

Surfactants: toxicity, remediation and green surfactants

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Abstract Surfactants toxicity has induced a worldwide alert followed by various regulations. There are still concerns about the biodegradability and ecofriendliness of surfactants. Reviews on surfactants are available, but a concise manuscript covering surfactant types, primary and secondary toxicity of surfactants, evaluating the level of surfactant pollution worldwide, is needed. We review here the safety of surfactants in the aquatic system, in terrestrial ecosystems and for humans. We discuss strategies to solve surfactant contamination. Remediation methods include ozonation, UV radiation and catalyst-coupled auto-oxidation. We focus on the biodegradation of the anionic detergents sodium dodecyl sulfate and linear alkyl benzene sulfonate. Finally, the relevance and role of biosurfactants as alternatives to synthetic detergents are also described.

Keywords Bioremediation · Biosurfactants · Sodium dodecyl sulfate · Linear alkyl benzene sulfonate · Pollution · Anionic · Methylene blue active agents

Introduction

Traced back from the ancestral Babylonian ash-oil soap formula to the currently available soaps, cleansers and detergents, surfactants appear in various forms. Of these, detergents indeed have become indispensable elements of

man's life all along his steps aiming cleanliness and tidiness. Apart from serving as cleansing agents, surfactants find many industrial applications as additives in paints, as textile softeners, as antistatic agents, in metal processing and in oil drilling operations. Some surfactants have antimicrobial properties which provide the basis for their utility as biocides (Ginkel 1989).

Industries worldwide discharge a wide range of surfactants, or surface-active agents, to their wastewater treatment facilities. Once used, surfactants enter the water bodies, where they can cause problems if they persist long, leading to the accumulation of potentially toxic or otherwise harmful substances (Deschenes et al. 1996) and cause serious environmental problems (Abd-Allah 1995). Surfactants are ubiquitous and in untreated effluents, certain classes of surfactants can be present in sufficient concentrations to constitute toxicity problems to aquatic organisms (Ankley and Burkhard 1992), even between 0.4 and 40 mg/L (Abel 1974).

Extensive research on the surfactant toxicity does exist (Lewis 1991; Schweigert et al. 2000; Chaturvedi and Kumar 2010a); however, assessment of contemporary pollution profile of surfactants is relevant. The toxicity and biodegradation of the most commonly used anionic surfactants sodium dodecyl sulfate (SDS) and linear alkyl benzene sulfonate (LAS) are detailed in this review, with special reference to its biodegradability and safe disposal. Information available on the metabolic pathway and molecular mechanism of surfactant degradation, methods and alternatives to combat the problem of surfactant contamination are also discussed. The relevance and utility of biosurfactants as an alternative to current synthetic detergents are also reviewed. This article is an abridged version of the chapter by Rebello et al. (2013) published in the book series Environmental Chemistry for a Sustainable World.

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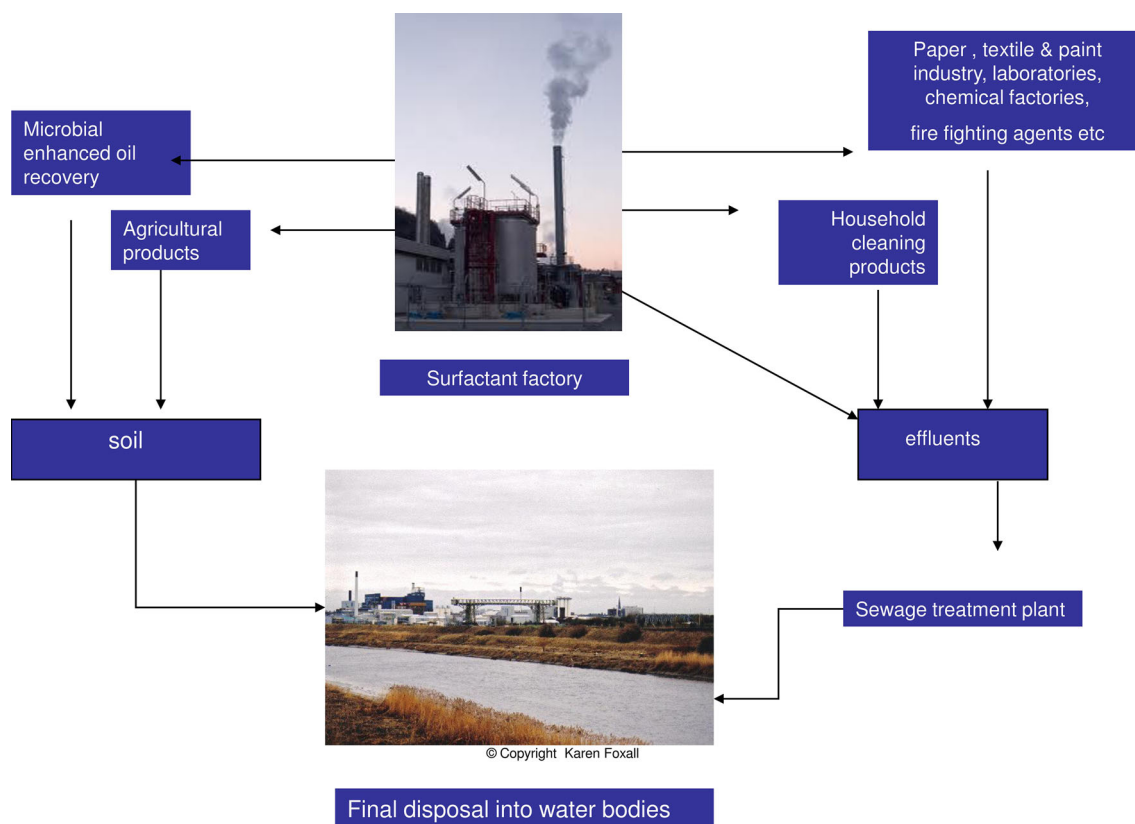


