BIODEGRADATION OF SURFACTANT IN THE ENVIRONMENT: A REVIEW

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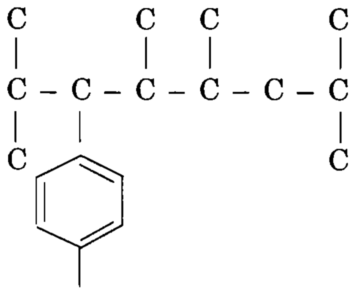
INTRODUCTION

Development of branched alkylbenzene sulfonate (BAS)

*The replacement of soap with surfactants achieved importance during World War II when oils and fats were in short supply and their replacement became technically and economically feasible (*Swisher, *1987). BAS, a synthetic surfactant derived from petrochemical, was the most widely used surfactant during 1950s and early 1960s because of its excellent detergent properties, its low cost and attractive physical properties of its formulation (*Hashim *et al.*, *1989). BAS manifests several advantageous characteristics such as good cleaning ability, good solubility and good foaming power. After a few years, the changeover was complete and BAS became the major surfactant used, first in the U.S. and later around the world.*

BAS contains a highly branched carbon backbone linked to a sulfonated benzene ring.



Branched alkylbenzene sulfonate

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*Alkylbenzene sulfonate is attacked by microorganisms through the alkyl chain, not through the sulfonate group or the benzene ring (*Nielsen *et al., 1985). In the case of BAS, the alkyl chain is resistant to microbial attack due to the highly branched hydrocarbon chains. Microorganisms are deficient of enzyme systems that can attack and biodegrade such highly branched alkyl chains when they are attached to a benzene ring, thus posing problems in the biodegradation of BAS.*

BAS began to be noticeable in waste waters, treated sewage and receiving waters because they retained their foaming properties in natural waters at concentrations around 1 ppm (Swisher, 1987). However, certain bacteria are able to degrade BAS up to 60% during the primary and secondary treatment processes. However this degradation is slow and consequently, measureable amounts (ppm) are present in treatment plant effluents and these normally enter water systems. In other words, BAS does not undergo complete biodegradation and persists in the environment.

ENVIRONMENTAL EFFECTS OF BAS

Surfactants enter waters and waste waters mainly by discharge of aqueous wastes from household and industrial laundering and other cleansing operations. Soon after the introduction of BAS, serious environmental problems in surface waters, groundwaters, drinking waters and in wastewater treatment plants appeared. These problems included (Nielsen *et al.*, 1985)

a) foam on rivers, streams and lakes
b) foam in drinking water
c) foam in waste water treatment plants
d) disease transmission by windblown foam
e) groundwater contamination
f) toxicity to aquatic life
g) inhibition of oxygen transfer to surface waters

Soon, the relevant authorities discovered the cause of these environmental problems and traced it to the occurance of BAS. A quick destruction of the surfactants in the environment, after the intended application is performed, was therefore needed. It was at this time (1950s) that interest on biodegradation (bioD) was developed in the chemical industry.

As the industry progresses and population densities increase, bioD and the effects of surfactants on the environment become increasingly important. Even though the concentrations of surfactants in public water supplies could be very low and essentially nontoxic to human, and the waste water is reused, there is a general agreement that their presence in drinking water is undesirable (Swisher, 1987). Today, the toxic effect of these surfactants on aquatic life (ecotoxicity) is of great concern too.

In contaminated waters, the presence of BAS, even at very low concentrations, can inhibit the clean-up processes (Nielsen *et al.*, 1985). Even at concentrations as low as 0.1 ppm, BAS can interfere with oxygen transfer to water and thereby depriving the microbial population of oxygen. A healthy growth of microbial population is needed for the clean-up processes.

In Japan, BAS was put to use around 1950 and around 1966 the foam pollution became apparent (Komeda, 1992). Foaming was observed in many rivers. This was the starting point for environmental measures for the control of pollution due to synthetic detergents.

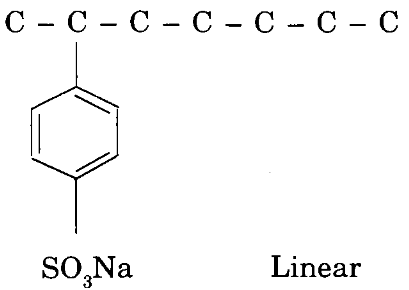
Surfactant molecules tend to congregate at the surface of the solution, i.e. the liquid-air interface. Foam is made up almost entirely of such interfaces, and consequently, foam from a dilute surfactant solution contains a much higher surfactant concentration than the main body of the solution (Swisher, 1987). Much of the surfactant content can be removed from the solution by generation and removal of foam.

Biodegradability data therefore, became an important parameter to decide the fate and persistence of chemicals in the environment (Gerike *et al.*, 1982). These information are used to decide whether or not a surfactant could be introduced into the market.

CONVERSION TO BIODEGRADABLE SURFACTANTS

Many of today's major foam-producing detergents resist chemical and biological degradation that could occur during sewage treatment, river self-purification processes and groundwater travel (Speel, 1963).

Research has shown that if the branched alkyl chain of BAS is replaced with a straight or linear alkyl chain, the surfactant can be easily degraded (Nielsen *et al.*, 1985). In many countries, environmental problems created by BAS are being solved by replacing it with linear alkylbenzene sulfonate (LAS).



