

#### Article Info

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### Biodegradability of Laundry Detergent Surfactants

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#### ABSTRACT

*The use of surfactants is increasing day by day. The byproducts of surfactants harm our atmosphere. Biodegradable surfactants are displacing conventional soaps and surfactants to control the harmful effects of uses of surfactants. This review paper describes the biodegradability of laundry surfactants. The main objective of this paper is to discuss the biodegradability of different type of surfactants approved by analytical data. This paper also discusses different analytical methods to tests the biodegradability of surfactants.*

**Keywords:** Surfactants; Anionic Surfactants; Cationic Surfactants; Biodegradability; Biodegradability Tests.

#### 1.0 Introduction

Surfactants (1) are the amphipathic molecules with polar (hydrophilic) and non-polar (hydrophobic) components within the molecule.

They tend to reduce surface tension of solution and thereby enhance surface active properties. Surfactants are broadly classified into four categories: anionic, cationic, zwitter-ionic and non-ionic.

Anionic and cationic have permanent negative and positive charges, respectively. Non-ionic detergents do not have any permanent charge; instead, they have weakly electronegative or electropositive atoms.

Zwitter-ionic has both the charges on the same molecule.

Anionic surfactants are the major cleansing agent in most of the laundry detergents and are able to remove oil and dust from the fabrics whereby cationic surfactants are used in detergents as fabric softeners and antistatic agents.

Nowadays, laundry detergents are the major components found in activated sludge and organic river sediments that need to be decomposed in sewage treatment plants before they are released into the environment. If they are not decomposed properly, they will be found within the water supply since they will not be absorbed by natural surfaces in the water ways.

#### 2.0 Biodegradation

Biodegradation (2) is the process by which organic matter get decomposed by the action of micro-organisms present in aerobic or aerobic environment. After treatment done by micro-organisms, 50-90% of these organic substances utilized to provide the energy necessary to sustain life. Remained carbon content is used as building material for the microbial cell constituents like proteins, fats etc.

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The final products of the microbial degradation of organic substances are generally mineralization products like carbon dioxide, water and mineral salts and newly formed biomass. The mineralization of organic materials consumed oxygen from environment that finally ends up in carbon dioxide, water and mineral salts etc. On the basis of results, biodegradation of surfactants are classified into three types

### **2.1 Primary degradation-**

This comprised of the transformation of surfactants by micro-organism resulting in the loss of its surface active properties.

### **2.2 Ultimate biodegradation-**

This comprised of the complete degradation of surfactants by micro-organism resulting in the release of inorganic substances such as CO<sub>2</sub>, H<sub>2</sub>O and mineral salts.

### **2.3 Ready Aerobic Biodegradation-**

In this type of degradation, surfactants rapidly and completely get degraded in aquatic environment under aerobic conditions.

### **2.4 Inherent Biodegradation-**

In inherent biodegradation, metabolites (non-surfactants) degrade into carbon dioxide and water within 24 days which could be extended up to 60 days depending upon different environmental conditions.

Inoculums, surfactants degrade under different temperature conditions and pre-adaptation of the micro-organisms can also be used in case of surfactant.

## **3.0 Biodegradation Tests**

As per Detergents Regulation proposed for the test methods, the achievement of a threshold level of 60% of the oxygen consumption or carbon dioxide production in a 28-day period was internationally recognized as it indicated a very high level of ultimate biodegradation.

According to the Detergents Directives, the extent of primary biodegradation of surfactants, measured as the removal of the parent chemical, is far

above the 90% pass level whereas, the 60% mineralisation requirement is far more demanding than the current 90% primary biodegradation requirement that provides a much enhanced level of environmental protection.

Several tests are used to determine the primary biodegradability of surfactants. Shake culture test, semicontinuous activated sludge (SCAS) test and continuous activated sludge (CAS) test are specified by detergent legislation in many countries i.e. US, Japan, Korea and Organization for Economic Co-operation and Development (OECD).

Shake culture test corresponds to surface water condition, SCAS and CAS tests stimulate the biodegradation that occurs in the communal sewage treatment plant.

A number of ultimate biodegradability tests have been used to estimate the environment compatibility of organic compounds.

