Review Paper:

Green Surfactants: Technological Innovations and Path Forward

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Abstract

Surfactants are surface active agents that reduce surface tension in water and other liquids. Surfactants are composed of both hydrophilic (lipopohbic) and hydrophobic (lipophilic) groups. The discharge of surfactants in water bodies has serious effects on the ecosystem if they persist long, leading to the accumulation of potentially toxic and harmful substances. To overcome these drawbacks of the surfactants, there is a great need of new alternate chemicals, effective and compatible with the environment. Green surfactants are surface active molecules synthesized using wide variety of natural resources. Their hydrophilic part contains polysaccharide, amino acids, peptide or protein, whereas the hydrophobic part is composed of saturated or unsaturated fatty acids, hydroxy fatty acids or fatty alcohols.

The development of surfactants based on natural renewable resources is a concept of green chemistry that is gaining recognition in detergents and cosmetics. In this study, attempts have been made to describe the type and classification, technological developments, global scenario of green surfactants followed by path forward.

Keywords: Surfactants, green chemistry, bio-surfactants, environment-friendly.

Introduction

Surfactants (also called surface active agents or wetting agents) are organic compounds. The most common applications of surfactants are as soaps, laundry detergents, dish washing liquids and shampoos. Other important uses of surfactants are in many industrial applications such as lubricants, emulsion polymerisation, textile processing, mining flocculates, petroleum recovery, wastewater treatment and agriculture etc [12]. Surfactants are compounds composed of both hydrophilic or lipophobic and hydrophobic or lipophilic groups. The hydrophobic part of a surfactant is generally derived from a hydrocarbon containing 8 to 20 carbon atoms (e.g. fatty acids, paraffins, olefins, alkylbenzenes) and hydrophilic parts are generally sulfates, sulfonates and ethoxylates etc.

Surfactants are classified as cationic, anionic, zwitterionic and non-ionic. The hydrophilic portion may ionise in aqueous solutions (cationic, anionic) or remain un-ionised (non-ionic). Major types of synthetic surfactants include linear alkyl benzene sulphonates, alcohol sulphates, alcohol ether sulphates, alcohol glyceryl ether sulphonates, alcohol ethoxylates and alkyl phenol ethoxylates etc.[41]

Surfactants have been widely used in personal care and cleansing applications. The major part of the surfactants reaches the environment after their use and residual surfactants are discharged into sewage systems or directly into surface waters and most of them end up dispersed in different environmental compartments such as soil and water.

Industries worldwide discharge a wide range of surfactants to their waste water treatment facilities. The discharge of surfactants in water bodies has serious effects on the ecosystem if they persist long leading to the accumulation of potentially toxic and harmful substances[17].

Most of the surfactants are petroleum derived synthetic compounds and are toxic to health and ecosystems and resistant to complete degradation. Water pollution caused by synthetic surfactants has been increasing during the past few years due to their extensive use in household, agriculture and other cleaning operations. Certain classes of surfactants are present in sufficient concentrations to constitute toxicity problems to aquatic organisms.

To overcome these drawbacks of the surfactants, there is a great need of new alternate chemicals, effective and compatible with the environment. The demand for green surfactants is increasing. Green surfactants have promising properties and fulfill the eco-friendly criteria.

The surface active agents that are produced from renewable resources that are environment friendly, are considered to be green surfactants[31]. These molecules can be used in various fields as multifunctional materials for new era. Green surfactants are surface active molecules synthesized by wide variety of natural sources. Their hydrophilic part contains polysaccharide, amino acids, peptide or protein whereas the hydrophobic part is composed of saturated or unsaturated fatty acids, hydroxy fatty acids or fatty alcohols.

Green surfactants have recently received much more attention in concern with the protection of environment, making them “green” chemicals, primarily because of their inherent good biodegradability and low toxicity. In the present study, an attempt has been made to review the types and classification of green surfactants, technological developments, global scenario and path forward.

Classification of green surfactants

On the basis of the origin, the green surfactants can be classified in two categories:

- ♦ Biologically derived (biosurfactants) green surfactants
- ♦ Chemically derived green surfactants

The classification of green surfactants is depicted in fig. 1.