Linear
alkylbenzene sulfonate

When BAS was replaced with LAS in England, the concentration of surfactant in rivers had decreased even though the volume of detergents used, and therefore the amount entering the environment, had greatly increased. The trend was similar in several countries such as U.S., Germany, Japan and Thailand. On the first of July, 1965, LAS totally replaced BAS as the principal surfactant for detergent production in U.S. (The Subcommittee, 1965).

In Japan, the detergent industry and the raw material suppliers made strenuous efforts for the conversion of BAS to LAS and it was completed in about five years (1968-1972). The government (The Environment Agency of Japan) measured water qualities of 23 water areas all over Japan in 1978 (Komeda, 1992). The change from BAS to LAS resulted in a substantial decrease in the foaming properties and methylene blue active substance (MBAS) of sewage treatment effluents and rivers. The biological oxygen demand (BOD) value had decreased after the conversion to LAS.

Figure 1 shows the biodegradation of BAS and LAS by river-die-away test, detected by MBAS. *Figure 2* shows the water quality of the Tama River in Japan. The MBAS value reached its peak in 1967 and as the conversion to LAS progressed, the value dropped sharply. The BOD value reached its peak in 1972 and gradually decreased thereafter. This value correlates with the increase of household waste water as a result of population growth. Although the BOD value increased slightly even after the conversion to LAS (both BAS and LAS were used during the 1968-1972 period), it gradually decreased since 1972.

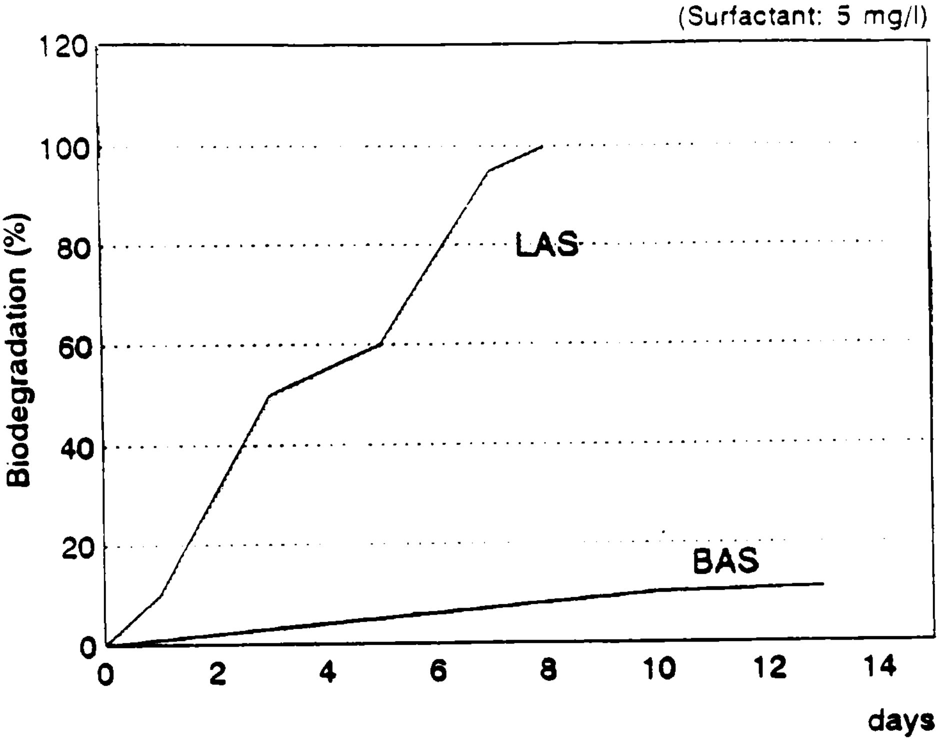


Figure 1. Biodegradation of BAS and LAS by river-die-away test, detected by MBAS. Source: Komeda, 1992.

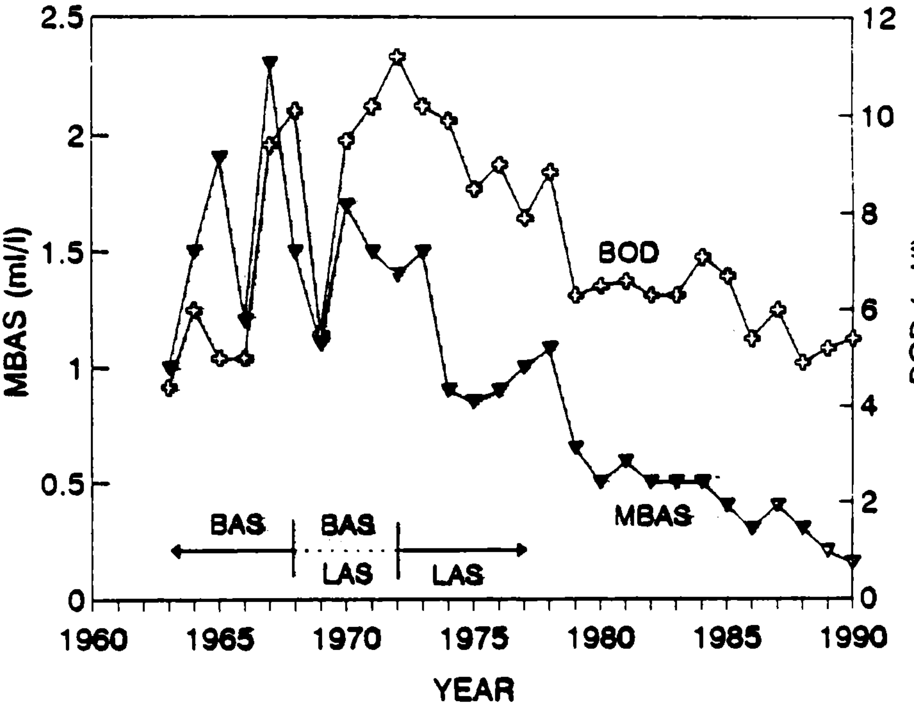


Figure 2. Biodegradation of BAS and LAS in Japan (Tama River) Source: Komeda, 1992.

