

# Biodegradation and the Evaluation of Chemicals in the Environment

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## INTRODUCTION

**E**very chemical substance has a unique set of characteristics that determine its distribution and fate in the environment (Cunningham and Saigo, 1990). Among the most important of these are solubility, bioreactivity and persistence.

Some of the most useful chemicals, such as chlorofluorocarbons, plastics and asbestos, are valuable because they are resistant to degradation (Cunningham and Saigo, 1990). However, this stability also causes problems because such materials persist in the environment and have unexpected effects far from the sites of their original use.

In industrialized nations, toxic chemical wastes have become an increasing problem. Agricultural and industrial chemicals have been released into surface waters and are seeping into groundwater supplies. Water pollution is a major source of human health problems: as much as 80% of all diseases and some 25 million deaths each year may be attributable to water contamination (Cunningham and Saigo, 1990).

The rapid rise in the use of synthetic detergents has caused some concern over the fate of these materials in wastewaters (Subcommittee, 1956). Detergent components are released into the wastewater either in unchanged form or as the products of reaction with other materials present (Jakobi and Lehr, 1987). These products

contain large amounts of environmentally relevant constituents, especially pentasodium triphosphate and surfactants.

Branched alkylbenzene sulphonates (BAS), widely used surfactants during the 1950s and early 1960s, were subsequently replaced by linear molecular forms of linear alkylbenzene sulphonate (LAS) in response to evidence that BAS were recalcitrant and xenobiotic in nature (Hashim and Kulandai, 1992). The presence of recalcitrant detergents in wastewaters is known to cause environmental problems in rivers and sewage treatment plants. These include:

- toxicity of the surfactant itself to microorganisms and fish
- toxicity of partially degraded surfactants
- reduction of oxygen transfer into water, which hinders self-purification processes
- foaming, which can result in the transmission of pathogenic microorganisms, the removal of active biomass into the foam layer, and reduction in visibility, which is aesthetically undesirable
- eutrophication, where a waterway is polluted by heavy organic growth stimulated by inorganic nutrients such as phosphate from the detergents.

Foam pollution became serious in some countries, such as Germany and Japan in the 1960s (Komeda, 1992). The publicity about water contamination by detergent foams has begun to awaken the public to the growing problems of air, water and soil pollution by all types of waste materials,

and work on resolving foam pollution led to measures for protecting the environment from the effects of synthetic detergents.

Microorganisms have mechanisms to minimize the effects of environmental hazards (Cunningham and Saigo, 1990). Among these are metabolic degradation, excretion and avoidance of toxins. Many microorganisms have enzymes that process waste products and environmental poisons, reducing their toxicity and biological activities.

Xenobiotic compounds are organic compounds not occurring in nature. They are normally introduced by man, often through industrial processes (Hashim and Kulandai, 1992). As living organisms have not been exposed to these compounds during their evolutionary history, they may not have evolved the enzymes for the metabolism of these compounds. Some xenobiotic compounds, such as chlorinated hydrocarbons and aromatic compounds, are known to be highly recalcitrant and tend to persist in the environment.

### **THE IMPORTANCE OF ENVIRONMENTAL EVALUATION**

The evaluation of the environmental compatibility of organic compounds is generally based on two crucial criteria, namely biodegradation and ecotoxicity (Gode *et al.*, 1987; Steber *et al.*, 1988).

Biodegradation, as the principal mechanism operating in sewage treatment plants and in the self-cleaning processes which occur in surface waters, decides the fate of a substance in the environment and indicates whether it is likely to have a toxic effect on aquatic organisms. Ecotoxicity refers to the entry of poisonous chemicals into the environment. The degree of ecotoxicity of a compound becomes significant when it is degraded very slowly or incompletely or is used in large quantities.

Toxic chemicals in the environment are becoming a source of increasing concern to people in industrialized countries

(Cunningham and Saigo, 1990). Some chemical compounds are very unstable and degrade rapidly under most environmental conditions, while others persist for long periods.

Unfortunately, many of the earlier foam-producing detergents resist chemical and biological degradation (Speel, 1963). Even if their concentration is too low to produce foam, the possibility of their combining with protein wastes and/or other water contaminants to produce persistent foam may remain.