The degradation of organic compound is measured using non specific parameters such as BOD/COD, CO<sub>2</sub> evolution and carbon removal.

Closed bottle test, modified OECD screening test, modified AFNOR test, modified STRUM test and modified MITI tests are specified in OECD

So many workers had worked to illustrate the different biodegradation tests for surfactants. Some of them are given as:

## **3.1 Primary tests for biodegradability (3)**

### **3.1.1. Shake culture test a**

Activated sludge microorganisms are inoculated into a flask that contains a microbial growth medium and the surfactants to be tested.

Following two adaptive transfers, biodegradation is determined by measuring the reduction in surfactant content during the test period.

### **3.1.2 Shake culture test b (37)**

A small no of polyvalent bacteria are inoculated into a flask that contains a chemically defined medium and the surfactant as a sole carbon source by simply adding a little sewage treatment plant effluent. Biodegradation is determined by measuring the reduction in surfactant content at fixed interval for up to 19 days.

### 3.1.3. Continuous activated sludge test (cas)

The surfactant to be tested is added in a concentration corresponding to 20 mg MBAS/liter to a synthetic sewage.

The sewage is fed into the activated sludge vessel of the model treatment plant where it remains for an average of three hours.

Sludge and supernatant are separated in the settling vessel and the effluent is collected. Biodegradation is determined by measuring the reduction of surfactant content.

### 3.1.4. Semi continuous activated sludge test (scas)

The activated sludge obtained from the sewage treatment plant, the surfactant to be tested, and the synthetic sewage as an energy source for the sludge micro-organisms are placed in an aeration chamber.

The mixture is aerated for 23 hours and then settling down followed by the removal of the supernatant material.

The remaining sludge is aerated and then brought back to volume with fresh surfactant and synthetic sewage with continuous repetition of the cycle. Biodegradation is determined by the reduction in surfactant content during each cycle.

## 3.2 Ultimate biodegradation tests (4)

A predetermined amount of the compound is dissolved in an inorganic medium providing a concentration of usually 2 mg of test substance per liter.

The solution is inoculated with a small no of microorganisms from a mixed population and kept in closed bottle in the dark in a constant temperature or enclosure at 20 to 21°C.

The degradation is followed by oxygen analysis over 28 days period. Closed bottle test was carried out based on the OECD guidelines.

## 3.3 Respirometry test (5)

The system Oxitop Control® (WTW, Weilheim, Germany) was used to determine the manometric changes, occurred during oxygen consumption for transforming the surfactant into CO<sub>2</sub> by the microorganisms inoculated (from a mixed population and aerated) in a mixture of nutrient solution and the surfactant.

The Oxitop system involved the number of reactors consisting of glass bottles (510 nominal volumes) with a carbon dioxide trap (sodium hydroxide) in the headspace.

The volume of the test mixture is usually 164 mL.

The bottles were furnished with a magnetic stirrer and sealed with a cap containing an electronic pressure indicator.

An incubator box was used to maintain the respirometer units at constant temperature (25°C) during a test run.

The decrease in headspace pressure in the closed test vessel constantly calculated the biochemical oxygen demand (BOD) using following equation:

$$DBO = M(O_2)R \cdot T \cdot V_{Total} - V_{Liquid}V_{Total} + \alpha \cdot T_{25}T_0 \cdot \Delta p(O_2)$$

Where,  $M(O_2)$  is the molecular weight of oxygen (32g/mol)

$R$  is the gas constant (83.144 mbar/(molK))

$T_0$  is the temperature at 0 °C (273.15 K)

$T_{25}$  is the incubation temperature, 25°C (298.15 K)

$V_{Total}$  is the total volume in the test vessel

$V_{Liquid}$  is the volume of the test mixture

$\alpha$  is the Bunsen absorption coefficient (0.03103)

$\Delta p(O_2)$  is the difference of the partial pressure of oxygen (mbar).

**Confirmatory Test:** The test was performed as per OECD 301 E test for ready biodegradability [21], which is used for those surfactants which have failed in the screening test of biodegradability.

It consists of inoculating a small amount of microorganisms, from a secondary effluent-treatment plant that works preferably with household wastewater.

The biodegradation process was performed on the small activated sludge plant at laboratory scale, where synthetic wastewater was used with a surfactant concentration of 10 mg/L at flow rate of 1 L/h.