DEVELOPMENT OF LEGISLATION

Laws regulating the use of chemicals are increasing (Idman, 1978). In many countries, public authorities have taken steps to prohibit the use of substances which are considered insufficiently biodegradable. These measures involve agreements concluded between governments and manufacturers on the application of regulations or legislation. Worldwide, groups of experts have developed and introduced several articles of legislation. Among them are :

GROUPS OF EXPERTS

EEC	- European Economic Community
EMPA	- Swiss Federal Laboratories for Materials Testing and Research
JIS	- Japan Industrial Standards
EPA	- Environmental Protection Agency (USA)
OECD	- Organization for Economic Co-operation and Development

LEGISLATION

- U.S. Toxic Substances Control Act
- U.S. Pesticide Registration Guidelines
- U.S. Food and Drug Administration Act
- EEC 7th. Amendment (OECD Guidelines)
- Chemical Substance Control Law (Japan)
- U.K.'s Safety and Health at Work Act
- La loi concernant le controle des produits chimiques (France)
- The Act on Products Hazardous to Health and to the Environment (Sweden)

(Painter, 1992)

One of the earliest pieces of detergent legislation was the German Detergent Law of 1961. The law, along with subsequent directives from the European Community and other countries (France, Netherlands, Switzerland and Austria), placed a strict requirement of more than 80% biodegradability on all types of surfactants (Jakobi *et al.*, 1987).

The statute that followed (1962) provided only for the control of anionic surfactants. This legal move successfully replaced the poorly biodegraded BAS from the detergent formulations by LAS. Legislation enacted in West Germany required their detergent makers to switch over by October 1, 1964, to products which were at least 80% biodegradable. Thus, by 1965, the foaming problems in German sewage treatment plants and surface waters had been eliminated. Pollution by detergent components had decreased considerably in Germany. Surfactants do not constitute a problem anymore due to legal biodegradability requirements and the modernization of sewage treatment plants (Gerike *et al.*, 1989). Also in that year, a 90% limit of biodegradability was agreed upon by the U.S. manufacturers (SDA 1965) (Swisher, 1987).

According to JIS, synthetic detergents to be used for home laundering should have a biodegradability value of 90% or more (Komeda, 1992). The legal limits of 80-90% mentioned above are realistic, high enough to accomplish the environmental objectives and still commercially attainable (Swisher, 1987).

Events leading to the introduction of various legislation are lengthy. A summary on the chronological development that took place are listed in *Table 1*:

TABLE 1 : EVENTS LEADING TO THE INTRODUCTION OF VARIOUS LEGISLATIONS

Year	Event
1950s	Serious environmental problems caused by the synthetic surfactants (in developed countries)
1961	German Detergent Law (one of the earliest pieces of detergent legislation)
1964	Legislation on anionic surfactants that required detergent manufacturers to switch to products of at least 80% biodegradable was enforced in Germany
1965	In U.S., LAS totally replaced BAS and detergent manufacturers agreed on the 90% limit for biodegradability
1966	Foam pollution in Japan became evident
1968	A "European Agreement on the restriction of the use of certain detergents in washing and cleaning products" was concluded
1968 - 1970	An OECD expert group developed a system of testing for estimating the biodegradability of synthetic anionic surfactants
1968 - 1972	Detergent industries in Japan made strenuous efforts to convert BAS to LAS
1971	The above agreement (1968) was enforced
1972	Some countries were considering the enactment of specific legislation on nonionic surfactant
	Development of a common test method for determining the biodegradability of nonionic surfactants
1973	The Council of the European Communities published a directive on this legislation
1974	France intended to publish a decree relating to specific legislation on nonionic surfactants
1978	The Environment Agency of Japan measured water qualities of 23 water areas

Japan Soap and Detergent Association (JSDA) conducts the following activities for the benefit of the consumers as measures for environmental protection and safety of synthetic detergent.

1. Publications
    a) periodicals
    b) opinion papers
    c) books
2. Research data
3. Cooperation with government
4. Other measures
    a) public relations
    b) lectures, meetings, pamphlets

The law to be imposed will eventually have to define biodegradability in terms of time, extent and current practice for water and sewage purification because all surfactants, including BAS, are biodegradable, given sufficient time and the right set of conditions (Speel, 1963). BAS is known to be degraded as they do not accumulate in the environment, although the biodegradation process may take a long time. This is in accordance with the principle of microbial infallibility in which the microorganisms are said to have a remarkable capacity for adapting themselves to a host of ecosystem, environmental conditions and substrates. Cain *et al.* (1972) reported that acclimatization of the microorganisms to a surfactant is generally achieved after a period of 5 to 6 days.