Interest in biodegradability testing is no longer new. The evaluation of raw materials in consumer products in relation to environmental water quality is now of critical importance in many industries throughout the world (Sturm, 1973). The chemical industry began looking seriously at biodegradability in the late 1950s, when a link was established between detergent surfactant residues and incidents of foaming in sewage treatment plants. Nowadays the biodegradability of a material to be used in a consumer product is considered as important as its performance.

The reason for determining biodegradability in the laboratory is, obviously, to predict the fate and persistence of chemicals in the environment (Gerike and Wierich, 1982). Under various national and international laws, when a new chemical likely to enter the environment is to be registered, information has to be supplied on its biodegradability. Evaluation of a major new organic material should therefore include biodegradability testing as an important first step in its environmental assessment. Special classes of environmental chemicals, pesticides and surfactants have been regulated effectively and satisfactorily for a long time in many countries (Gerike and Fisher, 1979).

### **DEFINITION OF BIODEGRADATION**

Some substances may be destroyed by either abiotic or biotic processes (Birch *et al.*, 1989). The former include processes such as

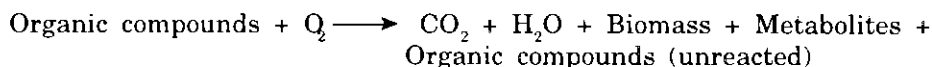
photodegradation, hydrolysis and oxidation or reduction reactions, but breakdown by living organisms, biotic processes or biodegradation, is considered to be the most important mechanism of removal for most organic chemicals likely to reach the aqueous and soil environment in significant concentrations.

Biodegradation can be defined as any process mediated by living organisms that results in the conversion of an organic chemical into organic and/or inorganic end-products that are chemically distinct from the parent material (Larson *et al.*, 1993). Biodegradability can mean susceptibility to complete decomposition to compounds such as carbon dioxide and water, or merely decomposition to a point where, for example, a detergent loses its ability to produce foam or act as a surfactant (Speel, 1963).

The chemistry of biodegradation can be represented by the equations in *Figure 1* below (Swift, 1993):

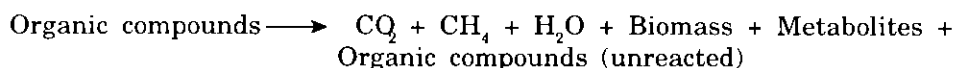
Equation 1

**Aerobic Environment**



Equation 2

**Anaerobic Environment**



Source: *Swift (1993)*

*Figure 1. Chemistry of Biodegradation*

The biodegradability of a substance cannot be assigned an absolute value since the result of a determination depends on the conditions under which it is made (Weaver and Coughlin, 1964). Biodegradation can occur either in the presence or absence of oxygen. Anaerobic conditions occur naturally in the lower layer of sediments in lakes and ponds, river beds and estuaries (Birch *et al.*, 1989). Any material released to the environment which is only slightly soluble

in water or strongly adsorbed on solids, is likely to become available as a potential substrate for anaerobic organisms.

Throughout the years, several terminologies describing biodegradation have been introduced (Larson *et al.*, 1993; Sturm, 1973; Swisher, 1987; Weaver and Coughlin, 1964; Birch *et al.*, 1989). Among them are:

**Primary Biodegradation**

Primary biodegradation occurs when the structure of a chemical is altered in such a way that basic physical and chemical properties are lost. This results in a decreased sensitivity of the chemical to a specific analytical method and a reduction in the analytical response relative to the parent chemical.

**Ultimate Biodegradation**

This is also known as mineralization, and it occurs when a chemical is completely broken down and metabolized to carbon

dioxide (and methane under anaerobic conditions), water and any other inorganic constituents.

Biodegradation cannot be considered a true environmental removal mechanism for chemicals that undergo only primary biodegradation or that are partially degraded to more persistent compounds. Accordingly, other terminologies are used to describe the biodegradation characteristics

of a compound in more detail.

### **Ready Biodegradability**

'Ready biodegradability' is the term applied to compounds which have passed certain specified screening tests for ultimate biodegradability. These tests are so stringent that it is assumed that compounds passing them will degrade rapidly and completely in aquatic environments under aerobic conditions.

### **Inherent Biodegradability**

'Inherent biodegradability' refers to compounds for which evidence of biodegradation (primary and ultimate) is uncertain in any test of biodegradability.

### **Recalcitrance**

This refers to an organic compound which resists biodegradation and remains unchanged.