The test was run at room temperature (18-25°C).

Finally, Chemical oxygen demand (COD), and dissolved organic carbon (DOC) were measured daily to determine the biodegradation efficiency.

### 3.4 Micro-organisms biodegradation tests (6)

Micro-organisms degrading surfactants do it to grow creation of biomass.

The biomass & metabolism cannot be measured by the biodegradability tests; only “CO<sub>2</sub> or O<sub>2</sub> level” is measured. Surfactant → CO<sub>2</sub> + H<sub>2</sub>O + mineral salts + biomass + metabolism

### 3.5 Analytical methods

Several analytical methods (7) of biodegradation tests were described in literature. Most of them were based on liquid chromatography with UV diode array and fluorescence (FLD), or mass spectrometric detectors.

The method detection limits (MLDs) of LC techniques employing direct injection of samples are too high for the detection of low levels allowed in natural waters.

Therefore, water samples require more pre-concentrations before analysis. Solid-phase extraction (SPE) is one of the most important techniques for sample enrichment because it overcomes many of the disadvantages of liquid liquid extraction.

But as SPE was time consuming and expensive it was further combined with HPLC, which deliver simple, rapid, and accurate means for determining biodegradability.

### 4.0 Biodegradability of Surfactants

Biodegradability can be defined as the ability of substances to be broken down into their basic components through natural processes by microorganism such as bacteria, fungi, yeast and other simple organisms.

Nowadays, biodegradability of surfactants and the treatment of sewage (8) is a major concern for the industries.

It has been reported that even after the sewage treatment, a high percentage of the anionic surfactant molecules remain unaffected which are continuously releasing into the environment; these molecules are found to be highly toxic even at low concentrations.

Moreover, surfactants which contain branched hydrophobes are not as easily biodegraded as surfactants which contain simple linear hydrophobes.

An example of a branched hydrophobe would be the cationic surfactant that is used as a fabric softener.

A much larger proportion of these surfactants will be released into the environment from sewage treatment plants.

Biodegradability of mainly used anionic, nonionic, cationic and amphoteric surfactants is given in Table 1 to table 3.

### 4.1 Linear alkylbenzene sulphonates (las)

LAS are the most commonly used surfactants that are found to get decomposed easily with a half-life of 1–87 days. Bacteria start metabolising LAS immediately after removing from the anaerobic environment of sludge digestion that leads to relatively short half-lives of the surfactants.

It has been noticed that high biodegradability of LAS suppresses the accumulation of LAS in soil.

### 4.2 Soaps

Soaps, still commonly used surfactants contain C<sub>12</sub>–C<sub>18</sub> chains are readily available to microbes [9] also gets precipitated with metal ions present in hard water and influences biodegradation rate.

Schoberl and his co-workers [10] reported 80–90% mineralization of Sturm-tested sodium soap salts whereas calcium soap salts showed significantly less biodegradability with only 67% of mineralization.

During waste water treatment, precipitation made by less biodegradable soaps leads to sedimentation in the primary settling tanks of WWTP that depends upon the hardness of water.

The effectiveness of WWTP and the degradation of these compounds can be determined by anaerobic degradation of soap.

