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A Review on the Degradation of Ionic and Non-Ionic Surfactants in Water

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ABSTRACT

Water contamination is a serious problem of current times that needs the immediate attention of mankind. With every passing day, the emergence of a variety of unaddressed contaminants poses a serious threat not only to mankind but also to the environment. Among the common contaminants are heavy metals, microorganisms, agricultural and pharmaceutical waste, radioactive elements, and industrial waste. Among these, surfactants are used widely by industries as well as households, have attracted the attention of agencies due to their inherent features/properties. Due to their specific chemical structure surfactants consisting up of a hydrophobic and hydrophilic part are difficult to degrade by environmental processes. Their presence in the soil and water adversely affects the species surviving in the near vicinity. Long-term consumption of surfactants contaminated water leads to serious consequences. It has become the need of the hour to devise a suitable technologies for degradation of surfactants. This paper gives a detailed account of surfactants, their applications/ uses, environmental impacts, techniques for surfactant degradation, and other mechanisms, current scenario along with future recommendations.

Keywords: Surfactant; Linear alkylbenzene sulphonate; Alkylphenol ethoxlate; Treatment of water; Treatment of water; Analytical method for surfactant degradation

1. INTRODUCTION

Water is a substance containing inorganic, odorless, tasteless, transparent, and almost colorless chemical substance which creates the majority of the fluids and the hydrosphere of all known living things of Earth. It can be said to be a necessary constituent for all the known life forms. In recent times, water pollution is a serious global environmental concern.

Our rivers, lakes, reservoirs, groundwater, and aquifers are all affected by water pollution, not to mention the seas and oceans that span the bulk of our world. However, not all types of water contamination are caused by the same thing. The water body is polluted mainly by surfactants in two distinct ways, natural and anthropogenic. So, in this review, we will discuss only the anthropogenic method of water pollution by surfactant. For example, pollution caused by chemicals, groundwater pollution caused by microbes, pollution of nutrients, pollution that depletes oxygen, and pollution of surface waters are the major reasons for water pollution and surfactant is one of the major pollutants[1].

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Surfactants are one of the most common and harmful pollutants found in both aquatic and terrestrial environments. Surface-active agents, or surfactants, are amphiphilic compounds. It has a polar head region and a non-polar tail region. Molecules which possess both hydrophobic and hydrophilic regions are known as amphiphilic molecules. So, it is also an amphiphilic molecule[2]. But we can't remove surfactants from our daily life due to their physicochemical properties[3]. These are compounds that lower water's surface tension, making the molecules less likely to stick together and more likely to interact with oil and grease. They're found in a wide range of cleaning products. Surfactant buildup in nature, in the other hand, is a major problem for environmental sustainability and a healthy ecosystem. Anionic, semi-polar, amphoteric, non-ionic, and cationic surfactants are the five types of surfactants available on the market, depending on the kind of modification on hydrophilic groups[4]. Surfactants for example LAS (linear alkylbenzene sulfonates) and ethoxylates of lauryl alcohol (LAEs)could not be determined earlier but this review states the detection methodology using mass spectroscopy with the reference from Motteran, *et al*. such analytical technique with its method of detection of the surfactants have been discussed in this review. Finally, surfactants are a growing market, with annual growth rates of 3 per cent to 4 per cent on a global scale. The global use of surfactants is approximately 9.3 million tonnes.

When compared to other synthetic organic compounds, such as plastics, this is a small amount (about 110 MT worldwide). Nonetheless, it seems worthwhile to examine the surfactant product group because it is one of the few areas where good know-how on the use of bio-based sources is accessible due to present practices. Furthermore, the technological obstacles to increasing the market share of renewable resource-based products are likely to be minimal. The worldwide surfactants market was worth $41.3 billion in 2019 and is predicted to increase at a CAGR of 5.3 per cent between 2020 and 2027, reaching $58.5 billion by 2027. The anionic and non-ionic groups make up most surfactants generated and account for roughly half of the total volume. The market share of different surfactants is shown in (Fig. 1).

The remaining surfactant kinds are made in far smaller quantities. In terms of manufacturing volume and captive use, non-ionic, particularly ethoxylates, have surpassed anionics. The applications of surfactants are depicted in Fig.2.

Usually, surfactants reduce interfacial tension and stabilise foams. They are often found in detergents, dishwashing liquids, shampoo, pesticides, and other consumer goods. Surfactants have a wide range of industrial applications, all of which are quite useful. Table 1 depicts some applications and risk of surfactant is shown.

Surfactants (surface-active agents) are mixed with other ingredients such as builders (e.g., tripolyphosphate), boosters, auxiliary compounds, and so on. The effects of the surfactant in a detergent composition have gotten the most attention in terms of environmental concerns[5].

The residual surfactants are discharged directly into surface waterways or sewage systems after use, and the majority of them end up in sediment, water, and soil. The harmful effects of surfactants on a variety of aquatic animals are well known. While the concentration of surfactant in water is too high, surfactants such as ethylene glycol monostearate enter the blood, kidney, gills, blood, gallbladder, kidney, and liver, poisoning the aquatic lifeforms. This review paper discusses surfactants, their applications/uses, environmental implications, surfactant degrading processes, and other mechanisms, as well as the current situation and future suggestions[6].

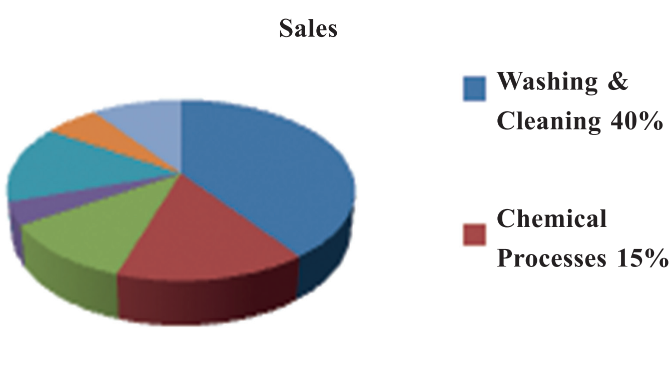


Figure 2. Distribution of surfactant production by field of application

1.1 Characterisation of Surfactant

Surfactants are compounds that form high-resolution self-assembled molecular clusters known as micelles that absorb to the interface between an organic and an aqueous component. A surface-active agent should contain a chemical with two completely distinct beneficial teams with varied affinities at consistent molecule intervals to highlight these two physical qualities. The molecules of surface-active agents also feature a helpful cluster known as the deliquescent cluster, which has a strong affinity for water. Associate in nursing amphiphilic structure is a small structure with two competing functions. Depending on the polarity of the head group, surfactants are classified as anionic, nonionic, cationic, or amphoteric. Surfactant's chemical structures are shown in Fig.3.