## **DEVELOPMENT OF TESTS FOR BIODEGRADATION**

Several countries have faced chemical crises in which there were widespread contamination by hazardous and persistent compound (Robra, 1986). As a result of these crises, government regulations have restricted the manufacture and use of certain chemicals including some surfactants, chlorinated hydrocarbons, pesticides, etc.

Various countries have passed environmental legislation which requires prescreening of new and some existing chemicals prior to large-scale manufacture and before they are introduced into the environment. In those laws and drafts, special methods are mentioned for measuring biodegradability as an essential item among the environmentally relevant properties of a chemical compound. One of the earliest pieces of detergent legislation was the German Detergent Law of 1961, which placed a strict requirement of more than 80% biodegradability on all types of

surfactant (Jakobi and Löhrr, 1987).

Biodegradation is the least expensive and most widely used method for removing organic compounds from wastewater and is the primary mechanism responsible for their destruction in nature (Mohd Naziruddin *et al.*, 1995). Test methods selected for the evaluation of biodegradability should reflect the characteristics of the environment to which the results will be related (Robra, 1986) and must be widely acceptable in the scientific community.

## **METHODS FOR TESTING BIODEGRADATION**

The special methods for measuring microbial degradation of substances require the exposure of the test compounds in suitable media to mixed populations of bacteria, and the application of analytical techniques to measure the disappearance of the test compounds or the metabolic activity of the bacteria (Robra, 1986).

One problem associated with current test methods relates to distinguishing between true non-biodegradability and inhibited biodegradability resulting from toxic effects of the substance tested (Reynolds *et al.*, 1987). In some instances, where high concentrations of test substances are required in order to achieve analytical precision, a toxic but biodegradable substance may be falsely identified as non-biodegradable, because of its toxicity to the microorganisms employed in the test systems.

Tests for potential biodegradability can be arranged in a sequence, determining ready biodegradability and inherent biodegradability, in which the first step is to discover whether the chemical compound is susceptible to breakdown by microorganisms.

Tests for ready biodegradability can be applied to a wide range of organic compounds without the need to develop specific analytical methods. The test conditions involve exposure of a relatively low concen-

tration of an organic substance to microorganisms.

Tests for inherent biodegradability include conditions which allow for a lower ratio of test substance to microorganisms, and prolonged exposure. If evidence of biodegradation is obtained, the test substance may be considered to be inherently biodegradable but it must not be assumed that rapid or complete biodegradation will occur.

Biodegradation may be assessed by measuring Biochemical Oxygen Demand (BOD), Dissolved Organic Carbon (DOC) and CO<sub>2</sub> evolution. These measurements can be made using a variety of test procedures, some of which have been standardized by various organizations, including the Organization for Economic Cooperation and Development (OECD), Environmental Protection Agency (EPA), Soaps and Detergents Association (SDA), American Society for Testing and Materials (ASTM), Ministry of International Trade and Industry of Japan (MITI), International Standards Organization (ISO) *etc.* (Swift, 1993).

Although in general the results from aerobic degradation testing allow a reliable prognosis of the fate of a chemical in the environment, in some cases consideration of the anaerobic degradability seems necessary as well for a complete evaluation. Because of the lipophilic structures of surfactants, and their often limited water solubility, they adsorb readily on to solid surfaces like those in sludges, and may reach anaerobic areas very quickly (Steber and Wierich, 1987). Test methods for anaerobic biodegradability are suitable for strongly adsorbing and poorly soluble compounds. Most methods described in the literature are based on anaerobic respirometric techniques which involve measurement of methane and CO<sub>2</sub> production (Birch *et al.*, 1989).

Recalcitrant metabolites with unknown ecological and toxicological properties which might arise from the incomplete biodegradation of chemicals are considered

a possible environmental problem (Gerike *et al.*, 1984). A test for detecting recalcitrant metabolites was developed on the basis of Coupled Units Test (Gerike *et al.*, 1989). The Coupled Units Test is a model of a communal activated sludge sewage treatment plant and has been used to determine the ultimate biodegradability of numerous environmental chemicals. The analytical approach best suited to the detection of recalcitrant metabolites is the determination of organic carbon.