**Table 1: Biodegradability of Anionic Surfactants (38):**

Surfactant type	Characterization	Test subs. In mg/l active matter	Test subs. In mg/l carbon	Inoculum in (dm) g/l	Test duration in days	Results in %
Soap	Na-palmitate Na-laurate Na-stearate	70-1000		1-5	28-54	>90
LAS	C <sub>10</sub> -C <sub>13</sub>	50			49	0
	C <sub>8</sub> -C <sub>12</sub>		50		60	0
	C <sub>10</sub> -C <sub>13</sub>	151	100	1.5	84	0
		75	50		119	0
SAS	C <sub>10</sub> -C <sub>14</sub>		10-200	3-4.5	78	0
	C <sub>14</sub> -C <sub>17</sub>					
SAS	C <sub>14</sub> -C <sub>17</sub>		20-100	3	17	0
					70	0
Alpha-olefin sulfonates	C <sub>14</sub> -C <sub>16</sub>		20-100	3	70	0
Methyl-ester sulfonates	C <sub>10</sub> -C <sub>16</sub>		20-100	3	70	0
Dialkyl sulfosuccinates	di-C <sub>8</sub> -SS		20-100	3	70	35-50
Monoalkyl ethoxy sulfosuccinates	C <sub>12</sub> - (EO) <sub>3</sub> -SS		20-100	3	23->80	0
Alcohol sulfonates	C <sub>18</sub>	50	29	3	5684	88
	C <sub>12</sub> -C <sub>18</sub>	239	100	1-5	42	59
	C <sub>12</sub> -C <sub>13</sub> linear	30		1-5	42	70
	C <sub>14</sub> -C <sub>15</sub> 80% linear	30		1-5	42	60
	C <sub>12</sub> -C <sub>13</sub> mid chain	30		1-5	42	40
	branched	30		1-5	42	25
	C <sub>12</sub> -C <sub>13</sub> mainly branched					
Alkylether sulfates Na salt	C <sub>12</sub>		20	0.15	56	0-30
Alcohol ether sulfate	C <sub>12</sub> -14, 2EO		50	1-5	41	75
	C <sub>12</sub> , xEO	40-100	20-50	0.06-0.12	55-56	14-41
	C <sub>12</sub> -14, 2EO	191	100	1.5	84	0
		95	50		119	60

**Table 2-Biodegradability of Nonionic Surfactants**

Surfactant type	Characterization	Test subs. In mg/l active matter	Test subs. In mg/l carbon	Inoculum in (dm) g/l	Test duration in days	Results in %
Alcohol ethoxylates	C <sub>9</sub> -11, 8EO		20-50	0.15-1.5	56-96	>75
	Isotridecanol,		20	2-3	110	0-30
	(5,10,20)EO		20	0.15		35
	C <sub>12</sub> -15, 7EO		20	2-3	110	29-94
	C <sub>12</sub> -14, (5,10,20)EO		20	2-3	89	0-23
	Mono Br C <sub>14</sub> -15, (10,20)EO		100	1.5	84	64
Alkyl phenol Ethoxylates	Dehydol LT7					
	Nonylphenol, 10 EO	50		1.5	84	20,5±12,6
	Nonylphenol, 9 EO	50		1	40-50	32-43 CH4
Glucosides	Ethyl 6-O-ecanoylglucoside	30-40	20	0.15	56	59-65
	APG branched C <sub>8</sub> , DP=1,6	30-40	20	0.15		22
	APG linear C <sub>12</sub> -14, DP=1,4		20	0.15	56-96	72
	C <sub>12</sub> -14 APG		100	3	56	>75
	C <sub>8</sub> -14 APG		203	1.5	84	>80
	Glucopon 215 CSUP		20-50	0.15	56-96	61
				0.15-1.5	56-96	>75
						>75
Alpha-olefin sulfonates	C <sub>14</sub> -C <sub>16</sub>		20-100	3	70	0
Methyl-ester	C <sub>10</sub> -C <sub>16</sub>		20-100	3	70	0

<b>sulfonates</b>						
<b>Dialkyl sulfosuccinates</b>	di-C <sub>8</sub> -SS		20-100	3	70	35-50
<b>Monoalkyl ethoxy sulfosuccinates</b>	C <sub>12</sub> - (EO) <sub>3</sub> -SS		20-100	3	23->80	0
<b>Alcohol sulfonates</b>	C <sub>18</sub> C <sub>12</sub> -C <sub>18</sub> C <sub>12</sub> -C <sub>13</sub> linear C <sub>14</sub> -C <sub>15</sub> 80% linear C <sub>12</sub> -C <sub>13</sub> mid chain branched C <sub>12</sub> -C <sub>13</sub> mainly branched	50 239 30 30 30 30	29 100	3 1-5 1-5 1-5 1-5 1-5	5684 42 42 42 42 42	88 59 70 60 40 25
<b>Alkylether sulfates Na salt</b>	C <sub>12</sub>		20	0.15	56	0-30
<b>Alcohol ether sulfate</b>	C <sub>12</sub> -14, 2EO C <sub>12</sub> , xEO C <sub>12</sub> -14, 2EO	40-100 191 95	50 20-50 100 50	1-5 0.06-0.12 1.5	41 55-56 84 119	75 14-41 0 60

