illustrated by the severe impact on survival rates (as shown in figure 3). They also reported other studies that have identified adverse effects on olfactory learning of bees. This is a major concern as bees are key to the pollination of plants, hence a reduction in bee population could lead to food shortages; some governments have already listed bees on the endangered species list.

There also is the matter of the effect on humans as some surfactants are toxic or irritant to humans (47). Some cleansing products are already marketed that do not use soaping agents (surfactants) but rather have a higher alcohol content for people with sensitive skin. Studies have shown that anionic and cationic surfactants are more toxic than non-ionic varieties, with cationic types being the most toxic (17,66). These cationic surfactants can cause burns and irritation to the eyes, skin and respiratory system in humans (as well as death in aquatic life as noted above) (51).

Figure 3: Displays survival rates of adult honey bees fed on 100ppm methoxy-capped Tri-siloxane surfactant (TSS), hydroxy-capped TSS or acetoxycapped TSS mixed in their sucrose/water diet for 10

days (originally published in “Are organosilicon surfactants safe for bees or humans?” by Elsevier B. V.) (50).

2.4. Effect on flora

It is not just animals and microorganisms that have been shown to suffer detrimental effects linked to surfactants. Masakorala et al. (67) also showed that these molecules reduce the efficiency of photochemical energy conversion, a process that is crucial for plant life. The use of grey water on crops reduces both cost and water waste; however, the presence of surfactants within grey water has been investigated by Bunenheim et.al. (68) where it was found that surfactant caused acute toxicity to lettuce. It was also noted that these effects can be mitigated by use of biological organisms to break down the specific surfactant investigated, although this is not the case for all surfactants in grey water which may be difficult to biodegrade and cause detrimental consequences to the crops. Ying et al. (69) noted that further toxicity data are needed to understand the effects surfactants have on plant life.

In addition, as noted in section 2.2, the presence of surfactants in water can lead to the formation of stable foam on the surface (2), which may reduce the amount of sunlight reaching the river/sea bed due to the opaque nature of foams with a very high liquid fraction, with consequent impact on photosynthesis processes in plants (5).

2.5. Persistence, accumulation and secondary effects

Synthetic surfactants show a lack of biodegradability in some parts of their molecular structure (38,44,46,70,71). When they are released into the environment they persist in the system for long periods and indeed accumulate, particularly where there is little material movement such as in sediment, or in slow-moving currents in rivers, and lakes. This was demonstrated by de Ferrer et al (72) who found a rapid decrease in concentration of linear alkylbenzene sulphates with distance from the sewage outlet during the winter months when the water flow was high, but the drop-off was more gradual in the summer months when the water flow was considerably slower (73). Even though surfactant concentrations in industrial and consumer use (typically 10-15% for dishwashing products) are below levels that are deemed harmful, the real risk arises as they accumulate in the environment, leading to the possibility of reaching concentration levels that may cause harm. Long-term exposure to these materials can lead to adverse effects such as bacterial resistance (see section 3.3 above).

Although some surfactants show little toxicity themselves, their breakdown products may have toxic effects, such as those affecting oestrogen production. A study of the oestrogenic effect of the major classes of surfactants found that whilst the original surfactants had no oestrogenic activity, some breakdown products did (74,75). Several of the products from the degradation of alkylphenol polyethoxylates (APEOs) in particular were shown to have oestrogenic activity, which has been linked to breeding failures and may be carcinogenic (50). Although research indicates that the usage of surfactants in some processes is at concentration levels that do not produce adverse effects (e.g. SDS and others) (45), the study did not account for potential anti-microbial resistance effects due to long term low-level exposure, nor the potential accumulation in the environment and the partial biodegradability of surfactants, that could lead to concentrations reaching toxicity levels.

Further “secondary” effects may result from the primary surfactant contamination. For example, synthetic surfactants may spread other contaminants such as heavy metals to a wider area. This is particular concern in developing nations where heavy-metal contamination is prominent (76). Owing to their surface-active properties, surfactants in the environment can also increase the solubility of

toxic organic compounds in soil, hence increasing the mobility of toxic agents and further contaminating the aquatic environment (51).