1.1.1 Anionic Surfactant

An anionic surfactant's hydrophilic component as a negative charge. Surfactant molecules are aided in raising and suspending soils in micelles by the charge. Because anionic surfactants can handle a wide range of soils, they are used in soaps and detergents.

Anionic surfactants are the most important surfactant used in laundry detergents: Soaps are a type of soap that is used to clean the body. At low concentrations, the anionic surfactant can be found in both polar and non polar liquids in monomeric form. They form regular aggregates at higher concentrations (critical micelles concentration, CMC) (micelles)[3].

- LAS which is the main example of Sulfonate of alkylbenzene
- Alkyl ether sulfates (AES)
- Alkyl sulfates (AS)
- The compound of the secondary methane series is called Sulfonate.

The cationic surfactants (cetyl trimethyl ammonium bromide, CTAB) and sodium benzene dodecyl sulfate (SDS) had a substantial impact on the chymotryptic degradation, dissociation, and the enteral absorption of an insulin hexamer, but Tween80 and polyoxyethylene lauryl ether had no effect. Anionic surfactants can generate micro-emulsions with a variety of chlorocarbons, increasing their water solubility. In Japan, synthetic anionic surfactants known as LAS have virtually replaced US soap. Linear LAS has excellent detergency properties, and because of their high solubility, they are widely utilised in liquid detergent compositions. LAS, like soap, is susceptible to water hardness; the detergency performance of LAS decreases as water hardness rises.

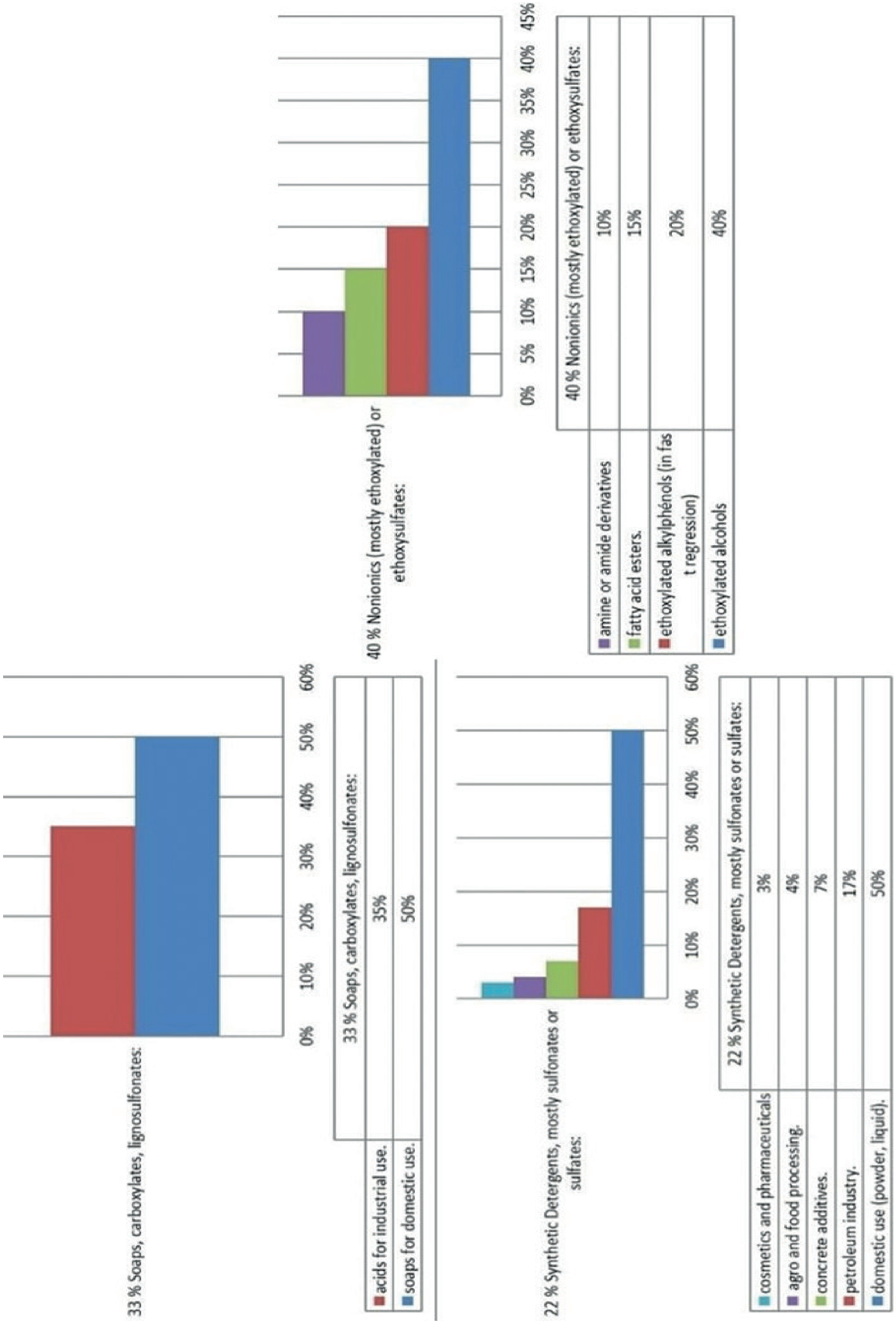


Figure 1. Market share of different surfactant.