**Table 3: Biodegradability of Cationic Surfactants**

Surfactant type	Characterization	Test subs. In mg/l active matter	Test subs. In mg/l carbon	Inoculum in (dm) g/l	Test duration in days	Results in %
<b>Alcohol ethoxylates</b>	C <sub>9</sub> -11, 8EO Isotridecanol, (5,10,20)EO C <sub>12</sub> -15, 7EO C <sub>12</sub> -14, (5,10,20)EO Mono Br C <sub>14</sub> -15, (10,20)EO Dehydol LT7		20-50 20 20 20 20 100	0.15-1.5 2-3 0.15 2-3 2-3 1.5	56-96 110 110 89 84	>75 0-30 35 29-94 0-23 64
<b>Alkyl phenol Ethoxylates</b>	Nonylphenol, 10 EO Nonylphenol, 9 EO	50 50		1.5 1	84 40-50	20,5±12,6 32-43 CH4
<b>Glucosides</b>	C <sub>14</sub> -C <sub>17</sub> C <sub>14</sub> -C <sub>17</sub>		20-100	3	17 70	0 0
<b>Alpha-olefin sulfonates</b>	C <sub>14</sub> -C <sub>16</sub>		20-100	3	70	0
<b>Methyl-ester sulfonates</b>	C <sub>10</sub> -C <sub>16</sub>		20-100	3	70	0
<b>Dialkyl sulfosuccinates</b>	di-C <sub>8</sub> -SS		20-100	3	70	35-50
<b>Monoalkyl ethoxy sulfosuccinates</b>	C <sub>12</sub> - (EO) <sub>3</sub> -SS		20-100	3	23->80	0
<b>Alcohol sulfonates</b>	C <sub>18</sub> C <sub>12</sub> -C <sub>18</sub> C <sub>12</sub> -C <sub>13</sub> linear C <sub>14</sub> -C <sub>15</sub> 80% linear C <sub>12</sub> -C <sub>13</sub> mid chain branched C <sub>12</sub> -C <sub>13</sub> mainly branched	50 239 30 30 30 30	29 100	3 1-5 1-5 1-5 1-5 1-5	5684 42 42 42 42 42	88 59 70 60 40 25
<b>Alkylether sulfates Na salt</b>	C <sub>12</sub>		20	0.15	56	0-30
<b>Alcohol ether sulfate</b>	C <sub>12</sub> -14, 2EO C <sub>12</sub> , xEO C <sub>12</sub> -14, 2EO	40-100 191 95	50 20-50 100 50	1-5 0.06-0.12 1.5	41 55-56 84 119	75 14-41 0 60

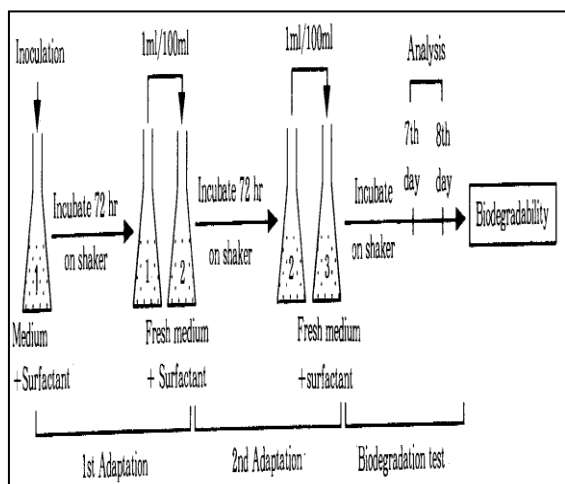
$\beta$ -oxidation of the alkyl chain (9) involved in soap breakdown does not require the presence of molecular oxygen and therefore they can readily biodegradable under anaerobic conditions. After placing the  $^{14}\text{C}$ -16 soap in anaerobic bioreactor for 28 days Steber and Weirich [11] suggested that the soap was 92–97% degraded with the evolution of  $^{14}\text{CO}_2$  and  $^{14}\text{CH}_4$ . Anaerobic degradation of 79–94% degradation of sodium palmitate 3-4 weeks was reported by Birch et al. [12].

