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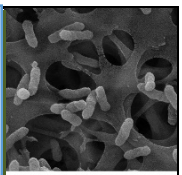

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# Biodegradation of Linear Alkylbenzene Sulfonates (LAS): A Mini Review

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**ABSTRACT**

The most common anionic surfactants in the formulation of detergents are Linear Alkylbenzene Sulfonates (LAS), with an anionic sulfonate head group and a hydrophobic alkylbenzene tail group. The two primary synthetic detergents, together with sodium laureth sulphate, have been around for quite some time and may be found in many personal-care items such as shampoos, soaps, toothpaste, and laundry detergent. LAS is a relatively recalcitrant compound and not easily biodegraded. It is a major source of environmental contamination. Bioremediation can potentially give a significantly higher removal efficiency than standard physicochemical techniques. This review aims to compile information on the toxicity, biodegradation and assimilatory pathway of this class of compound. One of the challenges in the bioremediation of this class of compound is that there have been limited SDBS-degrading bacteria isolated and characterized to date and further work in the field of bioremediation should focus on the isolation of more degraders and carrying out further trials with micro-and mesocosms.

## INTRODUCTION

In the case of synthetic detergents, anionic surfactants are the most often utilised and employed the most as additives in all of the components. Surfactants are extensively used in soaps and detergents as active components, and as such, shampoos and dishwashing solutions may be considered personal care products [1,2]. For many industrial applications, a major role is played by plastic and polymer particles in food, medicines, and the recovery of oil [3,4]. In the 1930s, alkylbenzene sulfonates were initially formed as branched alkylbenzene sulfonates (BAS). Many of them were replaced by linear alkylbenzene sulfonates (LAS) in the 1960s, due to environmental concerns.

Since the early 1980s, the manufacturing of this commodity has grown to approximately 3.5 million tonnes, making them the most manufactured anionic product. BAS initially appeared on the market in the early 1930s but experienced considerable development from the late 1940s forward. In early literature, BAS formulation or syndets (synthetic detergent) were often used as synthetic detergents [5–14]. The Friedel–Crafts alkylation of benzene with propylene tetramer followed by sulfonation was what they had planned. Propylene tetramer is a catch-all word that may be used to describe a complex combination of chemicals produced via the oligomerization of propene. While conventional soaps provided little resistance to hard water, BAS gave more resistance to it, plus improved frothing. As a result, this process was not completely biodegradable. In places such as lakes, rivers, and coastlines, where effluent is discharged, BAS was extensively criticised for causing huge stretches of stable foam to develop. Linear alkylbenzene sulfonates, which mostly superseded BAS, began to be phased out in detergent products in the 1960s (LAS). Where fast biodegradability is less essential, it is nevertheless important in some agricultural and commercial processes, where rapid biodegradation is required [5,15–20].

Anionic surfactants, including the most significant of them, linear alkylbenzene sulfonates, are extensively employed in their production. More than 40% of all surfactants used are LAS. Anionic surfactants, because of their widespread usage globally, are likely to enter water and land resources [21]. Surfactants are found in natural ecosystems in two ways: either wastewater flows cause surfactants to emerge (e.g. laundry detergent), or a direct application causes surfactants to be formed (for example, agricultural chemical sprays) [22,23]. These elements contribute greatly to the natural environment, where they are ultimately released into the rivers and the soil [24].

The most often utilised biodegradation technique for wastewater removal is surfactant dewatering [25,26]. It takes microorganisms thousands of years to break down detergent in nature. The need for alternative methods of water clean-up is on the rise, but researchers are becoming more interested in the utilisation of microbial degradation ability. Bacteria, which are both natural and sewage-related, are primary agents of surfactant biodegradation [23,27–29]. Biological degradation is environmentally friendly and cheap. Using bacterial communities to degrade Sodium Dodecylbenzene Sulfonate with greater efficiency [30,31] is one of the bioremediation techniques in the biological clean-up of industrial wastewater.