Table 1. Surfactant use and its venture into the environment

Common name	Abbreviation	Class	Application	Risk	Reference
Linear alkylbenzene sulphonic acid	LAS	Anionic	Personal care products and detergent formulation	Non-conservative conduct	[47]
Sodium dodecyl sulfate	SDS		-	-	
Alkyl sulfate	AS		-	-	
Sodium lauryl sulfate	SLS		-	-	
Alkyl ethoxy sulfate	AES		-	-	
Quaternary ammonium compound	QAC	Cationic	Fabric softeners, disinfectants, hair conditioners, cosmetics, biocides, and wetting agents are all used in the textile sector.	Very toxic in the nature	[48]
Benzalkonium chloride	BAC		-	-	[49]
Cetylpyridinium bromide	CPM		-	-	
Cetylpyridinium chloride	CPC		-	-	
Hexadecyltrimethylammonium bromide	HDTMA		-	-	[50]
Amine oxide	AO	Amphoteric	-	-	[51]
Alkylphenol ethoxylate	APE	Nonionic	Wetting agent, detergent, and emulsifier	Nonyl-/ octylphenolethoxylates (degraded and converted compounds) are hazardous and persistent in the environment.	
Alcohol ethoxylate	AE		-	-	

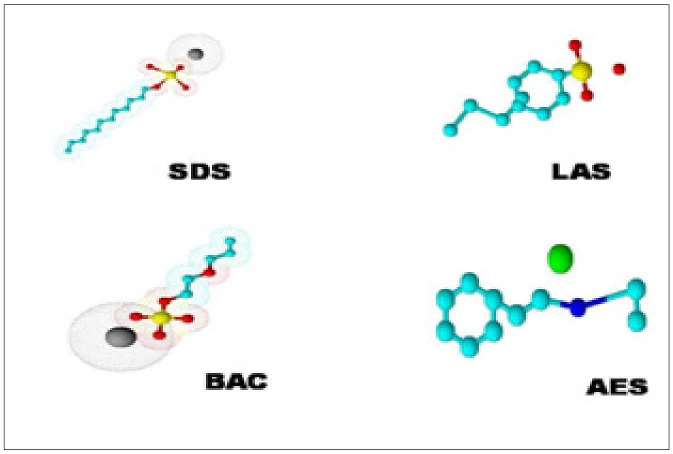


Figure 3. Chemical structure of some common surfactant.

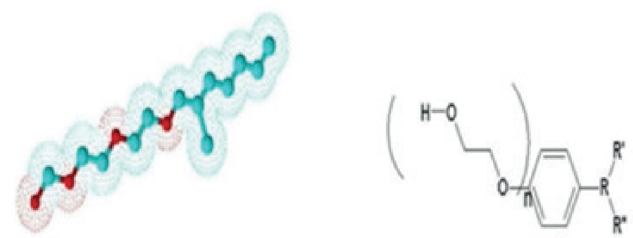
1.1.2 Nonionic Surfactant

Because of their hydrophilic group, non-dissociable surfactants like alcohol, phenol, ether, or amide do not ionize in solution. A great majority of non-ionic surfactants are hydrophilic because they include a polyethylene glycol chain which is formed by polycondensation of ethylene oxide. Because of the presence of a lipophilic group, it is often of the alkylbenzene or alkyl kind, with the derivation from natural fatty acids the former is formed. In contrast to polyethylene oxide, propylene oxide polycondensation produces a somewhat hydrophobic polyether. This polyether chain is employed as the lipophilic component in poly EO poly PO block copolymers, which are mostly classified as polymeric surfactants, which will be discussed later[4].

The trend toward washing at variations and lower temperatures within the production shares of various fibers has corresponded with the rising use of non-ionic surfactants in detergent compositions. The most common nonionic surfactants include alcohol ethoxylates (AE), fatty acid alkanolamides (FAA), Alkylamine Oxides (AO), Alkypolyglycosides (APG), Alkylphenol ethoxylates (APE), and n-Methylglucamides (NMG) as shown in Fig. 4

They are utilised in laundry detergents, home cleansers, and hand dishwashing solutions since they're great at removing oil. The inclusion of a polyethylene glycol chain, generated through polycondensation of ethylene oxide, makes a high fraction of these non-ionic surfactants hydrophilic. A non-ionic surfactant is perhaps the most employed in medication delivery applications. Polyolesters, polyoxyethylene esters, poloxamer, and pluronic (also termed poloxamer) are examples of Nonionic surfactants. Run Batch tests were run to see how surfactants affect PCP degradation rates in Sphingomonaschlorophenolicum strain RA2 as a function of surfactant type, concentration, and temperature. By attaching to different proteins and phospholipid membranes, non-ionic surfactant extracts antibacterial action.

Nonionic surfactants are less hazardous than cationic, anionic, and amphoteric surfactants. The order of cytotoxicity of surfactant determined on the corneal epithelial cells of the rabbit was non-ionic < amphoteric = anionic <cationic, according to another cytotoxicity test. Although it is known that non-ionic surfactants reduce the negative effects of anionic surfactants, which is the chemical basis for these phenomena, that is yet to be established. The water ozonation effect on the breakdown of cationic, anionic, and nonionic surfactants has been studied extensively. In the 1990s, a new form of a non-ionic surfactant called NMG was introduced into detergents. They're becoming more common in powder and liquid detergent compositions as co-surfactants. When coupled with an anionic surfactant, APG along with a hydrophobic alkyl chain and sugar derivates that are hydrophilic have different lathering capabilities. Because of its advantageous foaming properties, APG is extensively used in liquid, special, and dishwashing detergents.



Alcohol Ethoxylates (AE)　　Alkylphenol Ethoxylites (APE)

Figure 4. Schematic representation of non-ionic surfactant.

1.1.3 Cationic Surfactant

Cationic surfactants can be stated as a quaternary ammonia compound with surface-active molecules that are positive by charge (e.g., alkyl-dimethyl dichlorobenzene ammonium, dequalinium, benzalkonium, benzethonium, methyl benzethonium, cetyl pyridinium, and phenamylinium chlorides, cetrimonium, and cethexonium bromides). Cationic surfactants are utilised in detergent compositions as fabric softeners during the washing process. Quaternary nitrogen compounds are the most significant as Imidazoline derivatives.