Biologically derived (biosurfactants) green surfactants: Surfactants produced by biologically route are called as biosurfactants. They are produced by yeast or bacteria from various substrates including sugars, oils, alkanes and wastes. Biosurfactants are categorized as glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids, polymeric and particulate compounds[26]. The hydrophobic part of these surfactants is based on long chain fatty acids and the hydrophilic part can be carbohydrate, amino acid, cyclic peptide, phosphate, carboxylic acid or alcohol.

The examples of main biosurfactants are rhamnolipids, sophorolipids, surfactin and lecithin etc. Rhamnolipids are well-characterized and scientifically proven biosurfactants which are slowly and steadily becoming highly sought biomolecules.

Rhamnolipids: Rhamnolipid is composed of β-hydroxy fatty acid connected by the carboxyl end to a rhamnose sugar molecule. Rhamnolipid provides non-toxic and environmentally friendly biosurfactant applications and innovative technologies to various industries including agricultural and environmental[11]. Rhamnolipids have the highest number of patents and research publications as compared to other biosurfactants. However, cost-competitiveness is one of the major factors holding rhamnolipids back from becoming the champions of their field.

Sophorolipids: Sophorolipid is surface-active glycolipid compound composed of carbohydrate head and lipid tail[5]. This is a class of microbial biosurfactants which consists of a hydrophobic fatty acid tail of 16 or 18 carbon atoms and a hydrophilic carbohydrate head, sophorose.

They have gained increased attention as potential bio-surfactants due to their biodegradability and low eco-toxicity and renewable raw material based production. Today sophorolipids are considered promising bio-surfactants[34].

Surfactin: Surfactin is a lipopeptide-type biosurfactant that is generated by the gram-positive, endospore-producing, microorganism *Bacillus subtilis*. Surfactin consists of a peptide loop of seven amino acids (aspragine, L-leucine, glutamic acid, L-leucine, L-valine and two D-leucines)[40]. The potential applications of surfactin are therapeutic applications and environmental applications.

Lecithin: Lecithin is a multi-purpose food ingredient that primarily functions as an emulsifier and dispersing agent[15]. Lecithins are a complex mixture of glycolipids, phospholipids, triglycerides and carbohydrates. As such, lecithin interacts well with other substances in foods such as proteins, lipids and carbohydrates.

Lecithin is prepared by extracting and purifying phospholipids from naturally occurring products such as soybeans, eggs, sunflower and canola seeds.

The structure and applications of biosurfactants are summarized in table 1.

Green Surfactants

Biologically Derived

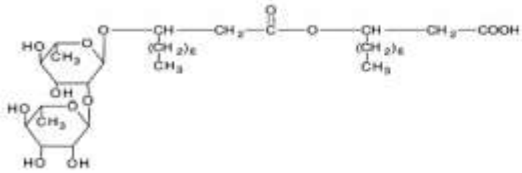
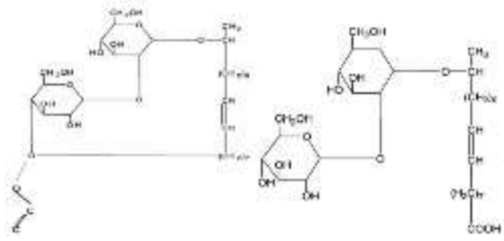
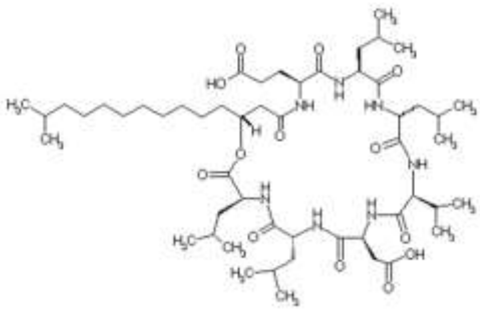
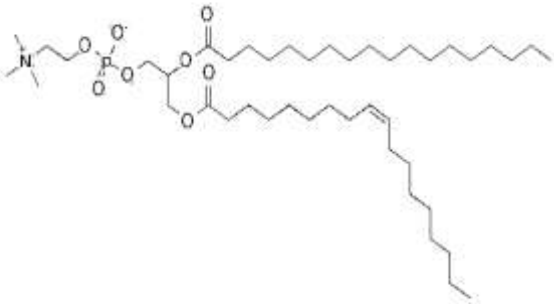
- Glycolipids
- Lipopeptides
- Phospholipids
- Fatty acids
- Neutral lipids
- Polymeric and particulate compounds