## CASE STUDY

### Methyl ester sulphonates

$\alpha$ -SME (sulphonated methyl esters) are made from renewable raw materials, exhibit good cleaning properties, are stable to hydrolysis and are largely unaffected by water hardness (Gode *et al.*, 1987). The biodegradation of  $\alpha$ -SME was found to start very quickly and then proceed rapidly to ultimate degradation at sewage treatment plants and in river water (Masuda *et al.*, 1993). The biodegradation of  $\alpha$ -SME does not leave any recalcitrant residues at all. By comparison with some other surfactants, smaller amounts are needed to obtain satisfactory detergency, thus lowering the organic load in wastes discharged to the environment.

Screening tests with a number of different types of soil demonstrated that the excellent aerobic biodegradability of the surfactants seen in all aqueous test systems is also relevant for soil (Steber and Wierich, 1989). Therefore, the  $\alpha$ -SMEs can be classified as readily biodegradable.

Microbial attack on the  $\alpha$ -SME structure starts with  $\omega$ -oxidation to form a carboxyl group and continues with  $\beta$ -oxidation, removing two carbons at a time, to form a transient intermediate, monomethyl  $\alpha$ -sulphosuccinate; degradation then proceeds by desulphonation (Masuda *et al.*, 1993). The desulphonation is assumed to take place prior to the scission of the methyl ester bond of the monomethyl  $\alpha$ -sulphosuccinate (*Figure 2*).