Because of its high-pressure hydrogenation process which is to be carried out during the synthesis process, these surfactants and often more expensive than anion zs. As a result, they are only used in two situations where there is no cheaper alternative, namely as bactericides and as positively charged substances capable of adsorbing on negatively charged substrates to produce anti-static and hydrophobic effects, which are often of great commercial importance, such as corrosion inhibition[5].

1.1.4 Amphoteric Surfactant

When a single surfactant molecule contains both anionic and cationic dissociations, it's termed amphoteric or zwitterionic. This category includes synthetic molecules like betaines and sulfobetaine, as well as natural chemicals like amino acids and phospholipids.Some commonly used surfactants and their chemical structure are given in Fig.5[6].

Several new cationic surfactants are being developed right now. Even in cold water, quaternary ammonium salts derived from long-chain guerbet alcohol create lamellae liquid crystals that are easily adsorbed onto hair. Surfactant-containing aminoguanidine cations and methylene groups as spacers between the amide and guanidine groups are employed to provide conditioning and great moisturising qualities even in low-humidity settings. Submissions to add shine, quaternary ammonium compounds have been combined with amine oxides and alkyl betaines, as well as hydrocarbons and vegetable oil.

2. EFFECT OF SURFACTANT ON ENVIRONMENT

The previous studies suggest about considerable amounts of surfactants and their products that are broken down are deposited in several environmental compartments, including terrestrial and aquatic compartments, due to their extensive usage[7]. In terrestrial compartments, sewage sludge and agrochemicals can introduce surfactants into soils. Sludge is increasingly being used as plant fertiliser on agricultural grounds. Table 2 shows study findings on toxicity for terrestrial compartments. During subsequent treatment, most surfactants are aerobically biodegraded. Sludge might be utilised to remove a substantial amount (16% – 36% in LAS to above 89% for the maximum of nonylphenols, hydrophobic).

After anaerobic digestion, sewage sludge is frequently utilised in agriculture. Sludge has the potential to contaminate soils, groundwater, and rivers nearby. The emergence and spread of surfactants in soil caused by sewage sludge application pose a possible ecotoxicological danger. The surfactant can be acquired from the ingestion of seafood or drinking water. Their ability to bind with existing proteins in the human liver and serum may cause long-term concerns regarding their metabolic consequences.

Table 2. Toxicity for terrestial compartments on different test organisms

Test organisms	Analyte	Parameter	Mean value (mg/L or mg/kg)	Reference
Bush beans, radish, and grasses			27	
Potatoes		NOEC/76 days	16	[52]
Sorghum	LAS		167	
Sunflower		EC50/21 days	289	
Mung bean			316	

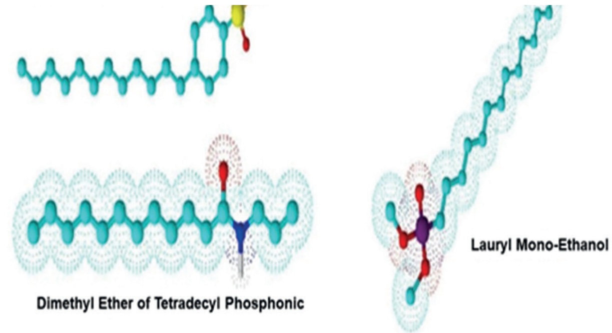


Figure 5. Commonly used amphoteric surfactant.

"Sewable sludge in agricultural water poses a risk to groundwater and neighboring rivers," according to the study. In the aquatic compartments, efficient treatment of water facilities will result in extremely low levels of surfactant being discharged into the environment; yet the enormous release of these chemicals present a risk to a wide range of aquatic ecosystems. It is seen that cationic surfactants were shown to be more hazardous than non-ionic and anionic surfactants. On *Dunaliella sp.*, a unicellular green alga, the detrimental effects of LAS and three QACs were detected. QACs have a strong biological activity. The action of this family of cationic surfactants against diverse aquatic bacteria has been extensively researched. Furthermore, QAC has the potential to reduce biological activity in water treatment plants[8].

Aerobic biodegradation is the most common breakdown mechanism in freshwater sediments. Sediment formation, transport, and erosion are all part of the dynamic processes that occur in rivers. If organic molecules that are biodegraded by aerobic bacteria pollute groundwater, it might turn anaerobic. In Table 3 the toxicity for aquatic compartments on different test organisms is shown.

The entry of surfactants can be from the environment via effluents industrial products, agrochemicals, and residential activities, causing environmental harm. Personal care wetting agents, products, emulsifiers, detergents, and softening of cloth or coating, paper, and carpets are some examples of agrochemicals, while personal care products, emulsifiers, wetting agents, and detergents are examples of industrial items that contribute to surfactant-assisted pollution. Surfactants are released into the environment by routine home operations such as laundry, disinfection, and fumigation. Surfactant fate, dispersion and persistence in the surrounding which is heavily influenced by the sorption and bio/photodegradation[9].

These processes are influenced by environmental factors like temperature, pH, and salinity. Surfactants and their breakdown products are commonly received in high quantities by municipal wastewater treatment facilities; however, following secondary treatment, surfactants and their degradation products are discharged in low amounts. Converted products include nonylphenol ethoxylates, octylphenol ethoxylates, sulfophenyl carboxylic acids