Owing to the concerns relating to the environmental impact of synthetic surfactants and the trend for consumer preference for more natural products, the potential replacement of *synthetic* surfactants with *biosurfactants* is being investigated (77). These surfactants offer improved biodegradability and low toxicity that avoid the adverse effects of synthetic surfactants. In the next section, the applications, advantages and challenges for these components is discussed in more detail.

3. Biosurfactants

3.1. Natural sources and natural function

Amphiphilic, surface active materials are abundant in nature, being produced by plants, animals and microorganisms including bacteria and fungi (38,78–82); these are referred to as biosurfactants. Whilst the term biosurfactant is sometimes applied to those surfactants produced specifically by micro-organisms, here we take the term in its most general usage to denote all naturally occurring surface-active species produced by living matter, covering the whole variety of natural sources. In chemical structure, they take a range of forms, such as polar lipids (particularly those from plant and animal sources), fatty acid esters of sugars, or amides of amino acids (82), all with the hydrophilic head-hydrophobic tail character that leads to their surface activity (83).

In natural biological systems, the surface-active agents function in very similar ways to synthetic surfactants such as to act as emulsifiers to overcome solubility limitations, and to modify surfaces for nutrient uptake (82). Indeed, for some micro-organisms, biosurfactants are essential to survival, supporting critical processes such as nutrient uptake, interactions with the host surface (attachment and detachment) and destruction of competing microbes (84). Their role in nutrient uptake mechanisms may include the increase in surface area to volume ratio of material (organic or otherwise), and enhancing bioavailability through solubilisation (i.e. by transferring hydrophobic, water-insoluble material into the aqueous phase) (85). In complex biofilm structures, biosurfactants are believed to support the maintenance of water- and nutrient-channels that are essential to the viability and successful attachment of the colony to the host (86). On the other hand, biosurfactants have been shown to disrupt biofilm formation of other microbes (87–89) and of exhibiting anti-microbial properties as a survival mechanism in densely populated environments (77), for example by the disruption of the viral lipid membrane (84). Biosurfactants are also used for foam formation; tropical frogs and African/Asian freshwater Labyrinth fish produce foams to protect their eggs (90), similarly to land animals such as lotuses and praying Mantis (56). Although naturally occurring foams can also be observed on the seashore, the function of these foams is not yet understood, but is believed to be caused by the reproductive cycle of marine life (90).

The vast majority of biosurfactants are produced by microorganisms (91), and the balance of metabolites produced (including the surfactants) are highly dependent on the type of microorganism and the environmental conditions, including its food source and the environmental pH and temperature (77). The implication of these dependencies is that the production of biosurfactants can be tailored to the intended application by changing the environmental conditions of the organism (92), although this may in itself create challenges for control and optimisation of biotechnological processes. However, it is notable that the properties of many of the resulting biosurfactants and their associated surface activity are not affected by environmental conditions such as temperature and pH (88).

3.2. Structure and functionality

Nearly all naturally occurring surfactants (biosurfactants) are of anionic or non-ionic type (93), with structural differences in the hydrophilic head group. It has been suggested that biosurfactants can be divided into low-molecular-mass (LMM) molecules (650-1126.4 g/mol) and high-molecular-mass (HMM) polymers (>45000 g/mol) (88,91,94–96). LMM surfactants can be further separated into glycolipids, lipopeptides and phospholipids (77,88,91,93,94,96–100), whilst HMM surfactants include polymers and particulate surfactants (77,79,80,84,88,91,93,94,96–105).

The main feature of surfactants, both synthetic and biological, is their ability to reduce surface tension; typically, a 'good' surfactant can decrease the surface tension of water from 72mN m⁻¹ to the region of 35mN m⁻¹ at the CMC (106). The biosurfactants rhamnolipids and sophorolipids can reduce the surface tension of water to 26 mN m⁻¹ and 33mN m⁻¹ respectively (107), similar to the reduction achieved by the synthetic surfactant SDS (25mN m⁻¹) with a CMC value of 2.36g L⁻¹(108). However, biosurfactants achieve this reduction in surface tension at CMC values 10-40 times lower than synthetic surfactants, indicating their greater effectiveness, and therefore the lower quantity of surfactant required to achieve the same results (6,93). These lower CMC values indicate that the number of molecules required to cover the whole interface is much smaller for biosurfactants than for SDS and this is related to their molecular structure. The biosurfactants are larger in size and have many branching chains so that the maximum number adsorbed onto the interface (i.e. at the CMC) is fewer than for smaller, less complicated compounds. For instance, rhamnolipids have CMC values in the range 10-20 mg L⁻¹, significantly lower than SDS. The precise properties depend on the growth environment of the microorganism which determines the molecular structures of the rhamnolipids produced (108). Biosurfactants also have a high temperature tolerance with some exhibiting unchanged surface activity up to 90°C (93), enabling their use in processes for which synthetic surfactants are unsuited.