Chemically derived

- Alkylpolyglycosides
- Fatty acid methyl ester
- Methyl ester sulfonate
- Fatty alcohols
- Fatty acid sulfates
- Sucrose esters
- Sorbitan esters
- Betains

Fig. 1: Classification of Green Surfactants

Table 1
Structure and applications of biosurfactants

Bio-surfactants	Type	Chemical Structure	Applications
Rhamnolipids	Glycolipids		Personal care applications Bioremediation of organic and heavy metal
Sophorolipids	Glycolipid	 **Lactone form** **Acid form**	Antimicrobial agents Foaming agents Cleaning applications Personal care applications Emulsifiers
Surfactin	Cyclic lipopeptide		Antibacterial, antiviral and anti-inflammatory applications Anti-adhesive applications
Lecithin	Phospholipid		Pharmaceuticals Animal feed and food additive Paint industries Release agent Anti-gumming agent, Emulsifier, spreading agent and antioxidant

Chemically derived green surfactants: Surfactants derived by synthetic route using natural and renewable resourcesare environment friendly are called chemically derived green surfactants. Chemically green surfactants are classified as alkyl polyglycosides, methyl ester ethoxylate, methyl ester sulfonate, fatty alcohols, fatty acid sulfates, sucrose esters, sorbitan esters and betaines.

Renewable sources of hydrophilic groups include carbohydrates, proteins, amino acids and lactic acid and sources of the hydrophobic moiety as steroids, monoterpenes, rosin acids, fatty acids and long chain alkyl groups as well as aromatic compounds. Chemically derived green surfactants have been synthesized using renewable resources such as amino acids, sugars and organic acids and they have been used in human life because of their low toxicity and high biodegradability.

Alkyl Polyglycosides: Alkyl polyglycosides (APGs) are non-ionic surfactants derived from sugars, mainly glucose or its derivatives and fatty alcohols[42]. For industrial manufacturing of APGs, the raw materials are starch and fat. Alkyl polyglycosides are nontoxic, renewable, green surfactants which are environment friendly and used in such industries as food, beverages, pharmaceuticals, cosmetics or detergents. They are used as foaming agent in detergents for cleansing applications.

Methyl ester ethoxylate: Methyl ester ehoxylates (MEE) are a type of renewable surfactant derived by ethoxylation of fatty acid methyl ester (FAME) (Fig. 2)[20]. Fatty acid methyl ester are synthesized (Fig. 3) by the reaction of fats with methanol in the presence of base such as sodium hydroxide, sodium methoxide or potassium hydroxide[7].