BIODEGRADATION FOR WASTE SURFACTANT CONTROL

The waste water problem is becoming more pressing as population densities increase. Use of biodegradable surfactants should minimize waste surfactant problems.

Detergent components are released to the waste water either in essentially unchanged forms or as the products of reactions with other materials present. The main contributions of detergent formulations to wastewater are surfactants and phosphates (Jakobi *et al.*, 1987). Surfactants and phosphates in particular became the subject of specific laws and regulations because of the magnitude of their contribution and their apparent ecological impact.

DEFINITION OF BIODEGRADATION

Biodegradability has been defined in many different contexts. In broad terms, bioD can be defined as any process mediated by living microorganisms that results in the conversion of an organic chemical into organic and/or inorganic end-products that are chemically distinct from the parent material (Speel, 1963; Swisher, 1963). The technical definition of bioD is the metabolism of organic chemicals as sources of carbon and energy by heterotrophic microorganisms which constitute bacteria and fungi to form microbial biomass and inorganic or organic end-products such as carbon dioxide (CO_2) or methane (from anaerobic process).

For a surfactant, degradation is achieved when there is a loss or a change in its properties such as surface tension and foaming tendency (Swisher, 1987). BioD of surfactants in wastewaters, in treatment plants and in ultimate receiving bodies is primarily the result of bacterial action, just as in the case of other organic components of the waste. The biochemical metabolic reaction involved appears to be the same whether the substrate is a surfactant or not.

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

PRIMARY BIODEGRADATION

Primary bioD, also referred to as biotransformation, occurred when a molecule has been oxidized or otherwise altered by bacterial action to such an extent that its surfactant properties are no longer evident or when it no longer responds to analytical procedures which are specific for detecting the original substance.

SECONDARY BIOD OR ULTIMATE BIODEGRADATION

Secondary bioD, also referred to as mineralization, is the complete conversion of a chemical molecule to CO_2, water, inorganic salts and products associated with the normal metabolic processes of bacteria. The overall bioD process normally consists of two steps, i.e 1° and 2° bioD as shown in *Figure 3.*

Biodegradability cannot be an absolute value, it depends on the conditions under which the determination is made (Weaver *et al.*, 1964). BioD can occur either in the presence of oxygen (aerobic) or without oxygen (anaerobic). Under aerobic conditions, microorganisms utilize molecular oxygen (O_2) as the hydrogen acceptor during the respiration process. Anaerobic conditions occur naturally in the lower layers of sediments to the environment which is slightly soluble water and/or strongly adsorbs on solids, is likely to become available as a potential substrate for anaerobic organisms (Birch *et al.*, 1989).

BioD is considered to be the most important removal process for most organic chemicals likely to reach the aqueous and soil environment in significant concentrations. Heterotrophic microorganisms which rapidly convert a wide variety of organic substances to simple compounds are by far the most important group of microorganisms which facilitate bioD.

BIODEGRADATION TESTING METHOD

An important reason for bioD study is to enable prediction of probable environmental consequences of widespread use of the surfactant or chemical in question. A second major reason for the study is to gain insight into the biochemical reactions involved in the introduction of the surfactant or chemical into bacterial metabolic reactions.

BioD is measured by exposing a test compound to microorganisms and analyzing the system at intervals to determine the disappearance of the test compound, the formation of degradation products or the uptake of O_2 (Swisher, 1987). Analytical techniques often used include the measurement of the loss of surfactant properties such as surface tension and foamability, dissolved organic carbon (DOC),