Fig. 1 Flowchart depicting course of surfactant pollution

Chemistry of surfactants

Surfactants are chemicals capable of reducing surface tension of liquids or interfaces of liquids, endowed by its hydrophobic tail and hydrophilic head. Surfactants do occur as simple monomers, but sometimes exist as more complex polymers. Based on the charge of the hydrophilic group of surfactants, they are classified as anionic (negatively charged), cationic (positively charged), nonionic (without any charge) and ampholytic/zwitter ionic (both charges). The anionic surfactant SDS is synthesized by sulfonation of petrochemical or oleo chemical-based lauryl alcohols, whereas LAS is exclusively synthesized from petrochemical by-products. SDS is linear molecule with an alkyl tail of 12 carbon atoms, attached to a sulfate group giving the molecule the amphiphilic properties required of a surfactant. LAS have a hydrophobic alkyl chain and a hydrophilic head with a benzene ring and a sulfonate group. It is not a single compound, but ideally a mixture of 20 compounds, of closely related homologs and isomers.

Surfactant pollution: worldwide and the Indian Scenario

The per capita detergent consumption in India is around 2.7 kg/year, whereas in places like Philippines and

Malaysia, it is 3.7 kg, and in USA, it is around 10 kg. The high consumption rates of detergents also develop a high detergent concentration in our water bodies (Gonzalez et al. 2012) as depicted in Fig. 1. The accumulation of surfactants in river sediments (Rico-Rico et al. 2009), marine water and sediments (Petrovic et al. 2002), infiltrated ground water (Field et al. 1992) and sewage effluents with concentrations up to 1,090 $\mu\text{g/L}$ (Holt et al. 1989) has been observed. LAS was found in treated sludge at high concentrations of up to 30,200 mg/kg dry weight (Berna et al. 1989) and in surface waters at concentrations of up to 416 $\mu\text{g/L}$ (Fox et al. 2000), which is quite above its predicted no effect concentration of 250 $\mu\text{g/L}$ (van de Plasche et al. 1999). In various developing countries, the usage of phosphate-based detergents continues at alarmingly high rates (Khurana 2002), leading to excessive growth of algae.

Most of the ponds in Varanasi city have become eutrophic and are highly contaminated especially with high amount of detergents (Chaturvedi and Kumar 2010b). Detergent pollution resulting from textile industry of Tirupur of Tamil Nadu also contributes to environmental pollution (De Neve 2009). Surfactants were detected in water samples collected from surface and ground (2–62 $\mu\text{g/L}$), bore wells and open wells (22–427 $\mu\text{g/L}$) in Tirupati of Andhra Pradesh, and open municipal drainage waste waters (50–720 $\mu\text{g/L}$) (Kanchi et al. 2012).

Safety concerns on surfactants

The cycle of surfactant toxicity starts from its very synthesis, disposal and subsequent exposure to the environment. Surfactant synthesis critically affects the environment aggravating the problems related to global warming, climate change, ozone layer depletion and greenhouse gas emission which cannot be totally avoided. Both petrochemical and oleo chemical-based surfactant production result in atmospheric emission (NO_x, CO₂, SO₂, hydrocarbons), waterborne wastes and solid wastes capable of causing eutrophication and acidification of rivers and lakes (Stalmans et al. 1995).

Toxicity on microbial world

The impacts of surfactants on the microbial world vary with each species and extend of pollution. Bacterial degradation of surfactants is well established (which will be discussed in biodegradation of surfactants). However, surfactants are also found to have deleterious effects on various other bacteria such as phosphate solubilizing *Acinetobacter junii* (Ivankovic et al. 2009), autotrophic ammonia oxidizing *Nitrosomonas* and *Nitrosospira* strains (Brandt et al. 2001) and bioluminescent *Vibrio fischeri* (Lima et al. 2011). Surfactant-based membrane lysis, DNA damage and starvation are found as counterparts even in bacteria capable of utilizing SDS as sole carbon source (Klebensberger et al. 2006). Effect of LAS on inherent populations of bacteria, fungi and actinomycetes in soil gave statistically significant results for bacteria and fungi (Asok and Jisha 2012b).