Above researches evident good biodegradability of soap in aerobic and anaerobic environments and found them ultimately treatable within the conditions and residence time of wastewater within a WWTP.

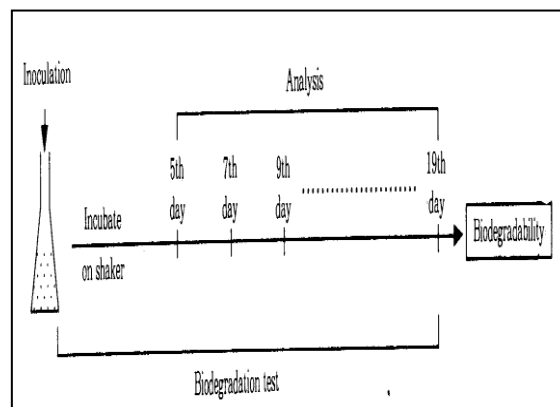
#### 4.3 Secondary alkane sulphonates

Many researchers [10] have reported that SAS is rapidly degradable with >90% removal in less than 3 days. Lotzsch et al. [13] incubated uniformly labelled  $\text{C}_{17}$  SAS and observed 61% ultimate degradation, producing  $\text{CO}_2$ . Neufahrt et al. [14] incubated  $^{14}\text{C}_{17}$  SAS for 3 days observing 47% degradation to  $\text{CO}_2$  and 25% incorporation into biomass. Several researchers [9, 12] reported that SAS might not be available for the anaerobic degradation of sludge, that is due to their similar biodegradation pathways arises from similar molecular characteristics of LAS and SAS. Absence of  $\text{O}_2$  resist the  $\omega$ -oxidation of the alkyl chains and their oxidative desulphonation.

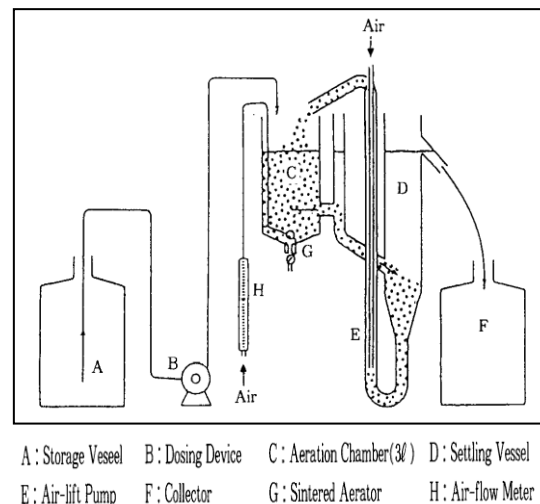
**Fig 1: Shake Culture Test A**



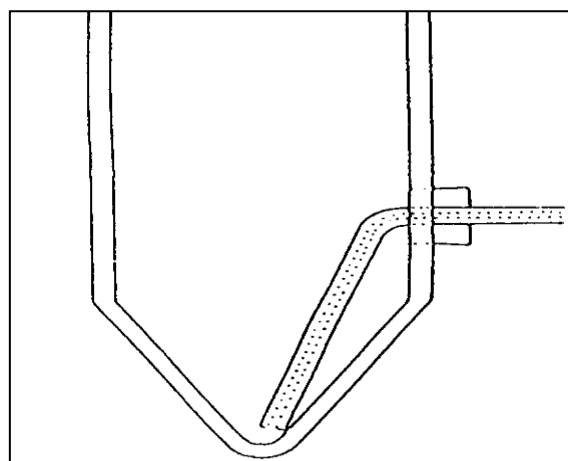
**Fig 2: Shake Culture Test B**



**Fig 3: Continuous Activated Sludge Test**



**Fig 4: Semi Continuous Activated Sludge Test**





#### 4.4. Fatty acid esters

Fatty acid esters (FES) are readily digestible under aerobic environment. Gode et al. [15] found 99% primary degradation and 76% ultimate degradation of FES in a closed bottle test under OECD (Organization for Economic Cooperation and Development).

Steber and Weirich [16] supported the above findings by their work. Similar degradation mechanism for FES and poor degradation under anaerobic conditions supported by many other scientists [9] suggests that any FES associated with sludge particles may pass through a WWTP being undigested.