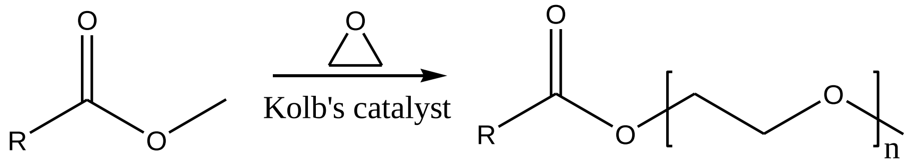
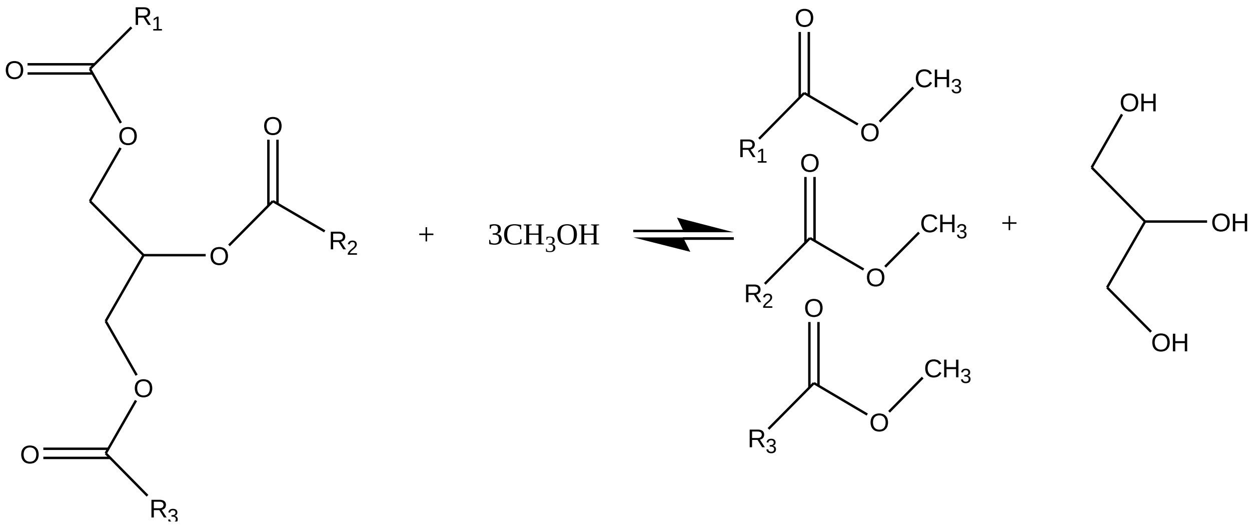
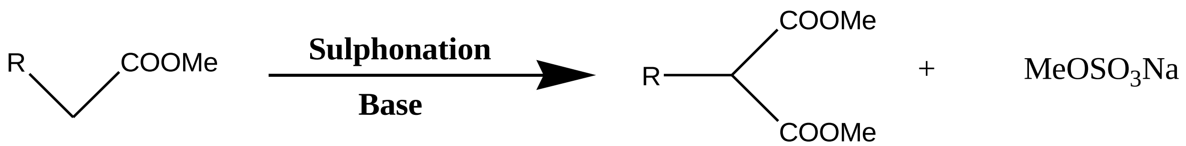


Fig. 2: Ethoxylation of fatty acid methyl ester (FAME)



Triglyceride **Methanol** **Fatty acid methyl ester** **Glycerol**

Fig. 3: Trans-esterification of triglycerides into fatty acid methyl ester



Fatty acid methyl ester **Methyl ester sulfonate** **Sodium methyl sulfate**

Fig. 4: Sulfonation of fatty acid methyl ester into methyl ester sulfonate

Methyl ester sulfonate: Methyl ester sulfonates (MES) are anionic surfactants that can be made by sulfonation of saturated fatty acid methyl esters derived from natural fats and oils[10] (Fig. 4). Because of these properties and because of the perceived potential for cheap availability of the feedstocks, interest has grown in using MES in combination with other anionic surfactants in laundry powders and soaps[35].

Fatty Alcohols: Fatty alcohols (or long-chain alcohols) are usually high-molecular-weight, straight-chain primary alcohols, but can also range from as few as 4–6 carbons to as many as 22–26 derived from natural fats and oils. The precise chain length varies with the source. The main sources and large-scale feedstock of fatty alcohols are various vegetable oils. They find use as co-emulsifiers, emollients and thickeners in cosmetics and food industry[13].