The structural differences between biosurfactants result in different functionality. For example, LMM molecules are effective at lowering interfacial tension and HMM polymers are more effective as emulsion stabilizers (88). One of the most widely studied biosurfactant classes, glycolipids (LMM type), includes rhamnolipids, trehalolipids, sophorolipids and mannosylerythritol lipids (MEL) (77,91,96) and their chemical structures and natural origin are shown in Table 1. As indicated by table 1, all of the biosurfactants listed show great promise due to their large reduction in surface tension achieving values similar to those achieved by SDS (25mN m⁻¹). Rhamnolipids are the most widely studied group of biosurfactants and show the most promise for application (77,97,108–112). They are produced predominantly by various strains of *Pseudomonas aeruginosa*, bacteria that are able to use a variety of water soluble and hydrophobic substrates as carbon sources in their production of rhamnolipids (79). Rhamnolipids have two hydrophilic head groups (i) a carboxylate group resulting in the anionic character of the biosurfactant and (ii) a rhamnosyl group that contributes to the bulkiness of the head group (97). These structural features lead to great versatility in function as foaming (113), detergency, (114) wetting, emulsifying (115,116) and demulsifying (77,93), with applications in cosmetic, agricultural and food industries (109). Their emulsifying properties play a key role in achieving the desired texture in food products. The same functional properties are of great interest to the petroleum industry for hydrocarbon emulsification, predominantly for enhanced oil recovery and bioremediation (109). For cosmetic applications, rhamnolipids show compatibility with skin and produce very low irritation (109). In their functional performance as surfactants, such as detergency, foam formation and emulsification, rhamnolipids have been shown not only to outperform other biosurfactants but also synthetic surfactants as well (77). In addition rhamnolipids show antimicrobial activities (97), and thermostability. However, in

contrast to synthetic surfactants, they are readily biodegradable, ecologically compatible and non-toxic.

Another class of biosurfactant, saponins, this time derived from plants (117), are non-ionic and have many useful properties such as foaming, emulsification, solubilisation and antimicrobial activity (118). This has led to their application in food, cosmetic and pharmaceutical industries (119). Surprisingly saponins were initially an undesired component in foods due to their bitter taste (120) and hence most early research was focussed on their removal (120,121). However, there are many useful benefits of saponins such as cholesterol-lowering and anti-cancer properties (122,123); these have led to attempts to utilize these biosurfactants in the pharmaceutical and food industries. Another plant-based surfactant that has been shown as a green alternative for the synthesis of gold nanostructures is VeruSOL-12, a biosurfactant derived from coconut and castor oils (124). Extracts from the plants Pyagi Phool and Ritha are traditionally used as cleaning agents in west Bengal (125). Surfactant extracted from Ziziphus Spina Christi has also been utilised in oil recovery (126,127) and has been investigated for its adsorption behaviour into carbonate rocks (128,129).

Table 1: Glycolipid biosurfactants, their structure and source (77,96,130–133).

Biosurfactant	Chemical structure and molecular weights	microorganism	Surface tension in water at CMC	Example application.
Rhamnolipid	504-650 g mol ⁻¹ (133)	Pseudomonas aeruginosa	29 mN m ⁻¹ (101)	Soil washing for the removal of crude oil: Rhamnolipids were observed to remove 44% of the crude oil from the investigated area, acting as an emulsifier to allow for the transport of the hydrocarbons out of the soil (134).
Trehalolipids	1211 g mol ⁻¹ (135)	Rhodococcus erithropolis	29 mN m ⁻¹ (136)	Biomedical: Trehalolipids can be utilized for their antitumor activities (137).