Surfactants primarily affect the growth, motility and photosynthetic ability of algae, the extent of toxicity dependant on the surfactants (type, concentration) and algal type (Lewis 1990). SDS even at 0.1 mg/mL causes inhibition of asexual and sexual reproduction of *Closterium ehrenbergii* resulting in no zygospore formation or defective/abnormal spores (Matsui and Park 2000). The photosynthetic ability of algae decreased exponentially with increasing surfactant concentration and decrease in algal biomass (Maksimov and Parshikova 2006), with cationic surfactants causing the most potent inhibition.

Toxicity on soil and plants

Even at low concentrations, surfactants seem to alter soil physics, soil chemistry and soil biology significantly, whereby sorption processes play a dominant role (Kuhnt 1993). Surfactants primarily affect the roots of plants suppressing or killing the roots, with comparatively less inhibition in the shoots of wheat seedlings (Rinallo et al. 1988). Use of detergent-contaminated water for cultivation

reduces the photosynthetic rate and chlorophyll content in bean plants (Jovanic et al. 2010). The continuous application of the anionic surfactant LAS to the soil increased the acid and alkaline phosphatase activity and arylsulfatase activity, whereas the soil dehydrogenase activity was decreased on continuous LAS exposure (Sanchez-Peinado et al. 2009).

Toxicity to aquatic system

Surfactant toxicity has been reported since late 1960s, during which it was observed that the exposure of fish *Ictalurus natalis* to detergent levels (0.5 ppm) even much lower than its sublethal concentrations caused disruption of chemoreceptors (Bardach et al. 1965). Chronic and sublethal toxicities of anionic and nonionic surfactants to aquatic animals occur at concentrations usually greater than 0.1 mg/L (Lewis 1991). Adverse biological effects on aquatic organisms occur especially when surfactants occur at relatively high concentrations (Romanelli et al. 2004).

The aftermath of surfactant exposure can be clearly visualized in various organs like gills (Mallatt 1985), liver, kidney (Rosety-Rodríguez et al. 2002), spleen and intestines (Ribelles et al. 1995) of fishes. Exposure to high surfactant concentration results in gill epithelial disruption causing subsequent asphyxiation or osmoregulatory failure (Mallatt 1985), while exposure to sublethal concentrations of surfactants causes gill epithelial hyperplasia, oxidative stress and mucus layer damage of fishes, which predispose them to microbial attack (Susmi et al. 2010). The detrimental effects of SDS on crustaceans are found to be less pronounced, yet reports on detrimental effects of this surfactant on filter feeding habits of bivalves (Ostroumov 2003) and mussel suspension feeding (Ostroumov and Widdows 2006) do exist.

Effect on higher vertebrates

In humans, anionic surfactants target mainly the stratum corneum of membrane bilayer of sensitive skin resulting in dermatitis (Marrakchi and Maibach 2006) and aphthous ulcers (Chahine et al. 1997). The American Cancer Society denied that SDS is carcinogenic and points out that the substance, while undoubtedly a skin irritant, is a strong detergent intended to remove oil and soil, but there is no link between use of this product and cancer risk (Doyle 2010). Thus, it is likely that the toxicity of these anionic surfactants is relatively low in human and wild animals as the molecular weight increases, probably due to lower adsorption in the intestine. An acute toxic effect by anionic surfactants is therefore not to be likely but a chronic effect can, however, be more possible since a regular dosage of a

human is about 5 mg/person from drinking waters, detergents, toothpaste and food.

Several cytotoxicity tests reveal that nonionics have the least toxicity in the order as cationic > anionic > amphoteric > nonionic (Grant et al. 1992). Some nonionic surfactants are found to anaesthetize the eye ball, and thus, combinations of nonionic surfactants with anionics would make many shampoos gentle to eye (Conry 1980).

Secondary toxicity of surfactants

Generally, the presence of surfactants helps in the degradation of polycyclic hydrocarbons, but the degradation of PAH was inhibited by SDS because this surfactant was preferred as a growth substrate (Tiehm 1994). This suggests that the presence of this detergent in the water bodies would indirectly lead to bioaccumulation of other hydrocarbons. Reports are also available that adding SDS and *Pseudomonas aeruginosa* UG2 biosurfactants inhibit polycyclic aromatic hydrocarbon biodegradation in a weathered creosote-contaminated soil (Deschenes et al. 1996). The presence of surfactants may be important for the fate of pesticides at effluent-irrigated sites because they may increase the apparent solubility of hydrophobic pesticides (Vigon and Rubin 1989).

Tackling surfactant pollution

Surfactant toxicity has aroused worldwide attempts to reduce after effects of these silent toxicants. The strict regulations on usage of phosphate free surfactants, remediation of waste water before disposal and promotion of green surfactants are manifestations of these attempts. The usage of liquid detergents than powder forms results in less surfactants toxicity according to a case study at Ludhiana (Goel and Kaur 2012). Interesting suggestions for hands on preparation of laundry and liquid detergents for hard and soft water could also add to our attempts to reduce surfactant toxicity (Khurana 2002). The use of nontoxic-biodegradable natural soaps and soapnuts is yet another promising approach (Ghai 2011).