Table 3. Toxicity for aquatic compartments on different test organisms

Test organisms	Analyte	Parameter	Mean value (mg/L or mg/kg)	References
Daphnia Magna	Diethyl ester dimethyl ammonium (DEEDMAC)	LC50/24 h	14.8	[52]
	Tetradecyl trimethyl ammonium bromide (TMABr)	IC50/24 h	0.14	
	BDSM		0.13	
	LAS		1.22-13.9f	
	NPEO9	LC50/48 h	14	
	Nonylphenol (NP)		0.19	
Dunaliellasp. (green alga)	TMAC	EC50/24 h	079	
	LAC		3.5	
	TMAC		1.21	
	LAS		3.63	
Salmo gairdneri (rainbow trout)	Fatty alcohol sulfates (AS)		33.61	
	Alcohol ethoxy sulfates (AES)		10.84	
	C12EO6		22.38	
	OPEO6		6.44	
	Tetradecyl trimethyl ammonium chloride (TMAC)		8.24	
Gambusia affinis (mosquito fish)	AS		40.15	
	AES	EC50/48	13.64	
	C12EO6		29.26	
	OPEO6		9.65	
	TMAC		3.58	
Carassius auratus (gold fish)	AS		38.04	
	AES		12.35	
	C12EO6		28.02	

and nonylphenol carboxylic acids. NPEOs (octylphenol ethoxylates or nonyl) are more dangerous than their forerunners of alkylphenol forerunners (APs). Several studies have discovered that toxic surfactants have major ecological and health implications on people, other animals, microorganisms, soil fauna, crustaceans and terrestrial plants. Surfactants have long been recognised to affect a range of aquatic creatures. Non-ionic surfactants produce toxic surfactants like ethylene glycol monostearate. Surfactant poisoning occurs when the quantity of surfactant is too high in water, allowing its entrance into entering the blood, kidney, gills, pancreas, gallbladder, and liver, resulting in poisoning for the aquatic animals.

The most essential elements for analysing the environmental risks connected with commercially available surfactants are biodegradability or photo adsorption effectiveness and toxicity behaviour. Surfactant foaming and sedimentation, for example, affect water quality by self-cleaning river capacity and reducing air or water oxygen transfer to varying degrees depending on the surfactant class. Surfactants also make persistent organic pollutants (POPs) more water-soluble, and the ensuing aerosol and surfactant products have a significant impact on the environment and climate. The physiological and biochemical impacts of LAS on aquatic animals damage cell membranes, decrease metabolism and growth and cause the breakdown of the chlorophyll protein complex.

The toxicity tests utilised in the procedures include Daphnia IQ Test, Daphtoxkit F, Rotokit F/M, etc. The toxicity of surfactants was shown to be influenced by physicochemical features of water (i.e., pH, suspended matter, DO), surfactants (i.e., surfactant absorption capacity and type and concentration), and the biological factors (i.e., surfactant absorption capacity and type and concentration) (sensitivity between species and their acclimatisation and the age and type of species). The median effective concentration (EC50) and median growth inhibition concentration (IC50) on animals, plants, and microorganisms, respectively are used to assess surfactant toxicity.

Surfactants can limit microbial growth while simultaneously boosting mutation and death. Nonylphenol ethoxylates (NPEOs) for example can disturb microbial growth and nitrification processes by decoupling energy production. Anionic surfactants disturb the microbiological functions and internal structures such as competitive stress, environmental resistance, reproduction, and growth. Surfactant absorption by a microbe can depolarise the microbial cell membrane, oxygen intake, limiting nutritional absorption and the release of toxic metabolites. Certain surfactants have major health repercussions for humans when consumed or consumed through contaminated food.

Surfactants have been related to skin irritation, as well as ocular and respiratory problems in humans. Carboxylates and Alkylphenol ethoxylate impede the penetration of therapeutic compounds below the surface. Surfactants like LAS harm and change the structure of the root cell membrane. As a result, nutrient and water transpiration and transfer were impeded. Surfactants and their breakdown products provide a significant environmental risk; hence their amounts must be measured in environmental matrices[10]. The analytical technique for various surfactants has been shown in (Table 4).

3. REMEDIATION METHODS

3.1 Physical Methods

3.1.1 Adsorption

Adsorption is a process that involves the surface area of a substance and involves the adherence of ions, atoms, or molecules of a gas, liquid, or dissolved solid to a surface. Because of its efficacy in surfactant removal, it is the most widely used physical approach. Nowadays, activated carbon, nanomaterials, zeolites, clay and resin are all being used as adsorbents. However, because of their high costs, the usage of these adsorbents is limited. Activated carbon is by far the most effective adsorbent material. On the other hand, it is frequently a difficult task to develop. In recent years, there has been a lot of effort in producing environmentally friendly, low-cost, and high-efficiency adsorbents as alternatives to activated carbon[11]. One interesting technique for overcoming the limits of employing adsorption to remove surfactants from wastewater is to manufacture green adsorbents from waste materials. It was hoped that by using these materials, waste management would improve, and economic growth would result. These materials can be used as - is, unmodified or modified adsorbents, or in conjunction with other surfactant removal methods[12]. Despite the potential benefits of employing green adsorbents, further research into the socio-economic and technological elements of the matter is needed. The greatest removal efficiency is influenced by these two criteria. Furthermore, the efficacy of this procedure is dependent on the mechanism utilised. The effect of surfactant removal efficiency on surfactant composition and physicochemical properties of nanomaterials has been extensively researched. CNT with more porosity and a larger surface area has been proven to be more efficient. Furthermore, the quantity of carbon nanotubes required to attain optimal efficiency has a limit. The performance of carbon nanotubes in terms of removal is governed by their outer diameter and functional groups[13]. Multiwalled carbon nanotubes effectively removed an ionic and non-ionic surfactants, whereas cationic surfactants were scarcely removed. However, the ability of cationic surfactants to remove carbon nanoparticles is highly dependent on the nanomaterials' physicochemical qualities as well as the composition of the cationic surfactant. Figure 6 depicts the adsorption system[14].