#### 4.5. Fatty alcohol sulphates (as)

Fatty alcohol sulphates (AS) are rapidly degradable under aerobic conditions. Swisher, Steber and Schoberl [10, 11, 7] reported 95-100% primary degradation of AS for the period of 1-5 days under OECD test.

Swisher [7] observed the rapid biodegradation of AS and stated that the primary and ultimate degradation of AS are effective in a broad range of microorganisms.

The end products of AS degradation are inorganic sulphate and fatty alcohol that resulted from the enzymatic cleavage of the sulphate ester bonds and the  $\beta$  Oxidation of fatty alcohol resulted in an aldehyde and subsequently to a fatty acid.

Thomas and White [12] observed that of  $^{14}\text{C}$  SDS was degraded upto 70% releasing  $\text{CO}_2$  whereas the remaining 30% was incorporated into the microbial biomass. Digestion of SDS is very fast under anaerobic conditions that doesn't require the presence of molecular oxygen.

Therefore, treatment in a WWTP is entirely sufficient to eliminate AS and little possibility exists for these surfactants to reach the environment via sludge amendment.

#### 4.6. Alcohol ether sulphates (aes)

Alcohol ether sulphates (AES) degrade well under aerobic conditions with comparable primary and ultimate degradation rates to AS.

Varied researchers [10, 15] tested such compounds in a close bottle test for 30 days and reported their 96-99 % degradation.

Three possible degradation pathways [4, 16-18] were suggested for AES viz. (i) oxidation of the alkyl chain at  $\omega/\beta$  position; (ii) break-down of the sulphate bond; and (iii) break-down of an ether bond.

Results suggested that breakdown of sulphate bond and ether bond doesn't require aerobic environment.

Oba et al. [24] also supported the above facts by their findings.

Itoh et al. [25] revealed that the degradation of AES evolved  $\text{CO}_2$  and  $\text{CH}_4$  production that supported their ultimate biodegradation.

Above data suggest that AES are readily biodegradable under aerobic as well as under anaerobic environments.

#### 4.7. Cationic surfactants

Due to the presence of positive hydrophilic group cationic surfactants have a strong attraction towards negatively charged particulates surface of sewage sludge.

Above fact was supported by the research of several scientists [27] that observed their 95% adsorption to the surface of particulate matter.

Huber [28] stated that 20-40% cationic surfactants were associated with particulate matter in primary settling tanks.

Cationic surfactants are biologically available surfactants [29], octadecyltrimethylammonium chloride have half-lives of 2.5 h. in waste water [30].

Krzeminski et al. [31] reported alkylbenzyltrimethylammonium chloride to be ultimately biodegradable with >80% of the  $^{14}\text{C}$  labelled compound being released as  $^{14}\text{CO}_2$ .

Sullivan [32] stated that ditallowdimethylammonium chloride (DTDMAC) in activated sludge was predominantly associated with the particulate matter and after digestion 40% was released as  $^{14}\text{CO}_2$ .

Easy adsorption of cationic surfactants to particulate matter increases their importance to understand their anaerobic degradation processes.



Janicke and Hilge [33] reported non-biodegradability of quaternary ammonium salts in the absence of molecular oxygen.

Battersby and Wilson [34] reported that 1-1 hexadecyltrimethylammonium bromide inhibited the production of methane when used in the concentrations of 200 mg.

However, no pathways for anaerobic degradation exist in the literature.

Therefore, it can be assumed that cationic surfactants are not anaerobically biodegradable either because of a lack of appropriate metabolic pathways and/or a possible toxic effect of the surfactant upon the relevant anaerobic microorganisms.

#### 4.8. Alkyl phenol ethoxylates (apes)

APEs are found to be rapidly degradable surfactants under aerobic conditions [35]. Though, research carried out by Jones and Westmoorland [36] on the biodegradability of During waste water treatment, precipitation made by less biodegradable soaps leads to sedimentation in the primary settling tanks of WWTP that depends upon the hardness of water.

The effectiveness of WWTP and the degradation of these compounds can be determined by anaerobic degradation of soap.nonyl phenol ethoxylate (NPE) revealed their 98% degradation due to the  $\omega/\beta$ -oxidation of the alkyl chain.