Remediation before disposal

The influence and relevance of surfactants in mans life are too immense, that totally avoiding them from our day-to-day life seems to be impossible and unpractical. Better management of surfactant use and disposal has become the need of the hour, both at industrial and domestic level. Strict regulations in the effective remediation of surfactants before disposal should be done. This section describes the various methods of surfactant remediation and various

steps that could reduce surfactant pollution at domestic level.

Physical and chemical methods

Various physical, chemical and biological methods of surfactant detoxification are reported. Physical treatment of surfactants by ozonation and advanced oxidation using various combinations of ozone, hydrogen peroxide, ultraviolet light irradiation and iron salts were found effective in degrading recalcitrant surfactants, including LAS, alkyl-phenol ethoxylates and quaternary ammonium surfactants (Ikehata and El-Din 2004). Various other techniques like electrocoagulation (Yuksel et al. 2009), nanofiltration (Korzenowski et al. 2012), sonochemical degradation, foam fractionation and wet air oxidation are also used.

Oxidation-based methodologies Detoxification of micropollutants such as surfactants, pesticides, herbicides and microtoxins from drinking water mainly relies on high oxidizing capacity of ozone (Beltran et al. 2000). LAS ozonation in surface waters intended for human consumption demonstrated that combinatorial use of O₃ and powdered activated carbon approach is the most efficacious than traditional O₃- or H₂O₂-based oxidation systems, considerably increasing the LAS removal rate and also reducing the concentration of dissolved organic carbon (Rivera-Utrilla et al. 2006).

Photocatalytic degradation The photocatalytic degradation of surfactants in water is done by solar fenton-like oxidation reaction (Bhatkhande et al. 2002). The photodegradation of SDS and LAS in reactors in presence of TiO₂ catalyst and UV light is also well studied (Hidaka 1998). According to this study, the surfactant competitively binds to TiO₂ and on exposure to UV light, radical attack on the aromatic ring and alkyl chain brings about degradation.

Foam fractionation Foam fractionation is a chemical process in which hydrophobic molecules are preferentially separated from a liquid solution using rising columns of foam. It has been shown to be an effective method of removing anionic or cationic surfactants from effluent streams. Cationic surfactants were easily removed from water by foam fractionation than the anionic surfactants studied (Tharapiwattananon et al. 1996).

Sonochemical degradation The utility of sonochemical reactors for anionic surfactant degradation from waste waters is well studied the rate of degradation proportionally increasing with sonication time, but decreasing with surfactant increase (Dehghani et al. 2010). The potential of using ultrasonic irradiation for the removal of LAS revealed that it increases with the frequency of radiation, and the addition of NaCl or H₂O₂ to this system had adverse effect on LAS conversion, while addition of Fe²⁺

either alone or in conjunction with H₂O₂ (fenton reagent) had a positive effect on degradation of LAS (Manousaki et al. 2004). Usage of 20 kHz ultrasound at 40 °C, pH at 2.5 throughout and addition of extra amounts of zero valent iron and H₂O₂ during the degradation resulted in 93 % reduction in LAS (Naldoni et al. 2011).

Electrochemical degradation Electrocoagulation can be addressed as a method of wastewater treatment when electric current goes through an electrolysis cell supplied with soluble electrodes (Sequeira 1994). This technique is also effective in the treatment of the strongly acidic effluents arising from electrokinetic surfactant-aided soil flushing of polluted soils using aluminum electrodes (anodes and cathodes) (Lopez-Vizcaino et al. 2012).

Biological methods

Microbial biodegradation provides a safer, environmentally benign and cost-effective alternative to physicochemical methods for surfactant remediation (Oya and Hisano 2010). Biodegradation of surfactants is most often performed by diverse soil or aquatic microorganisms leading to generation of water and carbon dioxide gas (Schleheck et al. 2000). Surfactant degradation is predominantly carried out by various species of *Pseudomonas*, yet many other bacterial species are also reported to participate in surfactant remediation as listed in Table 1.

Biodegradation of anionic surfactants was initiated in early 1960s (Payne and Feisal 1963), with the isolation of two unknown bacterial soil isolates capable of degrading short- or long-chained organic acids and alcohols of SDS and three of five phenyl placement isomers of dodecyl benzene sulfonate. But isomers with phenyl placement at carbon 4 or 5 were toxic and killed the bacteria. The primary SDS splitting enzyme was reported soon (Hsu 1963) and identified as a primary alcohol sulfatase. Anionic surfactant degradation is initiated by alkylsulfatases which convert them to corresponding alcohol by removing the sulfate/sulfonate moiety. Growth of the bacteria on SDS as the sole carbon source induced glyoxylate bypass enzymes, isocitrate lyase and malate synthetase, in addition to alkylsulfatases (Williams and Payne 1964).