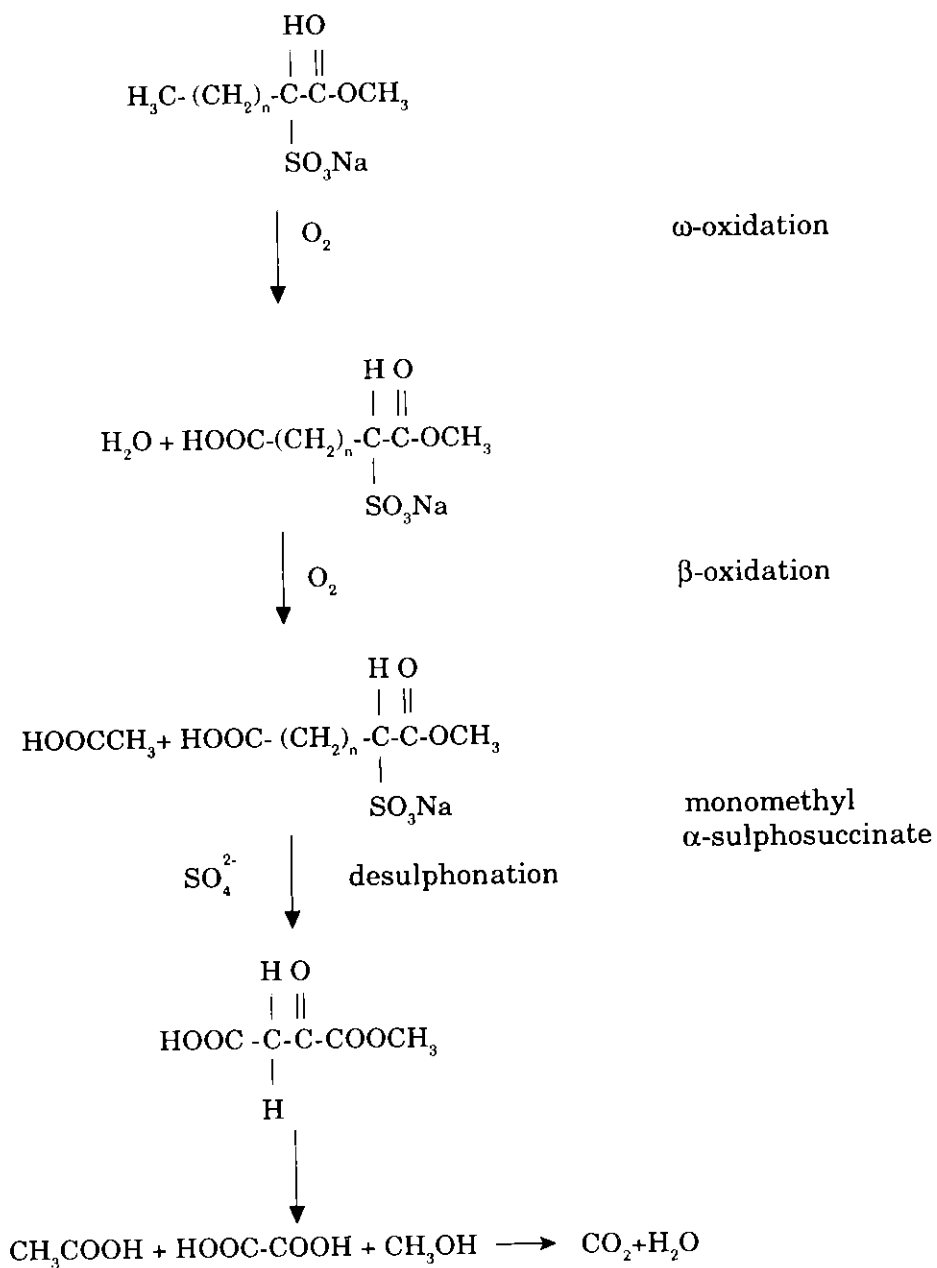


Figure 2. Biodegradation pathway of  $\alpha$ -SME

### Esterquats

Ditallowalkyl-dimethyl-ammonium-compound (DTDMAC), which has been used for more than three decades as a raw material for making softeners, is now regarded as a risk to the environment (Puchta *et al.*, 1993). A group of compounds ('Esterquats') containing ester groups, and quaternary or semi-quaternary species from alkanolamines, or imidazolines have proven very suitable as a substitute for DTDMAC.

The rapid biodegradation of the ester-bonded molecules of esterquats can be explained by imagining that the ester bonds act as potential breaking points (Figure 3).

The large molecule of DTDMAC could only be attacked slowly by microorganisms and was therefore only slowly degradable. (Figure 4).

### Linear alkylbenzene sulphonates (LAS)

During the search for a product to replace the first generation synthetic surfactants - branched alkylbenzene sulphonates (BAS) - the primary goal was to find an equivalent cleansing agent whose surface activity or foaming ability would not survive during the treatment of waste. Studies indicated that LAS would meet this requirement.

The biodegradation of LAS begins with

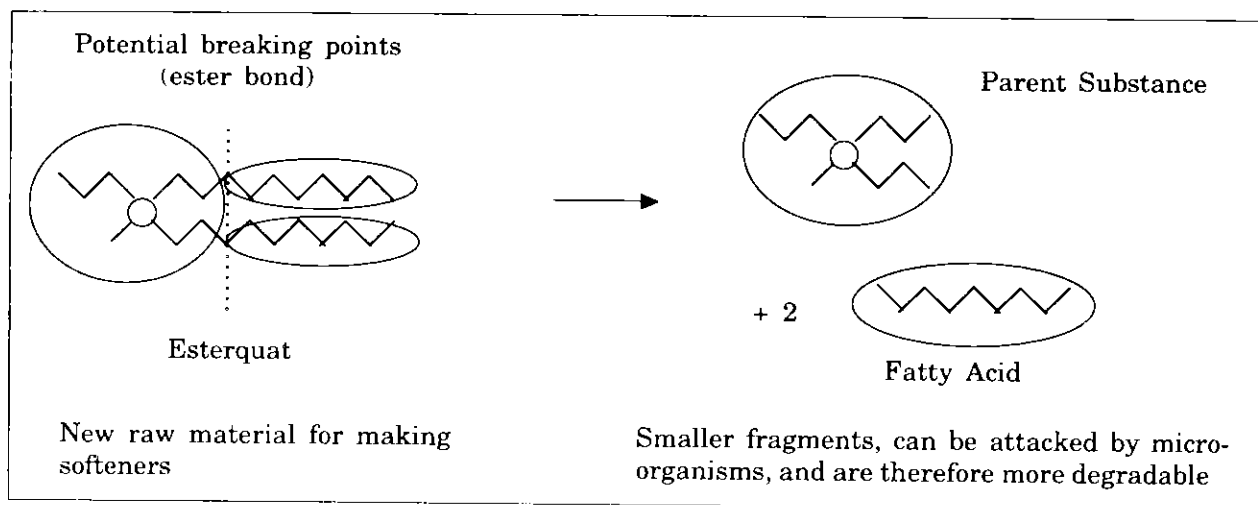


Figure 3.

One large molecule becomes several smaller ones, which are more easily accessible to attack by microorganisms.

a terminal alkyl carbon and proceeds towards the aromatic ring, cleaving each of the carbon segments at a time. Therefore, LAS is susceptible to complete biodegradation (Nielsen *et al.*, 1979) (Figure 5).