3.1.2 *Foam Fractionation*

To remove surfactants from wastewater, foam fractionation is a potential technology as shown in Fig. 7. Surfactants are therefore isolated from contaminated water based on changes in mass concentration. The employment of nanoparticles in the stabilisation of foam

Table 4. Reactive species for different Advanced oxidation processes (AOP)

Surfactant	Technique	Detectors	References
Methylene blue active substance (MBAS) and disulfide blue active substance (DBAS)	Potentiometry titration	UV-Vis	[53]
Linear alkylbenzene sulfonates (LAS) and lauryl alcohol ethoxylates (LAEs)	Gas chromatography	Mass Spectroscopy	[54]
Polyfluorooctane sulfonate (PFOS)	Liquid chromatography (LC)	UV	[55]
Linear alkyl benzenesulfonates (LAS)	High-performance LC	ELSD	[56]
Octylphenol ethoxylates (OPEOs) and lauryl alcohol ethoxylates (LAEs)	Supercritical fluid chromatography (SFC)	MS	[57]
Octylphenol (hapten)	ELISA (biological technique)	Monoclonal/ polyclonal antibody	[58]

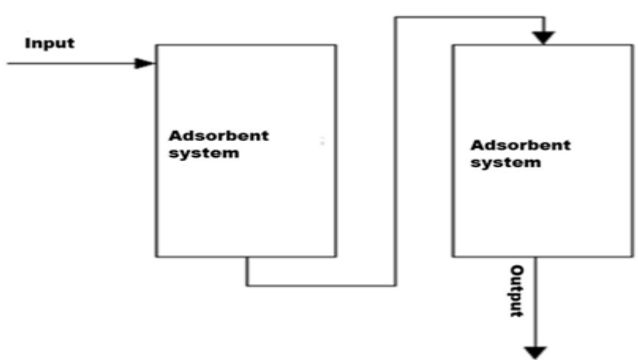


Figure 6. Adsorption system.

has led to advancements in the cleanup of surfactants from wastewater using this method. Foam properties are influenced by dual important factors: foam stability and formability. The increase in viscosity caused by activated silicon nanoparticles SNP harmed formability. Air entrainment will be hampered, and bubble formation will be reduced if the viscosity is high. As a result, the efficiency of surfactant removal will be reduced[15].

Low-cost and simple foam fractionation is one potential approach for recovering and removing surfactants from wastewater. The foam fractionation column, which can be single or multi-stage, can work in a batch or continuous mode. On the removal of anionic surfactants, feed flow rate, duration, the effects of airflow rate, foam height, and liquid height have been thoroughly researched (e.g., sodium dodecyl sulfate). Foam is a good medium for surfactant adsorption because of its large specific surface area and low interstitial liquid. Despite the extensive research on foam fractionation, efforts to commercialise it have yet to be realised. As a result, further research is needed to scale up and commercialise foam fractionation[16].

3.2 Chemical Methods

Chemical remediation is a viable solution to removing surfactants from waste streams. In practice, surfactant remediation using chemical technology results in the production of useful products like carbon dioxide, nitrogen, and water. Chemical treatments come in a variety of forms and variations[17.]

3.2.1 Coagulation

It's an effective strategy. This technology, which is based on iron and aluminum compounds, cleans extremely contaminated cosmetic effluent. Due to the bigger quantities and more diversity produced from sludge containing aluminum, aluminum-based coagulants function well. Coagulation is occasionally used in conjunction with other techniques including air flocculation and Fenton processes. For the removal of contaminants in high concentrations, coagulation-flocculation is very successful[18].

According to the study, the Fenton procedure, on the other hand, had the lowest removal efficiency when compared to the other listed techniques. The efficiency of the coagulation process is also influenced by the choice of coagulants. If the coagulants are not properly disposed of, they usually produce additional waste. As a result, more effort must be made into developing coagulants capable of selectively extracting raw surfactant from water and recovering it excluding polluting the influent[19]. (Fig. 8)

3.2.2 Advanced Oxidation Processes

When treating refractory surfactants from water, it is a viable remediation approach. Surfactant cleanup techniques include electrochemical, electro-Fenton, electroperoxide, and UV light irradiation. These techniques have several benefits over standard chemical processes, including the absence of carcinogenic chlorinated compounds and pathogenic bacteria[20]. Table 5 shows reactive species for the different advanced oxidation processes. Figure 9 shows the schematic for the Advanced oxidation process

3.2.3 Electrochemical Advanced Oxidation Processes

Electrochemical advanced oxidation procedures are one of the alternative remediation options for anionic surfactants (EAOPs). Electrochemistry methods are used

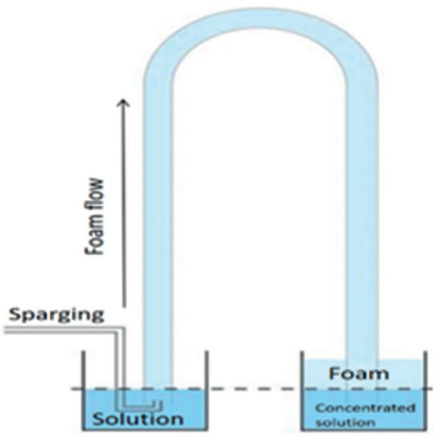


Figure 7. Foam fractionation.

to break down refractory surfactants from wastewater in this procedure. EAOPs are thought to be safe and environmentally friendly. The absence of chemicals in the procedure ensures its safety. This approach uses the transfer of electrons between the electrodes to break down toxic surfactants by generating hydroxyl radicals[21]. In all three procedures, increasing the applied current enhances COD (representing surfactant) efficiency to remove. It has been observed that a high electric current boosts the formation of BDD (OH) at a faster and larger rate. As a result, the surfactant molecules in the system can easily be oxidised. Increases in applied current density, on the other hand, result in unfavorable high energy consumption. When comparing the energy consumption of the three processes, the EF method uses the least amount of energy and has the highest current effectiveness. This is the case because both the radicals produced by the EF method destroy the organic molecule[22].

3.2.4 The Anaerobic/Oxic Method

It is also used to eliminate surfactants. The process is separated into six compartments, two of which are anoxic and four of which are oxic. Surfactant elimination is dependent on the anoxic treatment compartments. However, seasonal fluctuations in the location or nation in question have a significant impact on the removal efficiency of this operation[23,24]. However, information about the nature of the intermediates and products employed in this technique is still limited in the literature[25].