Metabolism of SDS by the detergent-degrading bacterium *Pseudomonas* C12B using a ¹⁴C radiotracer which showed that 70 % of the radiolabel was released as ¹⁴CO₂ at completion, where as the remaining isotope was incorporated cells (Thomas and White 1989). As depicted in Fig. 2, SDS was degraded yielding with the sequential production from [¹⁻¹⁴C] SDS of 1-dodecanol, dodecanal and dodecanoic acid. Biodegradation of LAS begins at the terminus of the alkyl chain with an omega-oxidation and is followed by successive cleavage of C₂ fragments (β-oxidation) (Huddleston and Allred 1963; Swisher 1963).

Table 1 Microorganisms involved in bioremediation of anionic surfactants sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS)

Sl. no.	Organism	Surfactant	Reference
1	<i>Pseudomonas</i> C12B	SDS, LAS	Payne and Feisal (1963)
2	<i>Hansenula</i> and <i>Candida</i>	LAS	Standard and Ahearn (1970)
3	<i>Vibrio</i> sp.	LAS	Bird and Cain (1972)
4	<i>Nocardia amarae</i> MB-11	LAS	Bhatia and Singh (1996)
5	<i>Bacillus cereus</i>	SDS	Singh and Kumar (1998)
6	<i>Spongia officinalis</i>	LAS	Perez et al. (2002)
7	<i>Phanerochaete chrysosporium</i>	LAS	Yadav et al. (2001)
8	<i>Parvibaculum lavamentivorans</i> DS-1 ^{and} <i>Comamonas Testosteroni</i> sp. B-2, KF-1	LAS	Schleheck et al. (2004)
9	<i>Acinetobacter calcoaceticus</i> , <i>Pantoea agglomerans</i>	SDS, LAS	Abboud et al. (2007)
10	<i>Pseudomonas beteli</i> , <i>Acinetobacter johnsoni</i>	SDS	Hosseini et al. (2007)
11	<i>Klebsiella oxytoca</i>	SDS	Shukor et al. (2009)
12	<i>Stenotrophomonas maltophilia</i>	LAS	Farzaneh et al. (2010)
13	<i>P. alcaligenes</i> and <i>P. mendocina</i>	SDS	Chaturvedi and Kumar (2010b)
14	<i>Pseudomonas aeruginosa</i> S7	SDS	Yeldho et al. (2011)
15	<i>P. aeruginosa</i> , <i>P. mendocina</i> , <i>P. stutzeri</i> , <i>P. alcaligenes</i> , <i>P. pseudoalcaligenes</i> , <i>P. putida</i> and <i>P. otitidis</i>	SDS	Chaturvedi and Kumar (2011)
16	<i>P. aeruginosa</i> MTCC 10311	SDS	Ambily and Jisha (2011, 2012)
17	<i>P. nitroreducens</i> (MTCC 10463), <i>P. aeruginosa</i> (MTCC 10462)	LAS	Asok and Jisha (2012a)
18	<i>Alcaligenes odorans</i> , <i>Citrobacter diversus</i> , <i>Micrococcus luteus</i> and <i>P. putida</i> consortium	LAS	Eniola (2012)

These intermediates are further biodegraded by oxidative removal of the aromatic ring and cleavage of the sulfonate group (Setzkorn and Huddleston 1965; Swisher 1967). Core research aiming optimized surfactant degradation has been carried out in the case of anionic surfactants SDS and