However, little evidence was found in the support of any degradation of the aromatic ether bond Kravetz et al. [37] also supported the above facts by studying on the degradation rates of APE. In their research, they placed tritium and C-14 labelled APE in a bioreactor and observed their terminal degradation products. Results revealed that only 29% of  $^3\text{H}$  label APE was converted to water and 58% of the  $^{14}\text{C}$  labeled APE was evolved as  $\text{CO}_2$ . They concluded that although APE are readily biodegradable however, degraded products were not consumable by microorganisms. APE are amphiphilic in nature and their breakdown products have affinity towards the negatively charged particulate surfaces of sludge fraction that leads to the higher concentration of APE in the sludge under anaerobic conditions and are restricted to aerobic degradation.

Consequently, relatively high concentration of APE was found in sludge which enters into the environment when used for agricultural applications.

#### 4.9. Fatty alcohol ethoxylates (ae)

Literature survey revealed the great extent of biodegradability of fatty alcohol ethoxylates (AE) that confirm them more eco-friendly when compared to APE.

Linear AE are considered readily biodegradable (>80% primary degradation in 28 days) [39] as compared to their branched derivatives (40%).

Balson and Felix [35] suggest that the breakdown mechanism of AE as their primary degradation that involves the breakdown of hydrophobe-hydrophile group of the

AE that resulted in a hydrophobe and a polyalkoxylate then the hydrophobe undergoes  $\omega/\beta$ -oxidation.

Concentrations ( $<700 \text{ mg kg}^{-1}$ ) of AE in sludge suggest that AE is not entirely degradable under anaerobic conditions [40].

Knaebel et al. [41] suggested that linear alcohol ethoxylates (LAE) are readily bioavailable in a variety of different soil types, suggesting that aerobic soil amended with sludge rich in AE will not accumulate the surfactants.

#### 4.10. Anionic surfactants

Hosseini et. al. (3) studied the biodegradation of anionic surfactants (Sodium dodecyl sulphate) obtained from isolated bacteria from activated sludge and will eventually end-up and accumulate in household or industrial sewage.

Anionic surfactants are considered as they are generally considered as serious pollutants due to their high foaming capabilities that causes many problems in sewage treatment and also give toxic effects on many different organisms in ecosystem.

In this study, biochemical tests along with 16S rRNA gene sequencing have been applied for identification of two different bacteria isolated from

Tehran municipal activated sludge and the extent of SDS were evaluated by HPLC method after optimizing their pH and temperature.

Degradation of bacteria were found to be dependent on their sole source of carbon; the tests indicated that the degradation of *Pseudomonas beteli* and *Acinetobacter johnsoni* were found to have 97.2% and 96.4% of the original SDS levels after 10 days of growth; respectively.

The mixture of above bacteria was tested, no significant increase was found. Above results suggest that simple bacteria present in household and industrial sewage are found to be cost effective method for the elimination of anionic surfactants.

#### 4.11. Biosurfactants

Biosurfactants or microbial surfactants are the diverse group of surface active substances synthesized from microorganisms such as bacteria, fungi and yeast or excreted extracellularly.

Biosurfactants are readily biodegradable and hence environmentally compatible. Bannat (2000) revealed that the addition of biosurfactant alone is capable to stimulate biodegradation of hydrocarbon contaminants in environment.<sup>7</sup>

Biodegradability tests performed over sphorolipids (a biosurfactant produced by *Candida bombicola*) showed that biosurfactants starts to biodegrade immediately after cultivation. Surfactin and arthrofatin also show easy biodegradation<sup>6</sup>.

Rhamnolipid showed easy biodegradation under both aerobic and anaerobic conditions, in the same environmental condition, synthetic surfactant was found non-biodegradable or partially biodegradable[42, 43].

#### 5.0 Conclusions

After literature review it can be concluded that LAS and soaps are found degradable under aerobic conditions whereas anionic surfactants and alcohol ethers are degraded readily in both, under aerobic and anaerobic conditions.

SAS, FES, cationic surfactants, APE and AE are either found to be very less degradable or almost non-biodegradable under anaerobic, during sludge treatment but degraded aerobically.

Fatty acid esters and secondary alkane sulphonates are poorly degraded under both environmental conditions

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