BIOSURFACTANT: CLASSIFICATION, PROPERTIES AND RECENT APPLICATION IN COSMETIC.

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Abstract: Biosurfactants are surface-active biomolecules that are produced by microorganisms from renewable resources as plant oils or sugar. Biosurfactants are used in cosmetic or in cleaning and laundry agents. One of the greatest strengths of microbially produced biosurfactants is their structural variety. They show various properties i.e. lower toxicity, higher biodegradability and environmental compatibility as compared to their chemical surfactants. Biosurfactants are commonly classified based on their biochemical nature or the microbial producer species with regard to structure .they have application in biotechnology and cosmetics because of their multi-functions i.e. detergency, emulsifying, foaming and skin hydrating properties. Some biosurfactant can be served as antimicrobials. Biosurfactants show very low critical micelle concentration (CMC) values if compared with synthetic surfactants and are stable at a wide range of temperatures and pH values . They show many promising characteristics for cosmetic applications. In this study the current status of research and development on rhamnolipids, sophorolipids, mannosyloerythritol lipids, trehalipids, xylolipids and lipopeptides particularly their commercial application in cosmetics is describe.

***IndexTerms* - Biosurfactants, lipopeptides, Manosyloerythritol lipids, Sophorolipids, Trehalipids, Xylolipids .**

I. INTRODUCTION:

Surfactants are amphiphilic molecules consisting of a hydrophobic head and a hydrophobic tail due to their amphiphilic nature, surfactants can decrease surface and interfacial tension in water-oil and oil-water systems[1]. These compounds find applications in variety of industrial processes involving emulsification, foaming, detergency, wetting, dispersing or solubilization. Surfactants produced from chemically-based materials are known as synthetic surfactants and those from biologically-based material are biosurfactants[1][2].

Biosurfactants are amphiphilic compounds produced in living surfaces, mostly on microbial cell surfaces or excreted extracellular hydrophobic and hydrophilic moieties that povide the ability to accumulate between fluid phases, thus reducing surface and interfacial tension at surface and interface respectively[3].

Biosurfactants have various physical and chemical properties, such as law toxicity, biodegradability, foaming ability, stable activity at extremes of pH, and temperature[4]. These biosurfactants has tremendous applications in various fields such as in oil recovery, cosmetics, agriculture, food, pharmacy and medicine. Biosurfactants has antimicrobial as well as anticancer activity. They are also used as anti-adhesive agents as they have ability to disrupt the biofilm. It also showed antiviral activity[5]. They also shown suitable application including as anti-aging and wound-healing agents and as cleaning products, emulsifiers in food, dispersants in pesticides, anti-fungal agents, and environmental bioremediation and enhanced oil recovery technologies[6].

Biosurfactants are structurally a very diverse group of biomolecules. Various methods for a general screening of biosurfactant producing strains are based on the physical effects of surfactants. Alternatively, the ability of strains to interfere with hydrophobic interfaces can be explored. The screening methods can give qualitative and quantitative results. The screening methods for biosurfactant producing microbes are based on the interfacial or surface activity[7]. The methods which are applied for screening of biosurfactant producing microbes are included Direct Surface/Interfacial Tension Measurements e.g Du-Nouy-Ring Method, Stalagmometric Method, Pendant Drop Shape Technique and Axisymmetric Drop Shape Analysis by Profile and included Measurements Based on hemolytic assay, bacterial adhesion to hydrocarbons (BATH) assay, drop collapse assay, oil spreading assay, emulsification assay[7][8].

II. PROPERTIES OF MICROBIAL SURFACE ACTIVE COMPOUND :

2.1 Surface and interfacial activity:

Biosurfactants produce a lower surface tension at a lower concentration, it gives greater effectiveness and efficiency in comparison to conventional surfactants.

2.2 Tolerance to temperature, pH and ionic strength:

Many biosurfactants can be used under extreme conditions like the lipopeptide from *Bacillus licheniformis* is stable at temperatures around 75°C for up to 140 hours and within a pH range of 5 to 12. Biosurfactants also tolerate salt concentrations up to 10%, whereas 2% NaCl is sufficient to inactivate conventional surfactants.