**Sodium Dodecylbenzene Sulfonate**

LAS is a category of xenobiotic chemicals that either has sulfonated or ester sulphate groups [32,33]. A linear alkyl chain (10-14 carbon atoms), a benzene ring, and a sulfonated group are present in commercial LAS (**Fig. 1**). Mixtures of various alkyl chain lengths (C10 to C13 or C14) and different phenyl positional isomers of 2 to 5-phenole (i.e., 2 to 5-phenyl-phenyl) are made by controlling the proportion of different starting materials and reaction conditions, and then the mixture is aromatized with a sulfonated para position with a linear alkyl chain and attached to an aromatic ring anywhere except for the terminal carbons (i.e., 1-phenyl) [34–37].


**Fig. 1**. Structure of Sodium Dodecylbenzene Sulfonate (DBS).

**Properties of Sodium Dodecylbenzene Sulfonate (DBS)**

Sodium Dodecylbenzene Sulfonate is a white or light yellow flake and melts at >300ºC. The important characteristic of DBS is their solubility in water. This molecule is characterized by having a hydrophilic head and a hydrophobic tail [1] facilitates the solubilization of hydrophobic substances in the water of 5-10 mg/ml at 20ºC. This molecule is stable under ordinary conditions. Besides that, DBS is also a nonvolatile compound produced by sulfonation.

**Sodium Dodecylbenzene Sulfonate (DBS) in industry**

Over 30 years, about 2.8 million tonnes of sodium dodecylbenzene sulfonate (or DBS) were utilised [38]. It is commonly used as additives in various industrial utilities, like in the cosmetics industry, as well as to make household primary cleaning agents such as laundry powders, laundry liquids, dishwashing liquids, and other household cleaners at concentrations of up to 25% in consumer products while as much as 30% in commercial products.

**Toxicity of Sodium Dodecylbenzene Sulfonate**

For Sodium Dodecylbenzenesulfonate, the oral $LD_{50}$ in rats was 1.26 g per kg. When rats were administered oral dosages of 1000 ppm SDDBS in water, no substantial toxic effects were detected. Dermal applications of 10% SDDBS to abraded skin caused no systemic toxicity in rabbits, although significant irritation at the site of application was noted. A formulation containing 15% SDDBS for 22 weeks was given in rats at 2.5–5.0 ml/kg/day [39]. Moderate necrosis of the intestinal mucosa, with hemosiderosis of the spleen, kidneys, and liver were seen. No lesions were found in rats given 0.5 ml/kg/day [40]. The findings of tests employing SDDBS to induce mutations were negative. LAS and TEA-DDBS and oral SDDBS and LAS dermal carcinogenicity tests produced negative results. According to the findings provided in this study, it is determined that Sodium Dodecylbenzenesulfonate, is safe in the current practices of use as cosmetic components [41].

Commercial surfactants are mostly manufactured organic chemicals and are thus classified as xenobiotics. surfactants are xenobiotics that contribute substantially to the pollutant profile of sewage and wastewater treatment plants, as well as wastewater treatment plant effluents. Surfactants are safe and non-toxic, however new research shows that some synthetic surfactants and their breakdown products may have potentially dangerous impacts on human health and the environment.

There is worry about severe environmental impacts because of the high amount of DBS. Re-mobilization of organic contaminants, suppression of biological processes, and toxic effects on organisms [23]. In addition to potentially being toxic to aquatic vertebrates and invertebrates, excessive use of these surfactants may also disrupt the hormonal systems of aquatic organisms, leading to ecosystem alterations [42]. One of the most prevalent contamination sources of a receiving water body is domestic and industrial wastewater.