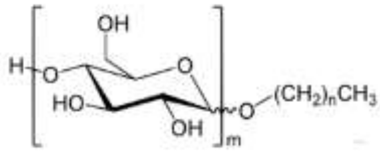
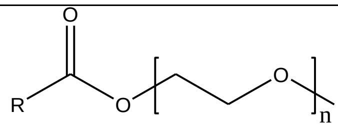
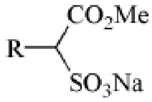
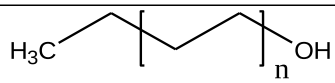
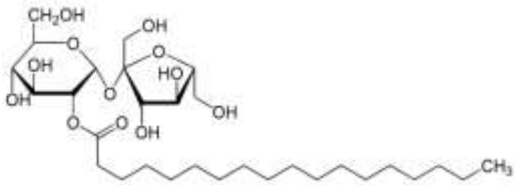
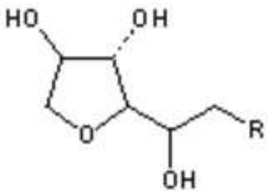
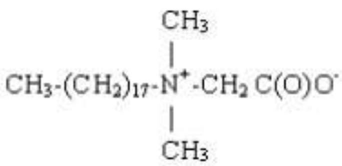
Sucrose Esters: Sucrose esters are a group of surfactants chemically synthesized from esterification of sucrose and fatty acids. These are biodegradable surfactants that can be manufactured in various hydrophilic-lipophilic balances (HLB) through the use of different fatty acids and they have the ability to bind both water and oil simultaneously and act as emulsifiers [38].

Sorbiton Esters: Sorbitan esters are nonionic surfactants used as emulsifiers in the preparation of emulsions, creams and ointments for pharmaceutical and cosmetic use. Sorbitan esters are well known emulsifiers and produce stable water-in-oil emulsions with a variety of textures and consistencies[14]. Sorbitan esters are synthesised from 1,4-anhydro-sorbitol and fatty acids. Ethoxylated derivatives of sorbitan esters can also be prepared by the reaction of various moles of ethylene oxide to the sorbitan monoglycerol ester and on the basis of various ethylene oxide (EO) moles, they have a wide range of HLB[18].

Betains: Betaine is one class of amphoteric surfactants. Because of its structure, it can exist in only two ionic forms, zwitterionic and cationic. Amphoteric surfactants are a class of compounds that have both a positive (+) and negative (-) charge in the same molecule. The structure shown is a zwitterionic form, having both positive and negative charges present in the same molecule.

As the pH is decreased, the carboxyl group is protonated and a compound with a positive (+) charge develops. Due to this behavior, betaines provide better conditioning in low-pH systems. Since the nitrogen is surrounded by carbon atoms, it cannot lose its positive (+) charge by pH alteration[28].

Table 2
Structure and applications of chemically derived green surfactants

Green surfactants	Chemical Structure	Applications
Alkyl polyglycoside		Cosmetic, household and industrial applications
Methyl ester ethoxylate		Cleansing and detergent applications
Methyl ester sulfonete		Laundry Detergent powders & detergent cakes
Fatty alcohol		Emulsifiers, thickeners in food and cosmetic industry
Sucrose ester		Cosmetics, food preservatives, food additives
Sorbitan Ester		Emulsifiers in pharmaceuticals and food industries
Betaines		Foaming booster in cleansing applications, emulsifying agents, thickener

The structure and applications of chemically derived green surfactants are summarized in table 2.

Technological Developments

The development of surfactants based on natural renewable resources is a concept that is gaining recognition in personal care and detergent industries. This new class of biodegradable and biocompatible surfactants is a response to the increasing consumer demand for products that are greener and more efficient. In order to achieve these objectives, it is necessary to use renewable low cost materials that are available in large quantities and to develop new green surfactants that show improved performance in terms of lower eco-toxicity and reduced environmental impact[4].

Microbially produced glycolipid biosurfactants / green surfactants comprise a hydrophilic carbohydrate section and a hydrophobic fatty acid chain. The sugar at the hydrophilic end is sophorose in the sophorolipids, rhamnose in the rhamnolipids and mannose and erythritol in MELS[22]. The sophorolipids are produced by yeasts of the genus Candida comprising usually 8 major and 15 minor components. The fatty acid chain typically has 16 or 18 carbon atoms with different degrees of saturation[39].