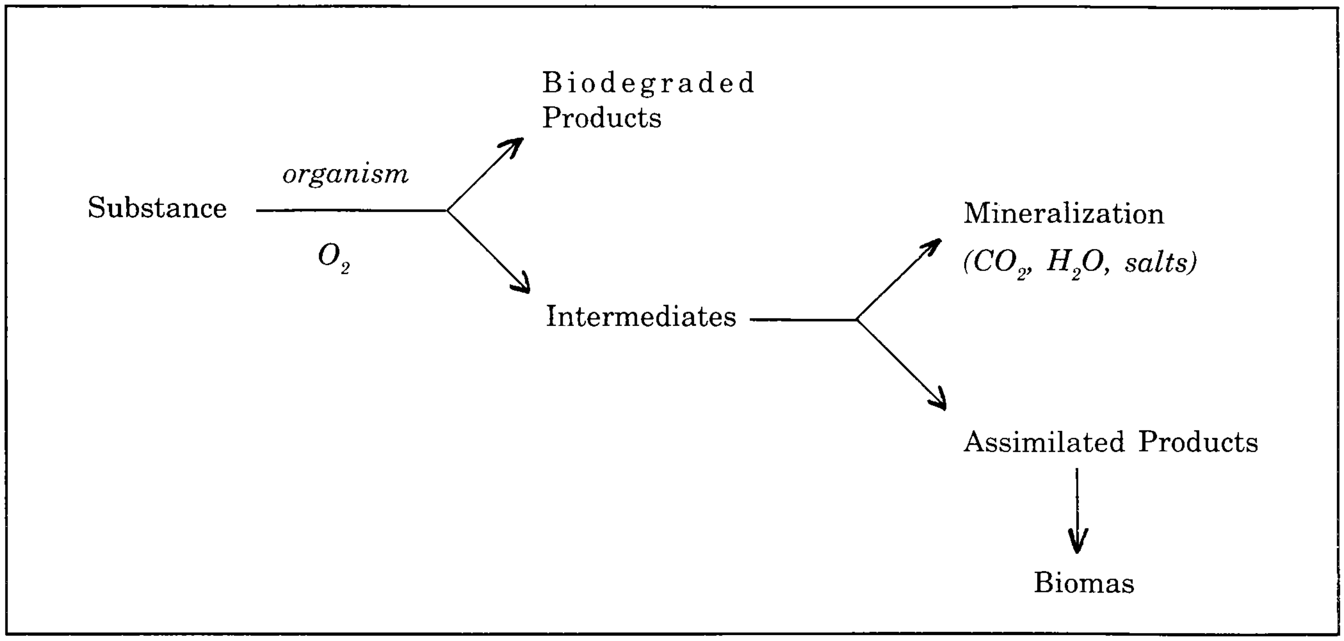


Figure 3. The biodegradation process

Source: Nielsen et al., 1985.

colorimetric determinations and O_2 uptake studies (BOD, COD). Brief description on the advantages and shortfalls of these techniques are summarised in *Table 2* (Gerike *et al.*, 1979).

Many factors have to be taken into account when considering events likely to take place in the environment. Some of these are important variables pertinent to bioD testing (Painter, 1992). These variables include :-

1. acceptable physical conditions
2. certain ranges of pH
3. temperature
4. dissolved O_2
5. salinity
6. redox potential
7. sorption
8. inorganic nutrients especially nitrogen and phosphorus, and other nutrients
9. analytical methods
10. concentration of test chemicals in the environment
11. presence of other organics
12. presence of natural or synthetic inhibitors (toxic or bacteriostatic agents)
13. microorganisms (nature, concentration and acclimatization)

The effects of these factors are further explained in *Table 3*. Depending on these and other unknown and unrecognized variables, the bioD results may vary.

These factors are not characteristics of a surfactant but of other organic compounds as well, including food products (Swisher, 1987). Further, these are characteristics not only of laboratory tests, but also of the larger scale operations. Because of such factors, the efficiency of removal of organics in sewage treatment plants may vary from process to process, and for a given process from plant to plant and for a given plant from day to day. In the wider and uncontrolled environment, the efficiency of the removal of organics on surface or river waters can be expected to vary even more widely from place to place and from time to time.

Many methods, such as OECD, JIS, EEC, EMPA and EPA, can be used as bioD testing methods. The OECD method is accepted worldwide and shall be described.

In their original report (1979) on the overall scheme for hazard assessment, OECD recommended a "flow scheme" (*Figure 4*) to be followed for bioD testing. It is a decision process based on three tiers of testing :-

READY BIODEGRADABILITY OR SCREENING

The conditions in the tests for ready biodegradability have been developed to devise screening methods, which can be easily and inexpensively carried out in the laboratory to decide whether a chemical has the potential to be easily biodegraded in the aquatic environment. The choice of which screening method should be used for a given chemical depends largely on its physical properties such as solubility, volatility and adsorptivity (Painter, 1992).

A substance may be considered to be readily biodegradable if the following levels of bioD are achieved in 28 days.

– Dissolved Organic Carbon (DOC)	70%
– O_2 uptake as a percent of Theoretical O_2 Demand (ThOD)	60%
– CO_2 generation as a percent of Theoretical Carbon Dioxide ($ThCO_2$)	60%

These levels of bioD must be achieved in a 10 days window within the 28 days period (OECD Guideline, 1992). The 10 days window begins when the degree of biodegradation has reached 10% of DOC, ThOD or $ThCO_2$ and must end before day 28 of the test. Chemicals which pass the first tier need not be tested further while those which fail are tested by a second tier method.

TABLE 2. TECHNIQUES USED TO MEASURE BIODEGRADATION.

Parameters Measured	Advantages	Shortcomings
Biological Oxygen Demand (BOD)	Operable regardless of the state of the test compound in the system, whether undissolved or dissolved, whether adsorbed or	Incapable of differentiating between say, 80, 90 and 100% biodegradation in the absence of independent data Extreme precision in the filtration, drying and weighing is necessary. Cannot be applied to mixture of test compounds with ordinary foods such as those in sewage.
Surface Active Properties		
ANIONICS Methylene blue active substance (MBAS)	Loss of MBAS parallels oxygen uptake as measured by BOD technique.	There are many microbiological processes that use O_2 which are not related to biodegradation.
NONIONICS Dragendorf Bismuth Reagent (BR)	Consumption of BR parallels oxygen uptake.	–do–
Oxidizable organic compound or Chemical Oxygen Demand (COD)	Eliminates much of the interference in interpreting oxygen uptake.	Non-selective.
O_2 uptake	Correlates well with biodegradation since the overall process involves uptake of oxygen.	Requires special apparatus and temperature control. Suffers from interference.
Carbon dioxide evolution	Gives direct evidence of oxidation of organic compounds. Applicable to inorganic carbon.	–
Dissolved organic carbon (DOC)	Determines with greatest precision especially when titration method is used	Removal of DOC could be due to some process other than biodegradation. Not applicable to inorganic carbon.
^{14}C radiolabelled compound	Most accurate, direct and efficient method.	Expensive.