2.3 Biodegradability:

Biosurfactants are easily degraded by bacteria and other microorganisms in water or soil, which makes them adequate for bioremediation applications and waste treatment.

2.4 Low toxicity:

Biosurfactants have received greater attention due to the increasing concern on the part of the population regarding the allergic effects of artificial product. Moreover, the low degree of toxicity of these compounds allows their use in food, cosmetic and pharmaceutical products.

2.5 Availability:

Biosurfactants can be produced from widely available raw materials and can even be produced from industrial waste.

2.6 Specificity:

As complex organic molecules with specific functional groups, biosurfactants are specific in their actions, which is of considerable interest regarding the detoxification of specific pollutants as well as in particular applications in the food, cosmetic and pharmaceutical industries.

2.7 Biocompatibility and digestibility:

These properties allow the application of biosurfactants in the food, cosmetic and pharmaceutical industries.[9].

III. CLASSIFICATION OF BIOSURFACTANT [10]

Biosurfactants can be classified according to their chemical structure and microbial origin. They are classified into two categories, first is high molecular weight and low molecular weight molecules. Low-mass surfactants include glycolipids, lipopeptides and phospholipids, whereas high-mass surfactants include polymeric and particulate surfactants[11].

3.1 Glycolipids:

Glycolipds are carbohydrates that combines with long-chain aliphatic acids or hydroxyl fatty acids that links with either ester or an ether group[11]. Examples: rhamnolipids produced by *pseudomonas aeruginosa* and sophorolipids produced by species of *candida*[9].

3.2 Lipopeptides and lipoproteins:

Lipopeptides and lipoproteins are a class of biomolecules known for their bio-surfactant activities. They are cyclic lipopeptide containing a lipid linked to a polypeptide or amino acid chain. Cyclic lipopeptides like gramicidins (decapeptide antibiotic) and polymyxins (lipopeptide antibiotic) show remarkable surface active properties[10]. Example: Surfactin produced by *Bacillus subtilis* is another well studied cyclic lipopeptide of this type and a powerful bio-surfactant, made of seven amino acid ring attached with fatty acid, hydroxy-methyl tetradecanoic acid. Lichenysinis another of this type which act synergistically and exhibit excellent temperature, pH and salt stability[10][9].

3.3 Fatty Acids:

Fatty acids produced from alkanes are also considered as surfactants.They have OH group and alkyl branch. Example is Corynomucolic acid. The hydrophylic and lipophylic balance of fatty acids are clearly related to length of hydrocarbon chain. For lowering surface tension most active saturated fatty acids are in the range of C12-C14.[13].

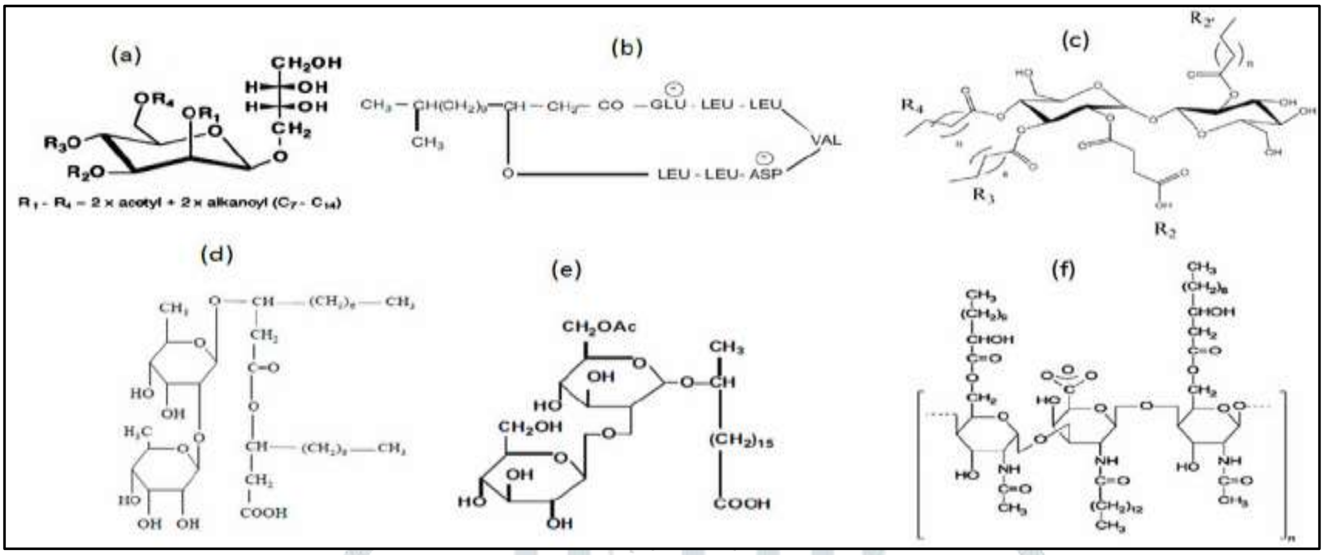
3.4 Phospholipids:

Structures common to many microorganisms. Example: biosurfactant from *Corynebacterium lepus*; Fatty acids, neutral lipids (some classified as glycolipids) and hydrophobic proteins[9].

3.5 Polymeric Biosurfactants:

Examples are Liposan, Emulsan, biodispersan, alasan, mannoprotein and polysaccharide-protein complexes. Liposan is composed of 83% carbohydrate and 17% protein and is produced by *Candida lipolytica*. Mannoproteins are produced by *Saccharomyces cerevisiae* and contain 44% mannose and 17% protein.[13]

Table 1: chemical structures of some common biosurfactants (a) monosylerthritol lipid (b) surfactin (c) trehalose lipid (d) sophorlipid (e) rhamnolipid (f) emulsan [12]



IV. MECHANISMS OF INTERACTION

Biosurfactants tend to interact with the phase boundary between two phases in a heterogeneous system, defined as the interface. Biosurfactants are amphipathic molecules with both hydrophilic and hydrophobic moieties that partition

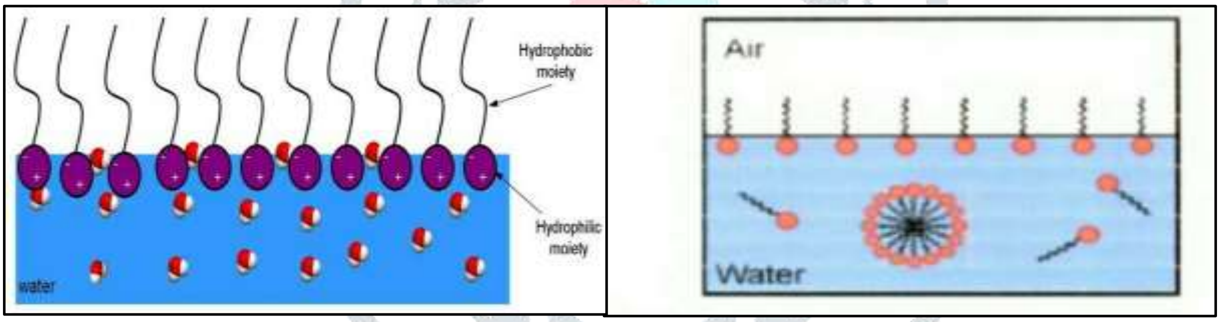


Figure 1: Biosurfactants at Water and Air Interface

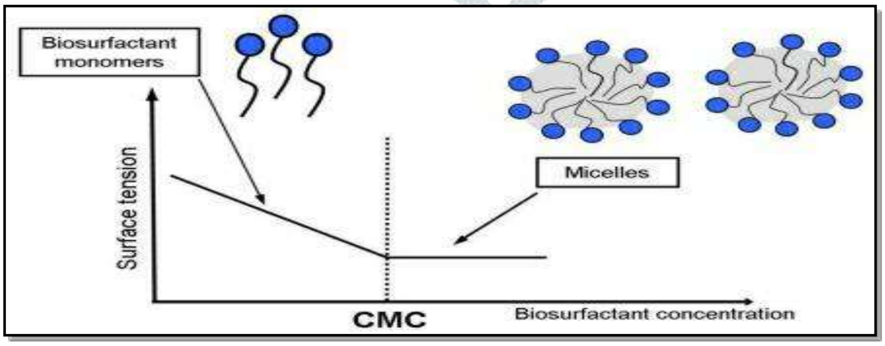


Figure 2: The relationship between biosurfactant concentration, surface tension and formation of micelles[14].