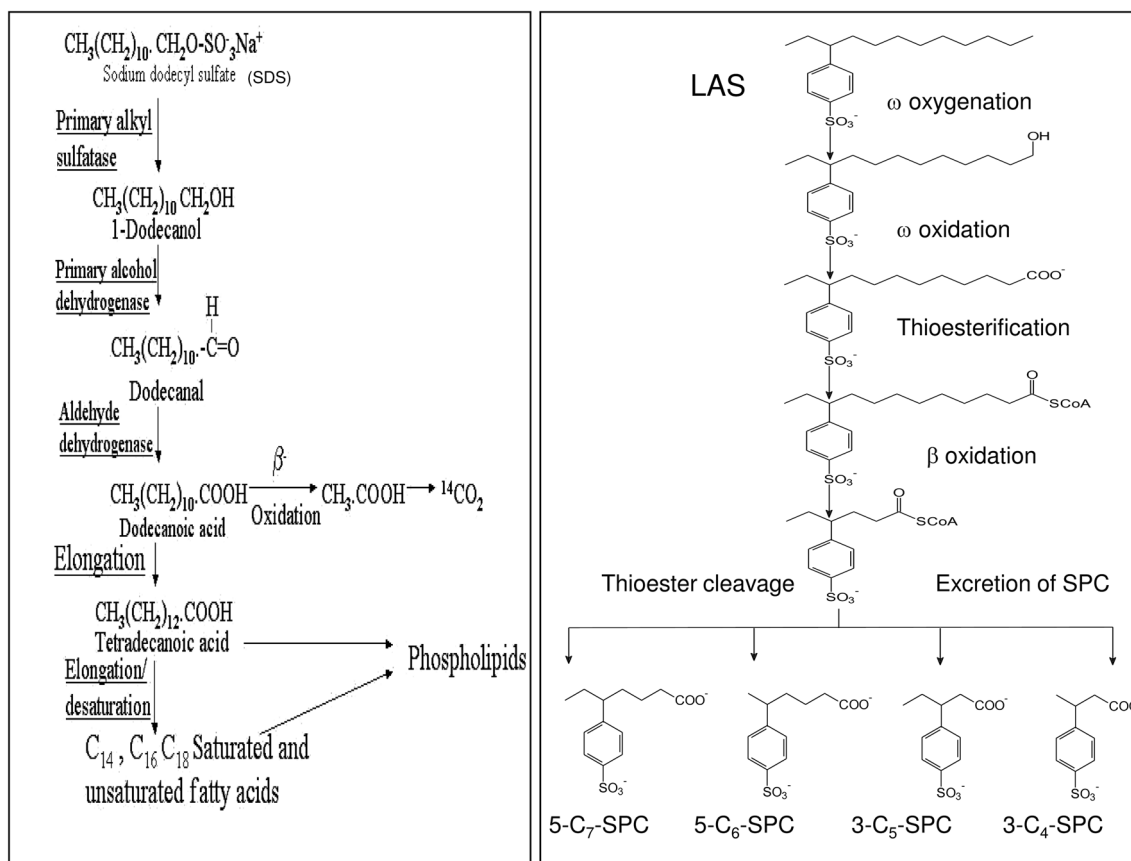


Fig. 2 Pathway of sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS) biodegradation as per Thomas and White (1989) and constructed as per Huddleston and Allred (1963), Swisher (1963), Asok (2011) respectively

LAS (Abboud et al. 2007; Asok and Jisha 2012a). SDS is found to be highly degradable both in aerobic and anaerobic conditions. LAS biodegradation in turn is found to be inhibited by anaerobic conditions (Mungray and Kumar 2009).

Analysis of alkyl sulfatase in parent and cured strains of *Pseudomonas* confirmed that both enzymes are encoded by the chromosome. The nucleotide sequence of two chromosomally located genes *sdsA* and *sdsB*, coding for alkylsulfatase and its transcriptional regulator, respectively, were identified to play significant roles in SDS degradation (Davison et al. 1992). Evidence to the transcriptional regulation of *sdsA* gene by *sdsB* protein was further proved (Jovicic et al. 2010). The ability of *Pseudomonas* C12 B to utilize alkyl benzene sulfonate also appears to be coded by the chromosome (Kostal et al. 1998). A novel alkylsulfatase gene, *sdsAP*, was cloned from a newly isolated bacterium *Pseudomonas* sp. S9 and expressed in a heterologous host of *E. coli* (Long et al. 2011). Plasmid-encoded character often plays a significant role in bacterial adaptation to xenobiotics in the environment (Kado and Liu 1981).

Reports on plasmid-encoded surfactant degradation also support this (Yeldho et al. 2011).

Sewage treatment plants

A sewage treatment plant represents the practical manifestations of biological surfactant degradation. The presence of surfactants (alcohol sulfates) in industrial effluents inhibited the anaerobic digestion of even readily biodegradable compounds like starch and other carbohydrates (Feitkenhauer and Meyer 2002), substantiating the need for remediation. The incorporation of surfactant-degrading bacterial cultures in household and industrial sewage could be a cost-effective method of anionic surfactant elimination, reducing the BOD, COD, and methylene blue active levels (Hosseini et al. 2007) in the water bodies. The presence of properly functioning sewage treatment plants in several places has resulted in low surfactant concentrations in the environment (van de Plassche et al. 1999). The use of fluidized bed reactors enabled the anaerobic degradation of LAS by microbial consortia (*Bacteroidetes*, *Firmicutes*,

Actinobacteria and *Proteobacteria*) in different support material giving 99 ± 2 % removal rates (de Oliveira et al. 2010).

Green surfactants

The idea of going green has launched the use of renewable materials for surfactant synthesis resulting in so-called green surfactants. This new class of biodegradable and biocompatible products is a response to the increasing consumer demand for products that are both “greener,” milder and more efficient (Benvegna and Sassi 2010). The use of renewable resources for surfactant synthesis rather than petrochemicals would reduce the liberated CO₂ levels by 37 % in EU (Patel et al. 1999). Green surfactants are defined as biobased amphiphilic molecules obtained from nature or synthesized from renewable raw materials. Various renewable raw materials particularly triglycerides, carbohydrate sources and organic acids (produced by fermentation) serve as starting materials in surfactant synthesis, of which, triglycerides/sterols contribute to the hydrophobic part while sugars/amino acids contribute to the hydrophilic part of green surfactants. Green surfactants can be synthesized from renewable raw materials either by chemical modification or utilizing the biosynthetic machinery of biotic community (plants, microbes, yeast, etc.) yielding biosurfactants.