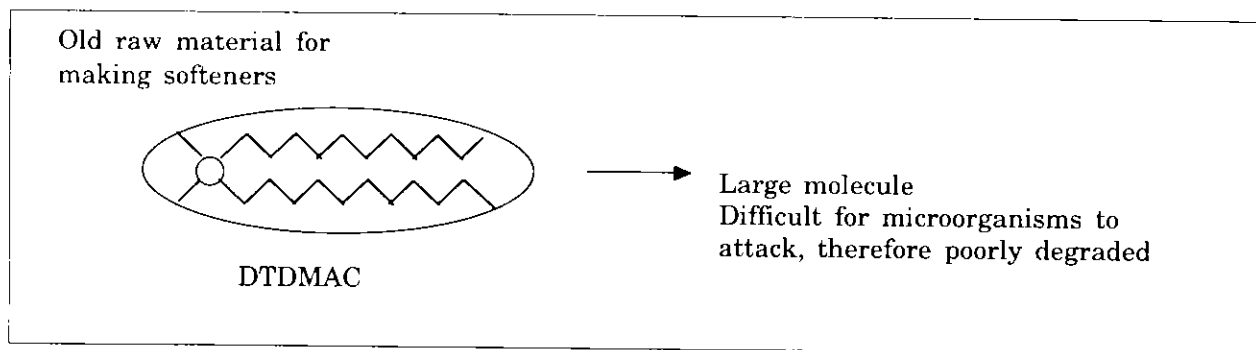


Figure 4.