preferentially at the interface between fluid phases that have different degrees of polarity and hydrogen bonding, such as oil and water or air and water interfaces (Fig 2)[15]. The most active biosurfactants can lower the surface tension and the interfacial tension. Biosurfactant activities depend on the concentration of the surface-active compounds until the critical micelle concentration (CMC) is obtained. At concentrations above the CMC, biosurfactant molecules associate to form micelles, bilayers and vesicles (Fig 3). Micelle formation enables biosurfactants to reduce the surface and interfacial tension and increase the solubility and bioavailability of hydrophobic organic compounds. The CMC is commonly used to measure the efficiency of surfactant. Efficient biosurfactants have a low CMC, which means that less biosurfactant is required to decrease the surface tension. Micelle formation has a significant role in microemulsion formation. Microemulsions are clear and stable liquid mixtures of water and oil domains separated by monolayer or aggregates of biosurfactants[14].

The CMC of biosurfactants (measure of efficiency) ranges from 1 to 2000 mg/L, their interfacial tension (oil/water) and surface tension are around 1 and 30 mN/m, respectively. Data on the CMC of biosurfactants are difficult to interpret or correlate. Table 1 offers as comparison of the CMC of biosurfactants and their chemical counterparts, demonstrating much lower CMCs for the former group. In principle, a lower CMC denotes greater efficacy of the surfactant and, from the economic standpoint, favours its use in industrial processes[9].

Table 1: Examples of critical micelle concentration of biosurfactants and chemical surfactants [9][17].

Surfactant	CMC (mg/l)
Sophololipids	43.0
Rhamnolipid	20
Sarfactin	9.4
Arthrofactin	9
Phosphatic acid	70
Sodium dodecyl sulfate	270
Sodium lauryl sulfate	2000 to 2900

Table 2. Examples of biosurfactant properties in the cosmetic field.

Bio-Surfactant Type	Bio-Surfactant Name	Name of microorganism	Properties	Reference
Glycolipids	Rhamnolipid	*Pseudomonas aeruginosa*	Foaming, Antibacterial, Anti wrinkles and Anti-aging	[18]
	Sophorolipids	*Torulopsisbombicola, Wickerhamielladomercqiae*	Moisturizing, Antibacterial, Antioxidant and Depigmenting	[19]
	Mannosylerythritollipid	*Candida Antarctica*	Antimicrobial	[19]
	Xylolipid	*Lactococcuslactis*	Antibacterial	[20]
	Cellobiolipids	*Ustilago maydis*	-	[21]
	Flocculosin	*Pseudozymaflocculosa*	Antifungal agent and Antimicrobial	[23],[24]
	Glucolipid	*Burkholderiacenocepacia*	-	-
	Glucose, Fructose Sucroselipids	*lArthrobacterparaffineus, Corynebacterium, Nocardia and Brevibacterium*	Flavoring agent, Skin conditioning agent,	[25],[26]
	Monoacylglycerol	*Candida ishiwadae*	-	-
	Diglycosyl diglycerides	*Lactobacillus fermenti*	-	-
	Polyol lipids	*Rhodotorulaglutinis, Rhodotorulagraminis*	Antifoaming agents and Antibacterial agent	[27]
	Lipopolysaccharide	*Klebsiellaoxytoca*	-	-

Table2. Examples of biosurfactant properties in the cosmetic field(cont.)