Sophorolipids	620-720 g mol ⁻¹ (138)	Candida bombicola	33 mN m ⁻¹ (107)	Dishwasher solutions: Sophorolipids have been utilized commercially by Saraya as a cleaning agent (a Japanese company) (139,140).
Mannosylerythritol lipids	634 g mol ⁻¹ (135)	Candida antartica	28 mN m ⁻¹ (141)	Skin care: Mannosylerythritol lipids showed potential for repair of damaged and dry skin, due its ability for water retention indicating high moisturization effect (142).

3.3. Advantages of biosurfactants

The main advantages of biosurfactants compared to synthetic surfactants are biodegradability (97,143,144), low toxicity (97,143,144), biocompatibility, digestibility, their effectiveness at a wide range of temperatures and pH values, the abundance of their natural sources, their adaptability and antimicrobial activity (77,97,144).

For products intended for direct human consumption or use (e.g. food, skincare products, pharmaceuticals and nutraceuticals), the characteristics of digestibility and low toxicity are of crucial importance, lending biosurfactants a key advantage over their synthetic counterparts. The use of biosurfactants to replace synthetic surfactants in foods has already been demonstrated (77,84,97,144), often utilising their emulsification and de-emulsification effects. The majority of synthetic surfactants have harmful effects on the human body, and their use in products for human consumption is therefore limited by regulation; the low toxicity of biosurfactant replacements reduces these limitations and biosurfactants are generally regarded as safe for foods (88). Biosurfactants also offer benefits in the production environment for products such as foods and pharmaceuticals, due to their antimicrobial properties and their ability to disrupt biofilm formation, thus preventing the establishment of microbes with potential health hazards in process equipment (88).

As noted in the introduction, the majority of surfactant material ends up in the aquatic environment, whether from usage and disposal of products, from industrial processes or from unintended events (Figure 1); such contamination can be direct or indirect (i.e. subsequent to waste-water treatment). The biodegradability of biosurfactants is therefore of great benefit since, even when released into the environment, these will breakdown rather than persisting and potentially accumulating to toxic levels as may be the case with synthetic surfactants (see section 2.5). Biosurfactants are therefore well-suited for applications such as cosmetic and detergent products (85,112), for example, where substantial quantities of product end up down the drain. Their low toxicity to flora and fauna means

that biosurfactants released into the environment present less of a threat than synthetic surfactants (96,145–147). In addition, biosurfactants have also been shown to have positive implications for water treatment. Perez-Ameneiro et al (148) found that applying a lipopeptide biosurfactant in water treatment improved the removal of sulphates. However, an area requiring further investigation is the potential effect the antibacterial properties of biosurfactants have on microorganisms in water treatment which may reduce their effectiveness.

Biosurfactants also offer benefits regarding the adaptability of their production and applications. The composition and structure of the biosurfactants produced by microorganisms can be modified by changing the environmental conditions of the organism (92). The properties of the biosurfactants produced by the microorganism can therefore be tailored to a particular application by adjusting the microorganism environment. This has been explored for use in the pharmaceutical industry in clinical trials by Reid et al (149) showing that probiotic lacto-bacilli was a possible treatment for bacterial infection providing a possible alternative to the antibiotic traditionally used. The fact that some biosurfactants exist that retain their surface-active properties even at relative extremes of pH and temperature permits their use in applications where the majority of synthetic surfactants would be poorly suited, whether those extreme conditions pertain to the processing stages or the final product application.

3.4. Potential applications of biosurfactants

Owing to their enhanced environmental credentials in addition to their effective surface-active properties, biosurfactants are currently being investigated as replacement for conventional synthetic surfactants in a number of industries including oil production, environmental remediation, industrial cleaning, foods, pharma and personal care.

In the oil industry, surfactants are utilised for oil extraction in both enhanced oil recovery (EOR), involving formation of foams, and bitumen recovery (93,150), where crude oil is extracted by surfactant. In the transportation of crude oil through pipelines, surfactants are used as emulsifiers to substantially reduce the viscosity to facilitate transportation (93). Using *biosurfactants* as emulsifiers enables the emulsions to be readily split by enzymes, thus allowing the oil to be dewatered easily. Another example where surfactants can provide benefit is for the cleaning of oil tanks; due to the highly viscous nature of the deposits, conventional pumps cannot remove them. Solvent washing and/or manual cleaning can be used but these processes are expensive and hazardous. Use of surfactants, whether synthetic surfactants or biosurfactants provides an alternative method for removal through formation of oil in water emulsions (93).