Source : Gerike *et al.*, 1979; Swisher, 1987 and Painter, 1992.

TABLE 3. FACTORS AFFECTING BIODEGRADATION IN THE ENVIRONMENT

Factors	**Possible Effects on Biodegradation**
a) Test Chemical	
- concentration	determines rate inhibition threshold - growth - maintenance
- availability	
- sorption	}
- speciation	} increase or decrease rate of removal
- conjugation	}
- emulsion formation	could increase rate
- duration of contact with microorganisms	opportunity for adaptation
b) Mixed substrates	
- concentrations	} simultaneous removal
- nature	} sequential removal
- temperature	} stimulation/inhibition
'secondary substrate utilization'	secondary substrate degrades below threshold
- primary-higher concentration	
- secondary-lower concentration	
c) Microbial populations	
- consortia, communities	degradation is absent or slow with single species
- interactions, mutualism	
- syntrophy, *etc.*	
- other microorganisms	
- protozoa	predation/inhibition
- exudates	{ inhibition
- products	{ inhibition
- eutrophic bacteria	active at higher concentrations, higher thresholds
- oligotrophic bacteria	active at lower concentrations, lower thresholds
d) Abiotic processes *e.g.* hydrolysis, photooxidation	can augment biodegradation

Source : Painter, 1992.

INHERENT BIODEGRADABILITY

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

Chemicals which fail a test at the second level (by showing < 20% mineralization) are considered to be not inherently biodegraded and are not tested further. If the degree of mineralization is between 20 to 70%, any metabolites (intermediates) must be identified while if it is more than 70%, the chemical is considered to be inherently biodegradable.

SIMULATION OF ENVIRONMENTAL CONDITIONS

An appropriate simulation test is applied in order to determine more precisely the degree of chemical removal. The principles used and relative stringency of each test is given in *Tables 4* and *5* (Guidance Document,79/831/ EEC) while *Table 6* gives the various methods often used for bioD, accepted by OECD, as well as EEC and ISO (Painter, 1992).

Various methods can be used to estimate the progress and extent of surfactant bioD, such as (Swisher, 1987).

a. physical or chemical properties imparted by the surfactant itself or by its intermediate bioD products

b. measuring related functions such as the amount of O absorbed or of CO_2 evolved by the organisms in the system.

OECD tests for surfactant bioD followed specific property (and therefore specific chemical test) of a surfactant. Therefore, it is necessary to classify surfactants into their characteristic chemical nature.

A qualitative estimate of surfactant degradation can be made by observing changes in surfactant properties during the test, for example, the surface tension and foaming tendency.

Quantitative analysis for anionic surfactants is accomplished by the methylene blue method. This is fairly specific for anionic surfactants. The method is simple to use, is readily adaptable to automation and is an acceptable method for measuring primary biodegradation (Linder *et al.*, 1982).

Dragendorf bismuth reagent is often used to analyze nonionic surfactants. Quantitative analysis for nonionics is much more difficult and no method is available which is comparable to the methylene blue method. The biodegradation of nonionic surfactants is generally more difficult to ascertain because of wide structural diversity and a usual lack of functional groups (Sturm, 1973). Paired ion extraction (PIX) and thin layer chromatography (TLC) are the two methods most favoured in current environmental and bioD work.

Determining the bioD of a substance under anaerobic conditions is important in predicting the compound's treatability by anaerobic municipal waste treatment systems and in predicting persistence in both ground and surface water systems. Many chemicals will eventually reside in anaerobic environments such as aqueous sediment layers, flooded soils and aquifer systems. Anaerobic tests are necessary especially for chemicals which are insoluble and/or adsorbed onto sludge and sediments (Birch *et al.*, 1989). Biodegradability is assessed by the net increase in pressure of gas during incubation and by the amount of methane produced as measured by GC or by adsorbing CO_2 in an alkaline suspension (Painter, 1992).

TABLE 4. RELATIVE STRINGENCY OF TEST METHODS FOR READY BIODEGRADABILITY.

Test method	Duration (days)	Determinant	
			Most stringent (test conditions less favorable to degradation of test substance)
Closed Bottle	28[a]	O_2 uptake	
Modified MITI(I)	28[a]	O_2 uptake/DOC	
Modified OECD	28[a]	DOC/Specific analysis[b]	
Manometric Respirometryanalysis)	28[c]	O_2 uptake(DOC specific	
Modified AFNOR	28[a]	DOC/Specific analysis[b]	
Modified Sturm	28[a]	CO /DOC/Specific analysis[b]	↓
			Least stringent (test conditions more favourable to degradation of test substance)

a : Test methods already published.
b : ^{14}C labelled test substances may be used in these tests.
c : A test protocol has been approved by the Co-ordinating Group but not yet published.
Source : Guiding Principles For A Strategy For Biodegradability Testing, 1979.

TABLE 5. TEST METHODS FOR INHERENT BIODEGRADABILITY.

Method	Determinant	Rank
Zahn-Wellens[a]	DOC/Specific analysis	Stringent
Semi-continuous[a] Activated sludge (SCAS)	DOC/Specific analysis	Less stringent than Zahn Wellens

[a] Test protocol for both methods have been approved by the co-ordinating group but have not yet been published.
Source : Guiding Principles For A Strategy For Biodegradability Testing, 1979.