Bio-Surfactant Type	Bio-Surfactant Name	Name of microorganism	Properties	Reference
Lipopeptides and lipoproteins	Surfactin	*Bacillus subtilis*	Anti-aging, Anti-wrinkle, Skin penetration agent, Foaming agent,Sunscreening agent and emulsifier	[28]

	Arthrofactin	*Arthrobacter sp*	Treatment of acne, moisturizer	[29],[30]
	Iturin	*Bacillus subtilis*	Antifungal, antibacterial	[31]
	Fengycin	*Bacillus subtilis*	Antibacterial	[22]
	Lichenysin	*Bacillus licheniformis*	Antibacterial	[22]
	Pumilacidin	*Bacillus pumilus*	Antibacterial	[32]
	Peptide-lipid	*Bacillus licheniformis*	-	-
	Serrawattin	*Serratia marcescens*	-	-
	Viscosin	*Pseudomonas fluorescens*	-	-
	Gramicidin	*Brevibacillus brevis*	Antibiotic	[33]
Fatty acids, Phospholipids and Neutral lipids	Fatty acids	*Corynebacterium lupus*	Cleansing agent, surfactant, opacifying, emulsifing agent	[34]
	Corynomycolic acid	*Penicillium*	-	-
	Spiculicporic acid	*Penicillium spiculisporum*	-	-
	Oleic acid	*Issatchenkiaorientalis*	Emulsifying agent and Emollient	[35]
	Neutral lipids	*Nocardia erythropolis*	-	-
	Phospholipids	*Acidithiobacillusthiooxidans*	Emulsifier,liposome former, solubilizer and wetting agent	[36]
Polymeric Bio-surfactants	Emulsan	*Acinetobacter calcoaceticus*	Emulsifier	[37]
	Liposan	*Candida lipolytica*	Emulsifiers and stabilizers.	[38]
	Alasan	*Acinetobacter radioresistens*	Emulsifier	[39]
	Mannan-lipid-protien	*Candida tropicali*	-	-
	Biodispersan	*Acinetobacter calcoaceticus*	Emulsifier, stabilizers	[40]
	Mannoprotein	*Saccharomyces cerevisiae*	Emulsifier	[41]
	Carbohydrate-protein-lipid	*Pseudomonas fluorescens*	-	-
	Protein PA	*Psedomonas aeruginosa*	-	-
	Bioemulsan	*Gordinia sp*	Emulsifier, stabilizers, antioxidant.	[40]

V. COSMECEUTICAL APPLICATIONS OF BIOSURFACTANT:

5.1 Anti-aging skin care products

There are two types of aging that the human body undergoes. first is the intrinsic aging and the other is the extrinsic aging. In case of intrinsic aging the collagen and elastin fibers become thicker, more clumped and looser, resulting in inelastic and brittle skin and eventually in wrinkling and sagging whereas extrinsic aging occurs due to the effect of environmental factors like smoke, pollution and ultraviolet rays which give rise to free radicals that binds with the skin layer and causes chemical changes that result in aging [10].

mannosylerythritol lipid (MEL):

To reduce or slower the effect of skin aging certain antioxidants containing products like anti-aging facial gel, anti-aging creams are used. Evaluated the antioxidant capacity of mannosylerythritol lipid (MEL) derivatives A, B and C by using a 1,1-diphenyl-2-picryl hydrazine (DPPH) free-radical method and superoxide anion scavenging assay with fibroblasts NB1RGB cells. MEL-C showed the highest antioxidant activity (50.3% at 10 gm/l) and also presented good protective effects in cells against oxidative stress (30.3% at 10lgm/ml of MEL-C)[16]. Based on their results, it is suggested that mannosyl alditol lipid (such as MEL and

MML) or triacylated mannosyl alditol lipid allows providing anti-aging agent effects on cells and that is safe enough to be used for a long time[21].

5.2 Sunscreen products

Exposure to natural light can cause harmful effects due to ultraviolet a (uva) radiation on skin**.** Skin protection from solar damage is crucial not only to minimize the immediate effects such as sun burn, but also to reduce the chance of developing skin cancer especially in white skin. For skin protection sunscreenings agents used. Sunscreening agents are available in various formulations including lotion, cream, wipes, lip balm and are incorporated into various other products such as moisturizers[42].