Rhamnolipid surfactant has been produced by the bacterium *Pseudomonas aeruginosa* using C10 and C12 fatty acyl chains by fermentation process[9]. MELs are produced by basidiomycetous yeasts of the genus Pseudozyma with medium chain length of fatty acyl esters[2]. Low cost fermentative medium using molasses and cheese whey was developed for biosurfactant production by L. Lactis 53 and S. thermophilus A.[36] Trehalose lipids synthesized by *Rhodococcus erythropolis* are typical compounds in which the fatty acid moiety depends on the carbon chain length whereas the hydrophilic moiety is not affected by the carbonsubstrates[16].

In the enzymatic reaction, the fatty acid is esterified to trehalose-6-phosphate which is subsequently subjected to dephosphorylation and further modification[8]. A pea protein isolate was hydrolyzed by enzyme treatment to obtain peptide sequences used as raw materials to synthesize lipopeptides-based surfactants. Pea protein hydrolysates were synthesized using the enzymes such as Alcalase and Flavourzyme.

The effect of the process parameters was studied to optimize the proteolytic degradation of hydrolysis. The average peptide chain lengths were obtained at 3–5 amino acid units after a hydrolysis of 30 min with the mixture of enzymes[3]. Green surfactants based on mannuronate moieties derived from alginates (cell-wall polyuronic acids from brown seaweeds) and fatty hydrocarbon chains were derived from vegetable resources. Controlled chemical and/or enzymatic depolymerizations of the algal polysaccharides give saturated and/or unsaturated functional oligomannuronates. An amino based surfactant was prepared by the reaction of cysteine with N-cetyl-N,N-dimethyl-N-ß-aminoethyl ammonium chloride[25].

Surfactants containing the sugar moiety as a hydrophilic group have been synthesized by many researchers and used as detergents, emulsifiers and cosmetics[36]. The syntheses and properties of anionic, cationic and amphoteric surfactants containing amino acid moieties such as arginine [24,30], tryptophan[29], lysine[37], cysteine[43], glutamate and aspartate[1] have also been reported. Polycarboxylate based surfactants with either sulfide- (S-) or imino- (N-) linkages were produced by addition reaction of fatty mercaptan or fatty amine with unsaturated polycarboxylic acids such as maleic, fumaric, aconitic, anditaconic acids. They exhibited surfactant properties and excellent biodegradabilities[27].

Green surfactants have been synthesized using renewable and sustainable resources as raw materials i.e. amino acids, sugars and organic acids etc. due to their low toxicity and high biodegradability. Several families of surfactants were prepared using environment friendly processes using by-products of sugar and oleochemical industries, glycins and betains with attractive surface tension, good foaming and emulsifying capabilities with potential applications in detergency and cosmetic industry[19].

Semi-natural, eco-friendly and biodegradable surfactant was developed using starch and some synthetic surfactants with good emulsifying efficiency and surfactant performance properties and analyzed by FT-IR, XRD and SEM[23]. Alkyl polyglucoside is a type of non-ionic green surfactant. Dodecyl polyglucoside was synthesized by glucose and dodecanol using P-toluenesulfonic acid as catalyst by one step process[21]. Green surfactants from waste biomass and agricultural raw materials are gaining attention as compared to petroleum feedstock. Personal care and homecare companies are looking at alternatives to synthetic surfactants and emulsifiers to use sustainable materials. The move towards green surfactants is due to consumer demands for sustainable products as well as industry pressure to adopt renewable feedstock.

Global scenario of green surfactants

With increasing demand for green products with favorable regulatory outlook in developed countries, the global green surfactant market is growing. Due to increasing consumer awareness and need for ecologically safe products, bio-surfactants is one of the alternatives. But the existing and potential demand for surfactants is very high and it cannot be catered by biosurfactants alone.

At the commercial level, green surfactants have been available since more than a decade now. Green surfactants are mainly used in personal care and cleansing applications due to mildness and low toxicity. Recent survey by transparency research market has revealed that the worldwide biosurfactants market volume is expected to be 476,512.2 tons by 2018. The global market value of biosurfactants was US$ 1735.5 million in 2011 and it is expected to grow at a rate of 3.5% annually and reach US$ 2210.5 million by year 2018[6].