Biosurfactants can also be applied to remediation processes, where their surface activity enables them to bind or emulsify pollutants (93,106,151,152). In the aftermath of the Deepwater Horizon oil spill in the Gulf of Mexico, synthetic surfactants were used as dispersants to break up the oil into droplets to increase the surface area to volume ratio so that the oil could be subsequently consumed by microorganisms in a targeted bioremediation strategy (151). However, the synthetic dispersants themselves were toxic; using biosurfactants as replacement, with their biodegradability and lower toxicity, would further reduce the environmental impact of such remediation processes.

Bioremediation is also applied to soil to remove hydrocarbons (109) by supporting their desorption, and to remove heavy metal contaminants; in both cases, the biosurfactants bind the pollutant to enable its transport out of the polluted soil (143,153–156). In a comparative study of soil remediation with biosurfactants and synthetic surfactants, by Wang and Mulligan (143), it has been demonstrated that the 0.5% concentration of the biosurfactant rhamnolipid (in water) was able to remove 61.7% cadmium (Cd) and 51% of nickel (Ni) whereas the same concentration of the synthetic

surfactant Triton X-100 removed only 52.8% and 45.2% cadmium and nickel respectively. In this instance, biosurfactants were more effective for heavy metal removal than synthetic surfactants.

Having already noted the advantages that biosurfactants present for the food industry, (section 3.3), it is worth considering the many applications in foods that offer potential for the replacement of synthetic surfactants by biosurfactants (88,95). Surfactants are already widely used as food formulation ingredients due to their emulsion formation and stabilization properties. In addition, surfactants improve texture and shelf-life of products; these properties pertain to both synthetic and biosurfactants. A lot of work has been concentrated on rhamnolipids but another important biosurfactant group are saponins which have recently been used for hygiene management against *E. coli* (157) and are being investigated for general use in food products as they are already naturally present in many food ingredients (158). Biosurfactants have many uses in the pharmaceutical industry due to their antimicrobial and antiadhesive properties thus providing an alternative to traditional antibiotics (84), as supported by clinical trials by Reid et al (149). There has even been suggested use of biosurfactants in treating SARS-CoV-2 (Covid-19) due to their antiviral properties, attacking the lipid membrane of the virus cell in a way that does not negatively affect the host (159). Due to their emulsifying properties and the low irritation caused by biosurfactants they have multiple uses when it comes to cosmetic applications (77,84,97,144,160). Rhamnolipids, for example, have been used as cosmetic additives (161) and were recently used to create lip gloss formulations (162) in combination with silica particles.

3.5. Biosurfactant production

It is clear that there are many applications where biosurfactants offer great potential as replacements for their synthetic counterparts, and indeed present additional benefits including the reduced environmental impact. However, the uptake of biosurfactants at industrial scale will be determined by the economic viability of their use (93). For the most widely studied class of biosurfactants, rhamnolipids, current challenges remain in relation to high production costs and low production yields (77,163).

A key target for enhancing the economic viability of biosurfactant production from microorganisms is the choice of raw material which the microorganisms consume, to both maximise yield of the biosurfactant (over other metabolites) and to reduce cost of that material for example by use of waste products (93). The production of rhamnolipids and surfactin has been demonstrated using agro-industrial wastes (111) and olive mill waste (112) as growing media, showing the potential for further environmental benefit by waste re-use in addition to the cost benefit. Other examples include producing rhamnolipids using waste frying oils (164), as well as other oil wastes such as corn, palm and soybean (165). Waste food products have also been investigated as growing media, such as distillery and curd whey wastes (166) and potato substrates (167). These studies focus not only on demonstrating biosurfactant production from waste products, but also on maximising the yield of the biosurfactant with particular feedstocks.

Optimization of reactor design is another key component to achieving economically viable production of biosurfactants, to ensure that the maximum amount of biosurfactant is extracted from the process and that the loss of material is limited (93). There is no surprise that this has directed current investigations to concentrate on streamlining the production process to make their use viable (163–170). Current investigations to maximise yield have been focused on the growing media; this cannot only reduce cost (by use of waste feedstocks) but the change in growing media also changes the amount of nutrients available to the organism, thus changing the yield of biosurfactant. A lot of studies including the two already mentioned are concentrated on the material on which the

microbes will grow to try and maximize the yield of biosurfactant produced using low cost materials. For rhamnolipid production, the choke point that restricts productivity in bioreactors is the severe foam formation during the fermentation process, which limits the working efficiency of the bioreactor, and leads to substantial product loss in the foam overflow (110).