**Treatment of waste product containing DBS**

After the usage of DBS, the waste product is disposed of and is sent to wastewater treatment facilities that may be filtered and cleaned to prepare for reuse (WWTP). Studies have shown that DBS removal in wastewater treatment is done via physical, chemical, and biological mechanisms. In the vast majority of activated sludge systems, microbial degradation is the primary pathway for LAS removal, resulting in a decrease in LAS overall. A combination of fuel oil and anionic surfactants is found in garages and car washes' wastewater. It may be possible to recycle polluted water in such cases (for example, for vehicle washing) and effluent from decontamination facilities may decrease the environmental pollution. Bio-augmentation methods may be utilised as effective approaches in the biological cleaning of industrial effluent [43,44].

**Principles of bioremediation**

Bioremediation methods may be utilised as effective remedies for the treatment of harmful or inexpensive industrial effluent. A definition of bioremediation is that it is a biological degradation process where organic waste is de-contaminated to concentrations below regulatory standards. This method seeks to accelerate the natural deterioration processes by eliminating environmental degradation factors. This may be either that the microbe is native to a polluted region, or that it was introduced to the polluted location.

As part of the microbe's metabolic activities, contaminated chemicals are converted. To boost the current microbial population at a polluted site, one would use bio-augmentation, which entails the adding of microorganisms to the site [45].

When the culture is sourced, and the temperature is high, the rate of biodegradation increases [46]. Genetically enhanced cultures, for example, are introduced via the technique of bio-augmentation because of the slow rate of destruction by indigenous bacteria. This may potentially create issues such as an inability to touch substances to be destroyed, or the attraction of laboratory-grown microbes as food for predators. The procedure must work because the microbe has to have enzymatic activity and be able to convert the pollutant into innocuous by-products. In order for bioremediation to be effective, the environment needs to provide both an abundance of microbial life and favourable conditions to promote microbial growth and activity.

As a result, implementation of bioremediation usually requires some adjustment of environmental factors to help microbes grow and degrade more quickly. Many types of pollution may be handled on-site, making the procedures less expensive than incineration and possibly decreasing danger to clean-up workers or even increasing it if there is a transport incident. The public would find it more tolerable because of bioremediation, which is based on natural attenuation. On the other hand, the disadvantages of bioremediation are a relatively slow reaction process and the failure of achieving the desired end-points [47]. Also, some metabolic products may be harmful and toxic to other organisms.

**Biodegradation of Sodium Dodecylbenzene Sulfonate by microorganisms**

Because microorganisms in the environment perform biodegradation and pollution clearance, they are involved in the degradation and removal of hazardous and non-toxic contaminants. Thus, biodegradation is the natural process of breaking down organic compounds (for example, materials containing carbon) into simpler chemical units by microorganisms. The term ‘biodegradable' describes a chemical that may be broken down in this manner. Surfactants that act on the surface, including emulsifiers, are more often known as surfactants. Biodegradation of detergents begins as soon as unclean laundry water with excessive foam produced by these chemicals is flushed down the drain with extra detergent.

Because of biodegradation, surfactants are readily biodegradable and, as a result, present low environmental concentrations [23]. One molecule's surfactant characteristics may be compromised and it will lose these qualities, including its capacity to foam. This causes the main degradation to proceed further breakdown of the molecules (sulfophenyl carboxylates). Carbon dioxide, water, bacterial biomass, and mineral salts all play a significant role in the ecosystem (ultimate degradation). Under some conditions, mineralization may mean the culmination of biodegradation.

One of the most often occurring disposal methods for LAS from contaminated environments is microbial biodegradation [28,48,49]. Enzymatic reactions of different bacterial groups take place at the same time. To combat anionic surfactants, microbes will breakdown them at a very slow pace in nature. Carbon source DBS is being consumed by microorganisms that are capable of using it for nourishment, while at the same time DBS is being destroyed. So, to maintain accuracy in determining the concentration of anionic surfactants, as well as to make it fast and easy to monitor their biodegradation over time, it is essential to know the actual concentration and to have accurate processes in place. Methylene blue is used to evaluate the surface agents in aqueous samples using spectrophotometry [50]. The ionic pair formed between the anionic surfactants, AS, and the methylene blue, MB, is used to evaluate the biodegradation of LAS. During the degradation process, an anionic surfactant level was found to determine the biodegradation profiles. The count of heterotrophic bacteria (CFU/ml) must be determined throughout these biodegradation tests.