STRUCTURE AND BIODEGRADABILITY

Links between chemical structure and biodegradability would be of use in the synthesis of new, biodegradable chemicals and in predicting the biodegradability of untested chemicals (Steinle *et al.*, 1964). Some structures like the quaternary carbon bondings; nitro, amino and sulfonic substituents on phenol, benzoic acid, aniline and toluene are nonbiodegradable or are very difficult to degrade (*Table* 7). Chemicals can be ranked according to their potential for bioD and a study by *Urano and Kato* (1986) showed that the ease of degradation of the following chemicals decreased in the order of (a) to (d) (Painter, 1992).

a) carboxylic acids, alcohols, esters
b) ketones, olefine sulfates, olefine sulfonates
c) diamines, amino-, nitro-, sulfonic aromatic acid
d) alkyl ethers, halo-, amino-, nitro-sulfonic benzenes and phenols.

In summary, the following generalizations relating to surfactant structure and bioD have been advanced and validated.

i) The structure of the hydrophobic group is an important determinant of biodegradability; bioD is promoted by increased hydrophobic linearity and deterred by hydrophobic branching, particularly by terminal quartenary branching.

ii) The nature of the hydrophilic has only a minor influence on the biodegradability.

iii) Increased distance between the sulfonate group and the far end of the hydrophobic group increases the speed of primary bioD of a surfactant.

(Swisher, 1987)

OLEOCHEMICAL-BASED SURFACTANT

The most important oleochemical-based anionic surfactants are fatty alcohol sulfates (FAS), fatty alcohol ether sulfates (FAES) and α-sulfonated methyl esters (α-SME) (Steber *et al.*, 1988). FAS and low-ethoxylated FAES are accessible even more easily than LAS to enzymatic degradation by microorganisms. α-sulfonated methyl esters (α-SME), in short ester sulfonates, are of considerable interest. They are made from renewable natural raw materials, exhibit good washing properties and are stable to hydrolysis and largely unaffected by water hardness (Gode *et al.*, 1987).

α-SME has been regarded as a potential surfactant for heavy-duty detergents because of its excellent detergent properties (Masuda *et al.*, 1993). Smaller amounts of α-SME are needed to obtain satisfactory detergency, thus lowering the organic load in wastes discharged to the natural environment. The bioD of α-SME was found to start quickly, and then proceeds rapidly to ultimate degradation at sewage treatment plants and in the river (Steber *et al.*, 1989). An effluent containing the breakdown products of α-SME should show low toxicity to fish.

Oleochemical-based surfactants exhibit better cleaning power than LAS in the absence of phosphates (Masuda *et al.*, 1993; Salmiah Ahmad, 1993). The better performance of α-SME at high washing temperature and FAS at low water temperature offer the flexibility in formulations, allow product formulation that is 100 % oleochemical-based and suitable for various ranges of temperatures (Salmiah Ahmad, 1993).

TABLE 6. LIST OF METHODS FOR TESTING BIODEGRADATION

Biodegradation Test	Methods		
	OECD	EEC	ISO (does not differentiate between ready and inherent biodegradability)
Ready Biodegradability	301A - DOC Die Away 301B - Modified Sturm Test 301C - MITI (I) (Japan) 301D - Closed Bottle 301E - Modified OECD Screening 301F - Manometric Respirometry	C.3 - Modified OECD Screening C.4 - Modified AFNOR (NF T90/302) C.5 - Modified Sturm C.6 - Closed Bottle C.7 - Modified MITI (I) C.8 - BOD	7827 - DOC. (1985), 1991 9408 - Oxygen demand respirometer (1991) 9439 - CO_2 release (1991) 9887 - SCAS 9888 - Zahn-Wellens
Inherent Biodegradability	302A - Modified SCAS 302B - Modified Zahn-Wellens-EMPA	Modified SCAS Modified Zahn-Wellens	
Simulations	303A - Coupled Units Test	Activated Sludge Simulation Tests	Activated Sludge Simulation Tests

TABLE 7. EFFECT OF CHEMICAL STRUCTURE ON BIODEGRADATION

	Factor	Effect	Chemical Concerned
1)	Number of C atoms in aliphatic chains	increased number of C atoms favors biodegradation	Imides and amides, C_3-C_{10} aliphatic ketones, C_1-C_8 alcohols, C_1-C_8 2,4-D esters and diamines.
		increased number of C atoms reduces biodegradation	Linear alkanes, fatty acids, adipic acid esters, C_9-C_{15} aliphatic alcohols,phthalates and C_{11}-C_{14} alkylbenzene sulphonates.
2)	Number of rings in cyclic compounds	increased number of rings impedes biodegradation	Heterocyclics with sulphur in the ring are more resistant than their nonsulphur analogues.
3)	Number of azo bonds in dyestuffs	increased number reduces biodegradation	–
4)	Substituents in aromatic and aliphatic structures	hydroxyl or carboxyl groups enhance biodegradation	-
		amino, chloro, nitro and sulphonic groups decrease biodegradation	-
5)	Number of substituents	increased number of substituents decreases the ease of biodegradation	-
6)	Structural complexity	higher molecular weight tends to reduce biodegradation	-

Source : Painter, 1992.