Chemically derived green surfactants Triglycerides, regardless of their source, utilize a variety of standard oleochemical transformations—hydrogenation, hydrolysis, trans-esterification as well as certain specific modifications to yield various surfactants and surfactant precursors including fatty acid methyl ester, methyl ester sulfonate, fatty alcohols, fatty amines, fatty acid anhydrides, fatty chlorides, fatty acids, fatty acid carboxylates and alkylpolyglucosides. (Foley et al. 2012). In recent years, due to the large increase in petroleum cost, there has been a re-emergence of interest in large-volume production of fermentation chemicals. Biotechnology is providing new, low-cost and highly efficient fermentation processes for the production of chemicals from biomass resources. Moreover, with a wide range of microorganisms available and many more recently discovered, fermentation of sugars represents an important route for the production of new bioproducts. On account of the performance and the high quality, regarding the light color and the good odor, alkylpolyglucoside is particularly appropriate to cosmetic lotions and creams (Weuthen et al. 1995). Alkylpolyglucosides are found to be superior to various carbohydrate based surfactants and are extensively produced on account of its good performance, mildness and completely renewable-based nature. Methyl ester sulfonate offers an environmentally friendly and viable alternative to the currently

used workhorse surfactant LAS due to its high biodegradability (Ghazali 2002).

As noted earlier, surfactants could be synthesized either from petrochemicals or natural oleochemicals, but the use of green surfactants does not always bring a solution to ecotoxicity as the surfactants chemically remains the same irrespective of the mode of its synthesis. For example, while surfactants like linear sulfate and secondary alkyl sulfonates are purely petrochemical-based surfactants like alcohol sulfates, alcohol ether sulfates and alkyl ethoxylates are partly fossil fuel based or partly oleo chemical based.

Biosurfactants as alternate to synthetic surfactants Biosurfactants are biological compounds with high surface-active properties (Georgia and Poe 1931), produced by microorganisms, plants, animals and humans (Christofi and Ivshina 2002). They are produced on microbial cells surfaces or excreted extracellularly and contain both hydrophilic and hydrophobic moieties. They have several advantages over the chemical surfactants, such as lower toxicity higher biodegradability (Zajic et al. 1977), better environmental compatibility (Georgiou et al. 1992), higher foaming ability (Razafindralambo et al. 1996), high selectivity and specific activity at extreme temperatures, pH and salinity (Velikonja and Kosaric 1993) and the ability to be synthesized from renewable feed stock (Desai and Banat 1997). In general, biosurfactants are more effective and efficient, and their CMC is about 10–40 times lower than that of chemical surfactants, i.e., less surfactant is necessary to get a maximum decrease in surface tension (Desai and Banat 1997), and biosurfactants also have higher EC₅₀ than synthetic surfactants (Poremba et al. 1991). Biosurfactants constitute an interesting alternative to the commercial chemical surfactants with potential use in several industries (Vaz et al. 2012).

Biosurfactants are of different types including glycolipids, lipopeptides, phospholipids, surface-active antibiotics, fatty acids/neutral lipids, polymeric surfactants and particulate (Muthusamy et al. 2008). These compounds are produced during the growth of microorganisms on water-soluble and water immiscible substrates. Diverse ranges of prokaryotic and eukaryotic microorganisms are capable of producing surfactants (Lang 2002). Bacterial surfactant—producing organisms—includes *P. aeruginosa* (mono- and di-rhamnolipid biosurfactants), *Corynebacterium*, *Nocardia* and *Rhodococcus* spp. (phospholipids, trehalose dimycolates/dicorynomycolates, glycolipids etc.), *Bacillus subtilis* (surfactin), *Bacillus licheniformis* (lipopeptide similar to surfactin), *Arthrobacter paraffineus* (trehalose and sucrose lipids) and others. Fungi involved in surfactant production include the yeasts *Torulopsis* spp. (sophorolipids) and *Candida* spp. (liposan, phospholipids) (Christofi and Ivshina 2002). The potential application of