Compared to SDBS, its sister compound SDS is easier degraded and numerous degrading bacteria have been isolated [51–56]. SDBS degradation as a sole carbon source is the ultimate tool for the degradation of this recalcitrant detergent. Very few microorganisms can do this. A bacterial strain, called WZR-A, was discovered from polluted river water, and it was shown to be able to use sodium dodecylbenzene sulfonate (SDBS) as the only carbon and energy source for growth. Based on the physical and physiological characteristics, strain *Ochrobactrum anthropi* was identified as the cause of the outbreak. To achieve maximum growth and SDBS degradation, the optimal pH and temperature are 7.0 and 30 degrees C, respectively.

When the concentration was less than 400 mg/L, the degradation rate of SDBS was 80% or higher. Proteins were found to vary in the total cell protein composition of the strain following SDBS induction. In the experiment with the enzyme distribution, the distribution of SDBS degradation was shown to be intracellular in the bacteria. The findings revealed that the strain of interest could use wider spectrum substrates via aromatic ring cracking of SDBS, as shown by the characterisation of degradation substrates and activity of relative catabolic enzymes in crude extracts. The genes involved in SDBS breakdown were discovered to be localised on the plasmid using the plasmid isolation and curing method [57].

Other SDBS-degrading bacteria requires supplementation with easily assimilable carbon sources. For instance, the consortium bacteria consisting of *Pantoea agglomerans* and *Acinetobacter calcoaceticus* were able to break down SDBS and sodium dodecyl sulphate (SDS). While growing in nutrient broth medium, the development of this consortium at 30 °C, pH 8.5, and 250 rpm resulted in the degradation and production of high biomass using the two surfactants. While just 60% of the SDBS biomass could be degraded under similar growing circumstances, the full breakdown of the SDS biomass was accomplished in 120 hours. Additional feeding of the mixed culture provided for the complete breakdown of LAS. Additionally, nitrogen nutrition addition has improved the SDBS biodegradation rate from 60% to 90%. Adding carbon and nitrogen nutrients to the mixed culture adversely affected the SDS degradation induction [58].

**Sodium Dodecylbenzene Sulfonate degradative pathways**

Most experts consider LAS to be biodegradable surfactants. certain effluent from wastewater treatment utilising aerobic methods has been shown to have very high biodegradation values [59]. The first step in the LAS biodegradation pathway involves the production of oxygen at the very end of the alkyl chain, followed by a shortening of the alkyl chain (β-oxidation) and aromatic ring breakage (desulfonation) [48]. Sulfophenyl carboxylate is an intermediate in this route. LAS biodegradation is preferred in aerobic than anaerobic environments [60,61].

When LAS breaks down, the straight alkyl chain is degraded, the sulfonate group is degraded, and the benzene ring is consumed [62,63]. When the terminal methyl group is oxidised (ω-oxidation), alcohol is formed and an aldehyde, which leads to the formation of a carboxylic acid (see figure 4). Enzyme-catalyzed processes (e.g. in alcoholic fermentation) include two dehydrogenases and an alkane monooxygenase. After carboxylic acid has been β-oxidized, the carbonyl carbon fragment enters the tricarboxylic acid cycle, which is subsequently followed by two carbon fragments β-oxidation and acetyl-CoA production. This occurs when a branched alkyl chain cannot undergo β-oxidation by microorganisms, and a side chain methyl group or a gem dimethyl-branched chain must be destroyed by loss of one carbon atom at a time (α-oxidation). In the degradation of LAS, the sulfonated component is lost [62]. Based on the current three following mechanisms, three methods for desulfonation of aromatic ring degradation products have been suggested.