3.2.5 Sonoreactor

The use of a sonoreactor is to remove waste water. It has several uses, including environmental friendliness, ease of operation, low chemical consumption, no sludge production, and no by-products[26]. The schematic of the sonoreactor is shown in Fig. 10. It is also an effective advanced oxidation treatment technology because of its minimal operating and maintenance costs[27]. In theory, this reactor works on the principle of free radical generation[28]. According to current research, LAS deterioration accelerates with time. In contrast, increasing the initial LAS concentration lowers the rate of LAS elimination. Increasing acoustic power, on the other hand, causes LAS to degrade faster[29]. This is due to the possibility of a response in the sonoreactor's cavitation[30]. High acoustic power, on the other hand, meant more energy[32]. As a result, a balance between efficiency and energy cost must be maintained.

3.3 Biological Methods

The advantages of biological treatment include decreased operating costs and the use of environmentally friendly procedures. Microorganisms such as algae, fungus, and bacteria are used to break down big molecular weight chemicals into smaller ones. Long operating times, inability to cure hazardous materials, and high surfactant concentrations are some of the disadvantages of biological treatment procedures[33]. As a result, the system suffers from biomass death.

3.3.1 Biodegradation

Surfactants are mostly destroyed in the environment by microbial activity[34]. The chemical structure of the surfactant and the physicochemical characteristics of its surrounding medium are the most important factors in biodegradation[35]. Synthetic surfactants, as well as any of their breakdown by-products, have some health and environmental consequences[36]. Because of the harmful effects on aquatic

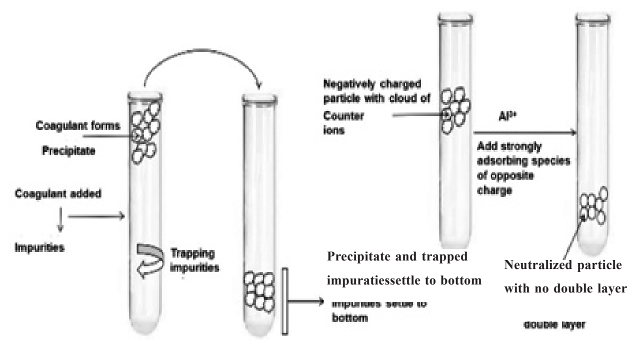


Figure 8. Coagulation process for surfactant removal.

life and the potential to alter hormonal systems in these aquatic creatures, these impacts are considered major issues[37].

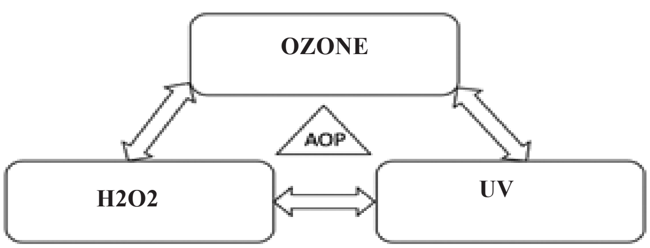
A biodegradable surfactant is commonly referred to as LAS[38]. Biodegradation values of 97 per cent to 99 per cent have been reported in some WWTPs that employ aerobic processes[39]. APE, on the other hand, has estimations ranging from 0 to 20 per cent based on oxygen consumption from 0 to 8 per cent with the help of spectroscopic techniques[40].

3.3.2 Sulfonation

It is one of the surfactant degradation processes. Sulfur trioxide and sulfuric acid are mixed to generate benzenesulfonic acid in a reversible process. The method

Table 5. Reactive species for different Advanced oxidation processes (AOP)

AOP	Reactive species	References
Ozone treatment O_3	$.{\cdot}OH$, $HO_2^{\cdot}$, $HO_3^{\cdot}$, $O_2^{-\cdot}$, $O_3^{-\cdot}$	[59]
O_2/H_2O_2	$\cdot OH$, $O_2^{-\cdot}$, O_3^{-}	
Fenton processes: H_2O_2/Fe^{2+}	$\cdot OH$, $HO_2^{\cdot}$	
Photo –Fenton processes	$\cdot OH$	
UV/O_3,UV/H_2O_2 and $UV/O_3/H_2O_2$	$\cdot OH$, $HO_2^{\cdot}$ / $O_2^{-\cdot}$, O_3^{-}	
V-UV(λ< 190 nm)	$\cdot OH$, H^+ , $e^{-\,aq}$	
Photocatalytic treatment	$\cdot OH$, h^+, $O_2^{-\cdot}$, e-, $^1O_2$, $HO_2^{\cdot}$, $HOO\cdot$	
UV/Vis light using TiO_2		
ZnO, etc as catalysts		
Ultrasonic treatment	.OH , . H	
ϒ-Radiolysis	$.{\cdot}OH$, $\cdot H$, e^-_{aq}	



AOP: Advanced oxidation process

Figure 9. The schematic for the Advanced oxidation process.

is reversed to make benzene by adding boiling aqueous acid to benzenesulfonic acid[41]. Sulfonation procedures consist of the reactions of sulfuric acid along with aromatic hydrocarbons, chlorosulfuric acid, or sulfur trioxide, as well as the reactions of organic halogen compounds along with inorganic sulfites and the oxidation of certain classes of organic sulfur compounds, such as disulfides orthiols. The desulfonation reaction is the hydrolysis of sulfonic acids in organic chemistry. It's the polar opposite of sulfonation[42]. The ease of sulfonation is related to the temperature of desulfonation. According to the reactions below, three processes for desulphonation have been proposed[43].

Hydroxyativedesulphonation:

$$RSO_3H + H_2O = ROH + 2H^+$$

Monooxygenase catalysis under acid conditions:

$$RSO_3H + O_2 + 2NADH \rightarrow ROH + H_2O + 2NAD^+$$

Reductive desulphonation:

$$RSO_3H + NADH + H^+ = RH + NAD^+ + H_2SO_3$$

3.3.3 Beta-oxidation and Omega Oxidation (-oxidation)

During surfactant breakdown, it is the L-oxidation and g-oxidation of the alkyl chain reaction pathways as shown in Fig. 11

Some of the drawbacks of traditional biological treatment technologies are being addressed by advanced technologies that combine a variety of different processes[44]. According to current research, TAMR can tolerate high-stress conditions and block high surfactant concentrations[45]. In addition, combining these three techniques improves surfactant removal. However, in terms of cost, TAMR +NF is the best option. Ultra filtration, which allows the reactor to store biomass and treat huge quantities of the target surfactants, can also increase the efficiency of the thermophilic aerobic reactor[46].