Table 2 Potential applications of biosurfactants

Biosurfactant	Organism	Potential use	Reference
Rhamnolipid	<i>P. aeruginosa</i> , <i>P. chlororaphis</i> strain NRRLB-30761, <i>Burkholderia thailandensis</i> , <i>Burkholderia pseudomallei</i>	Wound healing	Stipcevic et al. (2006)
		Stabilization of nanoparticles	Kumar and Mamidyala (2011)
		Preparation of microemulsion	Nguyen and Sabatini (2009), Xie et al. (2007)
		Antiagglomeration agent	York and Firoozabadi (2008)
		In cleaning soap mixtures	
		Cosmetic additives	Ishigami and Suzuki (1997)
		Biofungicide named Zonix	USEPA (2008)
		Pyrene degradation	Das and Mukherjee (2007)
		Degradation of hydrophobic compounds	Noordman and Janssen (2002)
		Sophorolipid	<i>Candida bombicola</i> , <i>Candida apicola</i> , <i>Rhodotorula bogoriensis</i>
Anticancer activity	Chen et al. (2006)		
Decrease pulmonary inflammation by decreasing IgE	Vakil et al. (2010)		
Antiviral activity against HIV, Herpes virus	Shah et al. (2005)		
Antibacterial activity of sophorolipid coated silver nanoparticles against both Gram-positive and Gram-negative bacteria	Singh et al. (2009)		
Surfactin	<i>B. subtilis</i>	Inhibits fibrin clot formation that indicates its potential use in the pharmaceutical sector	Rodrigues et al. (2006)
		Antiadhesive in surgicals	Mireles et al. (2001)
Cyclic lipopeptides	<i>B. subtilis</i>	In laundry detergent formulations	Mukherjee (2007)
Fengycin	<i>B. subtilis</i>	Antifungal agents of crop pathogens	Ramarathnam et al. (2007)
Iturin	<i>B. subtilis</i>	Antifungal agents of crop pathogens	Mizumoto et al. (2007)

biosurfactants in Table 2 depicts the various fields in which the use of synthetic detergents can be replaced by biosurfactants.

Some practical approaches have been adopted to make biosurfactant production process economically attractive including use of cheaper raw materials, optimized and efficient bioprocesses and overproducing mutant and recombinant strains for obtaining maximum productivity (Muthusamy et al. 2008). Agro-industrial wastes such as olive oil mill effluent (Mercade et al. 1993), soap stock (Shabtai 1990; Benincasa et al. 2002); molasses (Patel and Desai 1997), starch-rich wastes (Nitschke and Pastore 2004) and vegetable oils (Makkar et al. 2011) are used for surfactant production. Optimized biosurfactant production by an integrated rational whole-cell biocatalyst and bioprocess design methodology, termed systems biotechnology, has also been described

(Muller and Hausmann 2011). A novel method of SDS-based rhamnolipid synthesis is also been introduced yielding a high substrate to product conversion ratio (Rebello et al. 2013). However, current biosurfactant research has advanced far ahead providing significant opportunities to replace chemical surfactants with sustainable biologically produced alternatives in bulk commercial products. The growing demand for ecofriendly, truly bio-based surfactants, along with developments biosurfactant production has commercialized their production as shown in Table 3.

Conclusions

Tracing back from the ancient ashes, to modern petrochemical or nonrenewable raw material based surfactants,

Table 3 Commercially produced biosurfactants with their prospective uses

Company	Surfactant	Producer	Use
Ecover	Sophorolipids	<i>Candida bombicola</i>	Hard surface cleansers, laundry detergents
Jeneil	Rhamnolipids	<i>P. aeruginosa</i>	Zonix—biofungicide Reco—cleaning oil storage tanks
Urumqi Unite Bio-Technology	Rhamnolipids	<i>P. aeruginosa</i>	Microbial enhanced oil recovery, environmental remediation etc.
MG Intobio	Sophorolipids	<i>Candida bombicola</i>	Soaps
Kemin products	Lecithins	Plants	Lysoforte—changes the environment in the digestive tract to enhance absorption of nutrients, including fat-soluble vitamins of animals aiming profitability of animal production.
Athena Co. Ltd.	Saponins	Plant (<i>Saponaria officinalis</i>)	AT biosurfactant SP-
Etec environmental technologies	Nonionic biosurfactant	–	PetroSolv™ biosurfactant-remediate a wide range of contaminants like diesel, heating oil, and chlorinated solvents

the surfactant industry is constantly evolving and expanding to a highly competitive sector yielding a myriad of brands to meet the various demands of mankind. Their consumption is increasing day by day with no limits and restrictions, equally contributed by domestic purposes and industry. Such accumulation of these silent toxicants to the ecosystem could lead to drastic environmental problems including global warming, terrestrial and aquatic toxicity of the ecosystem and its inhabitants. Total banning of surfactants is impossible in such a modernized lifestyle needing surfactants in our food, cosmetics, cleansers, etc.

Surfactants are quite often regarded harmless, on basis of its biodegradability and speculated low concentrations in the environment. But statistical analysis of surfactant concentrations worldwide reveals the fact that these pollutants are found in concentrations higher than their predicted no effect concentrations. Thus, regarding surfactants as nonpollutants is a mistake. Visible manifestations of surfactant toxicity are available in the case of microbes, plants and animals.

The problem of surfactants toxicity should be thus addressed with cautiousness in every nation. Wise and limited usage of surfactants right from household level to large scale industries thus could reduce the intensity of surfactant pollution. The use of various physical, chemical and bioremediation strategies could help to reduce the toxicity of surfactants before their disposal into the environment. In such a scenario, going green by choosing the right surfactants, especially phosphate free and eco-friendly ones, gains relevance. Ultimately the utilization

of biosurfactants could lower the extent of synthetic surfactants prevalence in environment and its associated toxicity.

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