Europe and North America are the mainproducers and consumers of green surfactants. Asia Pacific has high potential for production and consumption of bio-based green surfactants due to more strict regulations about toxicity. Key players operating in the Green surfactants market include Tate and Lyle Plc, ADM, Cargill Inc., Du Pont, DSM, Ingredion Incorporated, Roquette Freres and Südzucker AG Company [32].

Jencil Biosurfactants, USA has become a renowned company in this field. AGAE Technologies LLC, USA and Rhamnolipid Inc, USA are main manufacturers of rhamnolipids. Fraunhofer IGB, Germany is invoved in production of mannosylerythritol lipids. Other manufacturers of biosurfactants are Ecochem Ltd., Canada, Sigma Aldrich Co., USA, Saraya, Japan, Intobio, South Korea, Solience, France and Allied Carbon Solutions, Japan. Evonik, Germany is main producer of biosurfactant sophorolipid[32].

India's Biosurfactants Market is expected to demonstrate moderate growth over the coming years owing to the increasing demand for green substitutes of synthetic and conventional surfactants in the country. The increasing applications in polymer, oilfields, construction chemicals, cosmetics and many other industries are probing the consumption of biosurfactants in the country. In India the major manufacturers of biosurfactants are– Evonik India Pvt. Ltd., Mitsubishi India, Vetline and Galaxy Surfactants Ltd., India etc.[33]

Total Indian surfactant market earned revenues of $2278 million in 2013 and was expected to reach $3748 million in 2017 approximately. India constitutes about 9% of total global surfactants consumption (volume basis). Multifunctional surfactants are gaining acceptance in Indian consumer segment[37]. Green Catalyst Processes for the manufacture of Amino Acid Surfactants (including, Glycinates, Sarcosinates, Taurates and Glutamates) were developed by Galaxy Surfactants[43]. In India, although some manufacturers are manufacturing the bio-surfactants but the research on green surfactant in India is in preliminary stage.

Path Forward

The development of surfactants based on natural renewable resources is a concept that is gaining recognition in cosmetics and detergent industries. Although worldwide various producers are involved in manufacturing of green surfactants, in India the production of green surfactants is at initial level due to which the cost of these surfactants is high and approachable to very few consumers. Green surfactants are not yet widely used in industry due to high production costs compared to synthetic surfactants associated to inefficient methods for product recovery.

Thus, it is a present need to use inexpensive natural waste sources as raw materials and to develop cost effective synthesis methods for increasing the yield of green surfactants. In order to achieve these objectives, it is necessary to use renewable low-cost materials that are available in large quantities and to design molecular structures that show improved performance, favorable eco-toxicological properties and reduced environmental impacts.

Conclusion

Surfactants have been widely used in personal care and cleansing applications. The major part of the surfactants reaches the environment after their use. The residual surfactants affect the ecosystem, as the biodegradability of synthetic surfactants is an issue of concern. The surfactants produced by renewable natural resources are the substitute over synthetic surfactants. The green surfactants mainly are classified as biologically derived (biosurfactants) and chemically derived. The main types of biosurfactants are glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids and polymeric surfactants and the example of these are rhamnolipids, sophorolipids surfactin and lecithin etc.

The chemically derived surfactants are categorized as alkyl polyglycosides, fatty acid methyl ester, methyl ester sulfonate, fatty alcohols, fatty acid sulfates, sucrose esters, sorbitan esters and betains. Various methods of synthesis of green surfactants have been described using renewable and natural resources as raw materials. Worldwide North America and Europe are the leading manufacturers and consumers of green surfactants. In India, Evonik India Pvt. Ltd., Mitsubishi India, Vetline and Galaxy Surfactants Ltd., are main producers of green surfactants. Due to high production cost and inefficient methods for product recovery, green surfactants are not yet widely used in industry compared to synthetic surfactants. Hence to overcome these drawbacks, it is needed to do research using cheap renewable resources such as natural waste and to enhance product recovery so that the cost of green surfactants is reduced and these can because approachable for surfactant consumers in diversified applications.

Acknowledgement

The authors wish to express their sincere thanks to Management of Shriram Institute for Industrial Research, Delhi, India, for their encouragement and support.

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(Received 29th May 2020, accepted 11th August 2020)

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