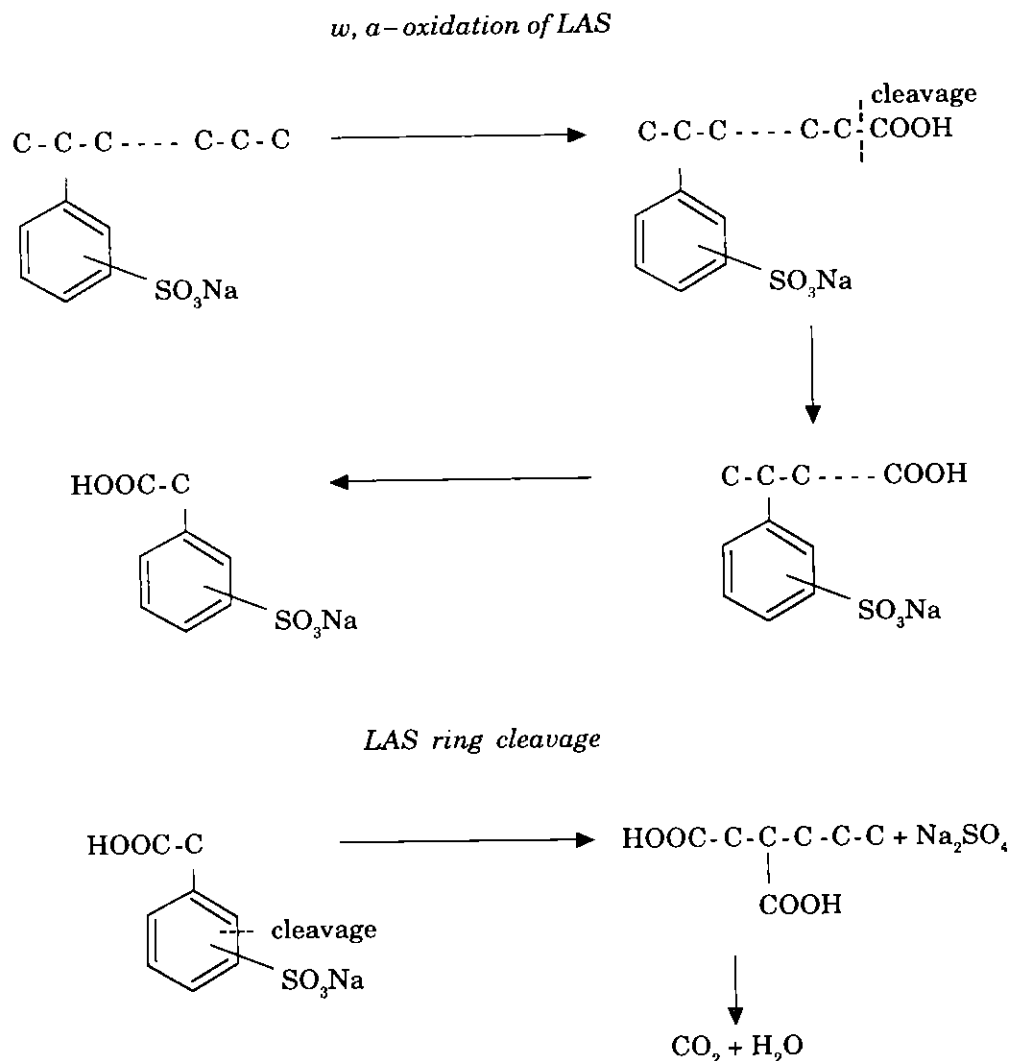


Figure 5.  $\omega, \alpha$ -oxidation of LAS

### Fatty alcohol sulphates

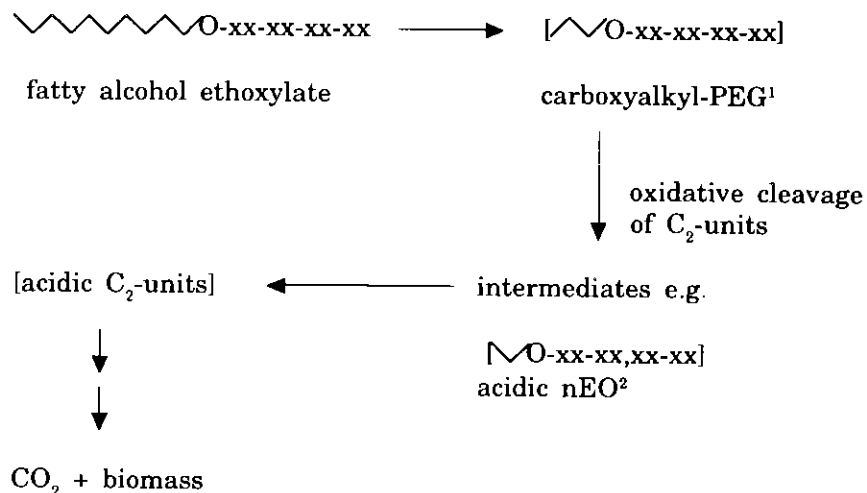
These materials showed a high degree of biodegradability, with average values around 96-98% being obtained in the primary degradation or screening test (Mann and Read, 1971). Not just primary degradation, but also ultimate degradation of these surfactants occurs rapidly and completely in sewage treatment plants and receiving waters. Furthermore, the excellent anaerobic biodegradability of fatty alcohol sulphates

indicates that they will be biodegraded under practically all environmental conditions (Steber *et al.*, 1988).

### Fatty alcohol ethoxylates

Linear fatty alcohol ethoxylates with the common structural formula  $R(\text{CH}_2\text{CH}_2\text{O})_n\text{OH}$  represent the economically most important group of nonionic surfactants and are highly degradable in sewage treatment plants and surface waters (Steber and Wierich, 1987). (Figure 6).





<sup>1</sup> Polyethylene glycol

<sup>2</sup> Acidic intermediates consist of carboxylated polyethylene glycols and low molecular weight acids

Figure 6.  $\omega, \beta$ -oxidation of alkyl chain

### CONCLUSION

The problem of the biodegradation of synthetic detergents in water and sewage systems appears to have been largely solved by substitution of BAS with LAS, by legislation requiring biodegradability and by investment in new sewage treatment plants and the modernization of existing ones. Vast changes have been made in recent years in the manufacture, formulation and evaluation of detergent products and their chemical intermediates. Natural processes and living organisms have a high capacity for removing or destroying water pollutants, but these systems become overloaded and ineffective when pollution levels are too high. Municipal sewage treatment is effective in removing organic materials from waste water, but the sewage sludge is often contaminated with metals and other toxic industrial materials. Reducing the sources of these materials is often the best solution to the pollution problems.

In the current state of knowledge, the prospects for the oleochemical industry in relation to environmental (or 'green') issues look promising. Neither the main raw materials, nor the main products, are toxic or dangerous. With respect to completeness of biodegradation, fat-based surfactants

really do seem to enjoy a distinct advantage.

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