3.6. Current challenges

The focus of research and development in biosurfactants has been on the biotechnology of their production. As a result, there has been a neglect of the study of *applications* for biosurfactants, in particular the selection of appropriate biosurfactants suited to particular applications and the direct comparison of the performance of biosurfactants with their synthetic surfactants in those specific applications (93). Without these studies, there is no indication of which biosurfactant or class of biosurfactants is best suited for each application. One example is the formation of foams for household cleaning applications. Not all surfactants are good foaming agents but a lack of research into this application means that it is not yet known which biosurfactants would be the best replacement for synthetic surfactants for stable foam formation. Although models have been developed for synthetic surfactant foams and their interaction with porous media (e.g. sponges) (12,171–175), similar studies with equivalent biosurfactants have so far been overlooked. There exists, therefore, a knowledge gap in appropriate biosurfactant selection for industrial and commercial applications and a full understanding of their performance. Research in this area would provide an indication of the most promising candidate biosurfactants and microorganism strains, thereby feeding into the optimisation of commercial production and selection of raw materials for *targeted* biosurfactants whose efficacy in the intended application has already been identified.

As biosurfactants are more widely adopted in industrial production, the lack of supply due to low production yields will become a serious issue. Since there is already some use within the food industry it may find itself competing for biosurfactants with the oil industry due to their increasing use of surfactants and interest in biosurfactants for EOR and bioremediation. The impact of the problem may be reduced by the recommended further research into applications which will help indicate the biosurfactants best suited to particular products. This could potentially increase the range of biosurfactant candidates, thus reducing competition for the same biosurfactant for use in different applications and industries. Future financial investment in the development of production methods to improve yields is predicated on the demonstration of biosurfactant effectiveness in relevant industrial applications. As indicated previously, one of the main advantages of biosurfactants is that they are readily biodegradable, but this may also prove an issue with the shelf life of biosurfactant products. Due to their relatively short life span there is a risk of the biosurfactants breaking down before making it to the point of use.

The high production costs of biosurfactants remain an issue, in spite of the environmental benefits presented by replacement of synthetic surfactants with bio alternatives, and the consumer push towards natural products. Costs of production for synthetic surfactants are considerably lower and yields higher, since they use well-established chemical processes and do not rely on the expensive culture of microorganisms for their production. As a result, companies have not yet been willing to switch from synthetic surfactants to safer and environmentally beneficial alternatives. However, a fair comparison of the costs must consider the total lifecycle costs not just the costs of production; this should include the costs of environmental damage and remediation, such as clean-up of synthetic surfactants and possible fines due to damages caused to the ecosystem. Further investigation of the full lifecycle costs should be conducted in relation to the case for biosurfactant use despite the higher economic cost of production.

4. Conclusion

Surfactants are widely used in many industries; presently synthetic surfactants are the most common surfactant type, but have been shown to cause adverse effects to the environment and detrimental effects when it comes to human consumption. The advantages of synthetic surfactants are that they are well established and cheap to produce. Biosurfactants have been shown to have a wide range of advantages including biodegradability and low toxicity, thus avoiding the problems that synthetic surfactants cause. However, the current challenge for biosurfactants is that they have a high production cost and are difficult to mass-produce.

Previous research on biosurfactants has focused on reduction of production costs and improvement of yields. This has led other important areas of investigation to be neglected, such as the demonstration of biosurfactant use in industrial applications and comparison with synthetic surfactants for example foamability, cleaning and wettability. Investigating these aspects of performance will help indicate which biosurfactants and strains are equally good or superior to the synthetic surfactants currently being used. This greater focus on industrial applications would lead to greater interest from companies to embrace the use of biosurfactants over synthetic surfactants, and potentially to further investment in optimising and expanding their production. A full consideration of the lifecycle costs of biosurfactants in comparison with synthetic counterparts is also needed to properly evaluate the relative costs of biosurfactants against the benefits. The main challenges for the widespread adoption of biosurfactants is to demonstrate that they are as effective as their counterpart synthetic surfactants and that they are economically viable.

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