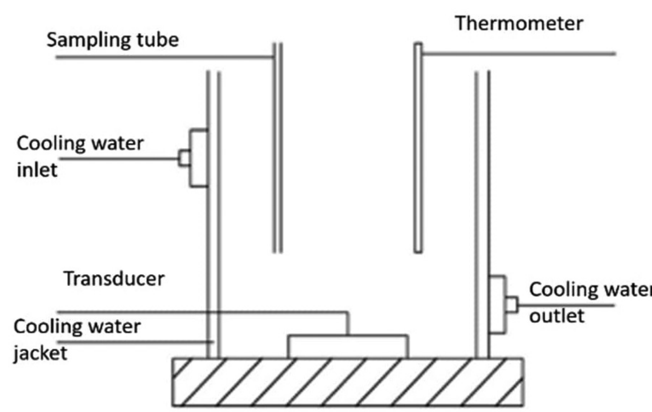


Figure 10. Basic design of a sonoreactor.

4. PROSPECTS

Surfactants are used as wetting, cleaning, dispersing, foaming, emulsifying and anti-foaming agents in a wide range of products and applications, including fabric softeners, detergents, motor oils, soaps, paints, adhesives, emulsions, inks, flotation, anti-fogs, snowboard wax, ski waxes, deinking of recycled papers, washing, and enzymatic processes, and laxatives.

Agrochemical formulations include biocides (sanitizers), herbicides (some), insecticides and spermicides (nonoxynol-9). Personal care products include cosmetics, shower gel, shampoos, hair conditioners, and toothpaste. Surfactants

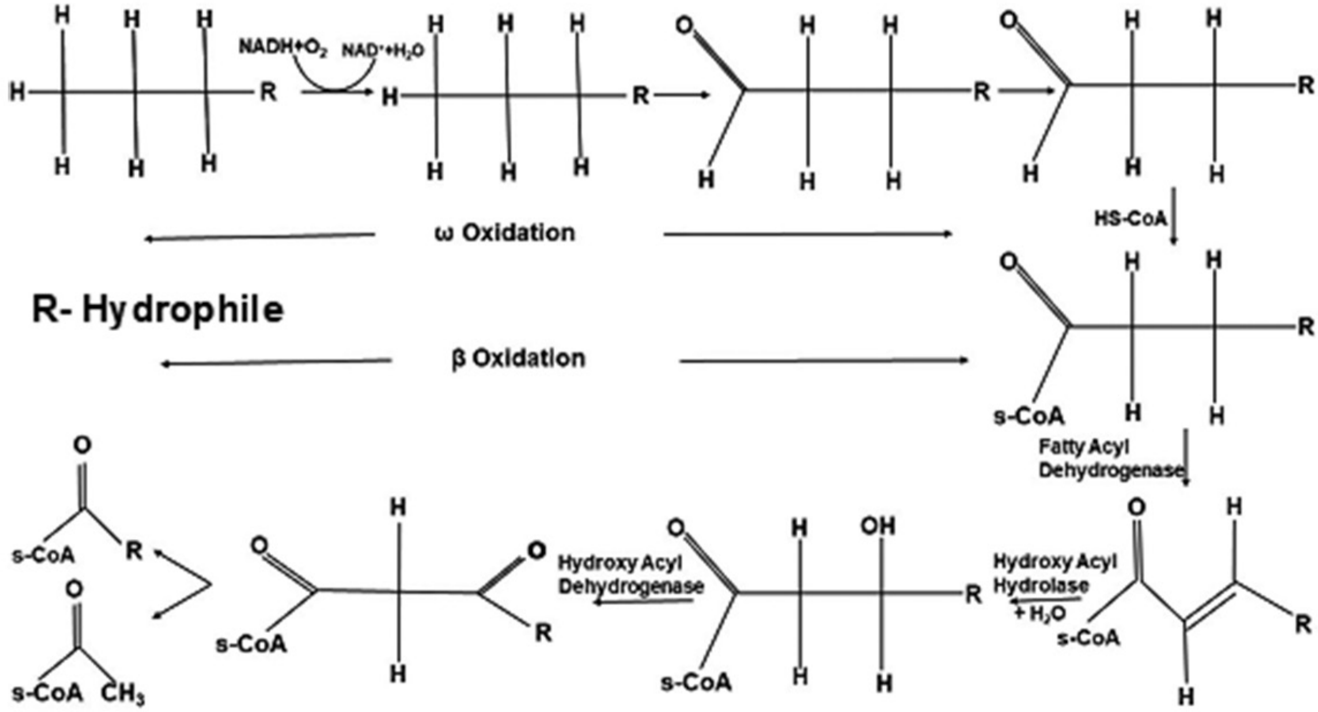


Figure 11. During surfactant breakdown, the chemical pathways L-oxidation.

are widely used in the pipeline building industries and firefighting (liquid drag-reducing agents). Alkali surfactant polymers are used in oil wells to mobilize oil.

It operates by displacing air from the cotton pad and bandage matrixes, allowing a solution that is medicinal to be absorbed and administered to different regions of the body. They also treat wounds with detergents and use therapeutic lotions and sprays to the skin's surface and mucous membranes to displace dirt and debris. Future potential includes detergents in biotechnology and biochemistry, surfactants in droplet-based microfluidics and quantum dot preparation.

5. CONCLUSION

The surfactant load in water effluent discharged into the environment appears to have been reduced to the point where harmful ejects on aquatic species are insignificant. Problems with APE breakdown products, particularly NP have led to a decrease in APE utilisation in recent years. When applied to aerobic soil, few surfactants which are not oxygen dependent during sludge treatment are unexpectedly eliminated.

Surfactants amphiphilic nature adds to their adsorption on the surface of the particle in sewage. Anaerobic soils might not be good candidates for amendment. Within the United Kingdom, there are three primary methods for sewage sludge disposal: landfill, soil application and incineration application. The requirement to dump waste on non-agricultural soils must be defined carefully.

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