Summary of The Biodegradation Data

For the benefit of researchers, attempts have been made by (Swisher 1987) to compile data on the biodegradation of various types of surfactants that have been produced world wide. For the researchers working on the oleochemicals derivatives from palm oil/palm kernel oil, the data in *Table 8* have been extracted from Swisher's compilation for a quick assessment. *Appendix 1* following *Table 8* explains it in detail.

TABLE 8. BIODEGRADATION OF VARIOUS TYPES OF SURFACTANTS

Substrates	Extent	Method	Time	Analysis
Alkyl benzene sulfonates				
C-10	36;72	BOD	5;16d	O_2
	98;77	BOD	4;15d	MB;O_2
	48	Wa	6h;8d	O_2
	66	Wa	1d	O_2
C-12	43;62	BOD	5;14d	O_2
	100;71	BOD	6;20d	MB;O_2
	38;60	Wa	6h;8d	O_2
	45	Wa	28h	O_2
Linear alkylbenzene sulfonates				
C-10	100	RW	15d	MB
	95*	RW	4d	MB
C-12	100	SF	7d	MB
	100	SF	3d	MB;
	98;79	In	20d	MB;O_2
	100;60	In	5;30d	MB;O_2
Olefin sulfonates				
C-16	100	CAS	3h	MB
	97;57	In	3;16d	MB;CO_2
Sulfonated methyl esters				
C-16	80*	RW	4d	MB
	78	In	22d	C
C-18	99;91	CAS;RW	3h;4d	MB
	80*	RW	4d	MB
	83	In	22d	C

* *Extent of degradation chosen by the researcher for the termination of his test (usually 50, 80 or 90%) and not necessarily the full extent possible.*

Table 8. (cont.)

Substrates	Extent	Method	Time	Analysis
Alkyl sulfates				
C-12	100	CAS	3;6h	MB
	95-100	CAS	1h	MB
	100	In	1d	MB
	97;100	In	2;9d	MB
C-16	100	RW	28d	MB;r;F
	100	RW;AnRW	1;3d	MB
	100	In	2d	MB
	98	In	7d	MB
Alkoxylated sulfates				
C-12(18EO)	88-92	CAS	3h	MB
Soap	84;83	BAS	1d	COD;C
	100	RW	20d	C
	100;98	In	10;15d	$C;O_2$

* *Extent of degradation chosen by the researcher for the termination of his test (usually 50, 80 or 90%) and not necessarily the full extent possible.*

CONCLUSION

The activities to protect the global environment and saving the natural resources are becoming more and more important worldwide. For these, cooperations among the governments, the consumers, the industries and the scholars are required. In Malaysia, BAS is being used by the detergent, pesticide, metal finishing (degreasing), petroleum and textile industries. But recently, the usage of BAS has been banned and several alternatives such as LAS and oleochemical-based surfactant has been suggested to replace BAS. The use of BAS has yet to be banned in developing countries, hence, special attention should be given in the treatment of this detergent prior to discharge into the environment. Various alternatives are available and these have been briefly outlined in this article.

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NOTES ON *TABLE 8*

1) Substrates - chemical nature : Column 1

The chemical structures of the compounds tested are indicated in the column. The term 'linear' is often applied to commercial products which may still contain as much as 5-10% of branched or cyclic structures. Incomplete biodegradation in commercial types of LAS, for instance, may only reflect the presence of such impurities rather than any failure of the truly linear components to degrade.

2) Extent of biodegradation : Column 2

The second column shows the percentage of biodegradation found (or simply percentage removal in many cases where biodegradation was not explicitly proved), using the indicated conditions of exposure and analytical methods. With non specific analytical methods, the figure given is a percentage of the theoretical amount. In some cases, the percentage is based on the experimentally determined COD of the substrate rather than calculated theoretical figure.

In some cases, the extent of biodegradation tends to level off. Where possible, the 'level value' is the one entered in the table. If no level value is reached, or if the extent of biodegradation is low, the extent given is that found at the end of the run.

In some situations, the figure for extent of degradation is an arbitrary value chosen by the researcher for the termination of his test (usually 50, 80 or 90%) and not necessarily the full extent possible. In *Table 8*, such values are indicated by asterisk.

3) Conditions and test methods : Column 3

The following are the abbreviations used in this column.

Appendix 1

An	Anaerobic
BAS	Batch or semicontinuous activated sludge
BOD	Standard BOD bottle procedure
CAS	Continuous-flow activated sludge
In	Natural or synthetic medium inoculated with acclimated organisms; although the shake-culture, BOD and Warburg procedures also fall into this category, they have been designated individually
RW	River water die-away
SF	Shake-flask culture
Wa	Warburg respirometer.

4) Biodegradation time : Column 4

This column gives the time (h, hours; d, days; y, years) corresponding to the extent of degradation entered in column 2. In the case of continuous-flow tests, this is usually the average retention time in the aeration section, and in the batch (semicontinuous) activated sludge test, it is the time for one cycle.

The times cited for tests of die-away type are those at which the extent of degradation levels off to a relatively constant value. If no levelling off occurs, or if the extent is low, the time and extent given usually correspond to the end of the run.

5) Parameters analyzed : Column 5

The abbreviations used in this column are :-

C	Organic carbon; ^{14}C, radiocarbon studies
COD	Chemical oxygen demand
F	Foaming properties
MB	Methylene blue, methyl green, and other paired-ion extraction (PIX) methods for anionic surfactants
O_2	Oxygen uptake
r	Surface tension

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