Surfactin biosurfactant;

Biosurfactant from agro-industrial stream as sunscreen agent, biosurfactant which could possibly be used to increase the protective effect of mica minerals against ultraviolet light (uv light). The sunscreen protection factor (SPF) of different biocomposites based on different mica minerals alone or mixed with a biosurfactant extract obtained from the corn industry. In corn industry, surfactin production by *b. Subtilis* may be used [42][43]. The SPF values of water-based formulations containing mica with and without the biosurfactant extract were determined by means of a standardized method in which the absorbance was determined at wavelengths between 290 and 320 nm. The SPF values obtained for the mica minerals in the absence of biosurfactant ranged between 0.2 and 11, and in some cases the addition of biosurfactant increased the SPF values of the micas by more than 2000% [42].

5.3 Toothpaste

Sophorolipids (SLPs) biosurfactant ;

Biosurfactant is obtained from *Nocardiopsis* VITSISB and which is from marine actinobacteria . it is used in cosmetic formulation of toothpaste, replacing Sodium Lauryl Sulphate which is normally used in commercial toothpaste as a surfactant. This biosurfactant toothpaste was qualitatively analysed by several tests like Spreadability Test, Foaming ability Test, Abrasiveness Test, Brine shrimp Hatchability Test and cleaning ability test. The results indicate that biosurfactant are more efficient and less toxic surfactant compare with chemical surfactant [44]. Sophorolipids (SLPs) are the glycolipid biosurfactants produced by *Candida bombicola ATCC 22214* also used in toothpaste[45].

5.4 Face wash

Rhamnolipid:

NatSurFact is a Rhamnolipid-based line of biosurfactant products. Rhamnolipids are a naturally occurring class of compounds that have surface active (surfactant) properties. Rhamnolipid is made from a renewable source – vegetable oil – in a natural fermentation process. It is mild when we use it to wash our skin and hair. Rhamnolipid surfactant can replace conventional surfactants, such as Sodium Lauryl Sulfate [46].

5.5 Shampoo

Rhamnolipid biosurfactant :

In a recent study conducted by Desantoet al. proposed the use of rhamnolipid bio-surfactant obtained from *Pseudomonas aeruginosa* to formulate a shampoo comprising 2% of rhamnolipid dissolved in water. The antimicrobial effect of the said bio-surfactant kept the scalp free from odour for three days and maintained a lustre [10].

5.6 Hair Conditioners

hair conditioners is used to improve the feel, appearance and manageability of hair and also protect from UV rays.

Mannosylerythritol lipids (MELS) biosurfactant:

Mannosylerythritol lipids (MELS) are produced by the *genus Pseudozyma*, and MELS have a hair care properties like Repair the Damaged Hair MELS are proposed to be the new hair care ingredient, which are the highly useful agent for not only for the recovery of damaged hair but also for providing the smooth and flexible hair. [47]

5.7 Skin moisturizing Creams

it is used for protecting, moisturizing, and lubricating the skin. Water constantly evaporates from the deeper layers of the skin, an effect known as transepidermal water loss (TEWL). Since dry skin is brittle and rigid, any increase in the water content of skin is believed to improve the skin quality.

Sophorolipids biosurfactant ;

Sophorolipids biosurfactant ability to retain moisture. The Sophorolipids produced by *Torulopsis Bombicolu* is reacted with alkylene oxides to produce a group of long chain Alkyl-Sophorolipids. These chemically modified compounds is found to complement the natural moisturizing factor. The Oleyl- Sophorolipid had an HLB Value of 7-8 and showed specific compatibility and excellent mossisturizing properties to the skin.[48]

VI. CONCLUSION:

Biosurfactants produced by micro-organisms from renewable sources, they are non-toxic and inexpensive to produce and have excellent surface properties and biological activities. They also have the potential for wide spread use in personal care and cosmetic products because of their low toxicity, biological activity, biocompatibility and biodegradability and clearly benefit product efficiency, efficacy and the economy. Application of biosurfactants instead of synthetic surfactants in many branches allows to fulfil more and more restrictive environmental expectations and simultaneously ensures very good efficiency and In future synthetic surfactant could be replace by biosurfactant.

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