Hydroxyative desulfonation:
$RSO_3H + H_2O \qquad ROH + 2H^+ + SO_3^{2-}$ (i)
Monooxygenase catalysis under acidic conditions:
$RSO_3H + O_2 + 2NADH \qquad ROH + H_2O + SO_3^{2-} + 2NAD^+$ (ii)
Reductive desulfonation:
$RSO_3H + NADH + H^+ \qquad RH + NAD^+ + H_2SO_4$ (iii)

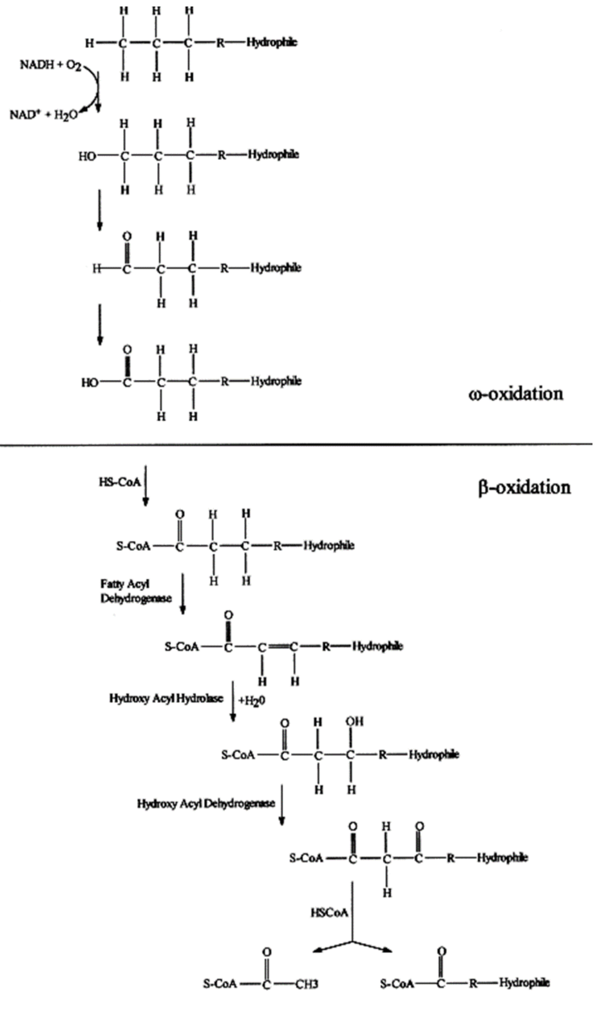


**Fig. 2**. The reaction pathways of ω- and β-oxidation of the alkyl chain during surfactant degradation [65].

The break-down product of LAS is sulfite that may be oxidised into the environment to sulphate. LAS removal of both alkyl and sulfonate leaves either benzoic and phenylacetic acids. Phenyl acid microbial oxidation may lead to fumaric, acetoacitic acids, and catechol benzene [62]. The pace and degree of individual LAS molar degradation relied on the length of the alkyl chain and the sulphophenyl composition in the molar [48]. For the longest alkyl chain LAS and for the LAS isomers with the mid-alkyl chain, degradation rates were quicker. the sulphophenyl group was slower. The decline of alkylic chain and lack of capacity to cleave the sulfone aromatic ring of LAS are typically confined to single bacterial strains [64]. In addition, full biodegradation indicates that the bacterial consortium which has been created has all enzymes necessary for the metabolic breakdown (**Fig. 2**) of these structurally diverse surfactants [23].

## CONCLUSION

SDBS is a relatively recalcitrant LAS and is ubiquitous environmental pollution. It is one of the highly utilized synthetic surfactants, where bioremediation presents a much better removal method compared to physicochemical methods. The primary disposal method for LAS from the contaminated environment is the microbial biodegradation route. In addition, bacterial community's breakdown DBS with higher efficiency; use it as their only carbon source at concentrations that are frequently quite high in terms of energy in the environment, supporting its development which is less dangerous and cost-efficient. Unfortunately, not many SDBS-degrading bacteria have been isolated and future remediation works should concentrate on the isolation of more degraders and more micro- and mesocosm works should be carried out.

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