Biodegradation of Nonionic Surfactants

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ABSTRACT

This paper discusses the biodegradability of alcohol-based nonionics measured by the recommended legislative test procedures and how the results obtained are affected by the chemical structure of the surfactant, and thus provides guidance on the selection of materials. More detailed studies on the biodegradation of alcohol ethoxylates during the activated sludge sewage treatment process are also reported. Examination of a wide range of alcohol ethoxylates in the legislative tests shows that the majority of those nonionics of practical importance will be extensively biodegraded. Although the mathematical model used to design the treatability test is very simple and has frequently come under criticism, the predictions seem to be upheld and the results obtained appear to provide a reliable guide to what is likely to happen in practice. The sludge residence time, which has long been regarded as of particular importance by those involved in the field of sewage treatment, is clearly demonstrated to be a highly significant factor whose influence should be taken into account in any detailed laboratory study of treatability. The study of alcohol ethoxylates indicates that extensive primary biodegradation will occur even in overloaded treatment plants where sludge retention times (SRT) are likely to be short. The effect of temperature on the biodegradation is small and suggests that effective treatment will be achieved in such plants even at the lower temperatures experienced during winter. Ultimate biodegradation of alcohol ethoxylates was shown to be extensive under practical conditions and levels of "polyethylene glycol" intermediates discharged to surface waters will be low. Although alcohol ethoxylates are rapidly and extensively absorbed on activated sludge, this does not play a significant role in the removal process which is essentially one of biodegradation.

INTRODUCTION

Within the EEC, a directive which provides the basis for legislation to control the use of nonionic surfactants has now been issued. The directive recommends standard tests by which the biodegradability of nonionics may be determined.

A simple die-away procedure provides an initial test by which materials may be screened, and those meeting the requirements of the test are considered to be acceptable. Nonionics failing the test may be subjected to the confirmatory test, a more comprehensive continuous flow activated-sludge test using a synthetic wastewater. In the event of any dispute, the confirmatory test is used as the reference procedure. The directive also specifies that the analytical method described by Wickbold (1) be used to follow the degradation process and, since this measures only intact nonionics, both tests measure primary biodegradation.

A comprehensive study of nonionic biodegradability using these two procedures has been reported (2). The behavior of a wide range of materials was examined and the results are summarized in Tables I and II.

Both sets of data lead to the same conclusion, that the effect of the hydrophobe structure is small until the rate of biodegradation is reduced by the increasing ethoxylate (EO) chain length, and differences due to increased branching of the hydrophobe then become apparent. For those materials of major interest to the detergent industry, i.e., with EO chain lengths below ca. 20 units, materials based on linear, oxo or secondary alcohols are acceptable. If materials with longer ethoxylate chain lengths are required, they must be based on an essentially linear primary alcohol.

Clearly, these results give no cause for concern about the continued use of alcohol ethoxylates following the introduction of the controlling legislation.

TABLE I

Biodegradation of Alcohol Ethoxylates in OECD Screening Test

Alcohol	% Removal				
	10 EO	20 EO	30 EO	40 EO	50 EO
Linear primary alcohol	99	99	98	98	98
Linear primary oxo alcohol 25% branched	100	98	93	88	92
Linear primary oxo alcohol 50% branched	84	83	79	–	69
Linear secondary alcohol	96	64	59	65	–

TABLE II

Biodegradation of Alcohol Ethoxylates in OECD Confirmatory Test

Alcohol	% Removal				
	10 EO	20 EO	30 EO	40 EO	50 EO
Linear primary oxo alcohol (25% branched)	93	83	85	89	86
Linear primary oxo alcohol (50% branched)	97	89	75	71	68
Linear secondary alcohol	87	85	72	54	–

Experience with both anionic and nonionic surfactants suggests that results obtained by these procedures predict the behavior of the materials in practice with reasonable accuracy. However, as might be expected, in developing a simple and widely applicable test method which incorporated a significant safety margin, there were of necessity a number of potential problem areas which could not be taken into account.

The following are among the principal shortcomings.

—The possible effects of temperature and variations in plant operating conditions are not taken into account.

—The synthetic wastewater used produces a sludge with a lower biodegradation potential than sludge growing on domestic sewage.

—The test only measures primary biodegradation and "polyethylene glycol (PEG)-like" residues have been reported in confirmatory tests on nonionics (3).

For relatively high tonnage materials having considerable potential for widespread distribution in the environment, more detailed studies were considered desirable. This paper reports studies of the behavior of alcohol ethoxylates in the activated-sludge process under a range of conditions which may be encountered in practice.

MATHEMATICAL MODEL OF ACTIVATED–SLUDGE PLANT

The theory of the activated-sludge plant and the resulting mathematical models (4) seemed a rational starting point for the design of a more comprehensive treatability test.

A flow diagram of a completely mixed activated-sludge process is shown in Figure 1.

The net change in the concentration of microorganisms, X, as a result of synthesis and decay can be expressed by:

$$\frac{dX}{dt} = uX - KdX$$

where u is the specific growth rate and Kd is the specific decay rate, and the effect of substrate concentration, S, on the specific growth rate is given by the Monod function:

$$u = \frac{\hat{u}S}{Ks + S}$$

where $\hat{u}$ is the maximum specific growth rate and Ks is the saturation constant, i.e., the concentration at which

$$u = \frac{1\hat{u}}{2}$$

A mass blance of the active solids across the system gives:

$$\frac{VdX_1}{dt} = u\,X_1\,V - KdX_1\,V + Q_0X_0 - (Q_0 - Q_1)X_2 - Q_1X_3 \ldots \quad [1]$$

For most of the materials for which detailed biodegradability studies are necessary, efficient treatment only occurs after a period of acclimatization, i.e., when a significant population of competent microoraganisms becomes established in the activated sludge. Hence it is not unreasonable to assume that the levels of competent organisms in the influent sewage are low, i.e., $X_0 = 0$.

At steady state $dX_1/dt = 0$ and, since $u = \hat{u}S_1/(Ks+S_1)$, Equation 1 reduces to:

$$\frac{\hat{u}S_1}{Ks + S_1} - Kd = \frac{(Q_0 - Q_1)\,X_2 + Q_1\,X_3}{VX_1}$$

Since $VX_1/[(Q_0 - Q_1)\,X_2 + Q_1X_3]$ is the mean sludge retention time (SRT), then:

$$\frac{1}{\theta s} = \frac{\hat{u}S_1}{Ks + S_1} - Kd$$

where θs is the mean sludge retention time.

On rearrangement, the following expression for the level of substrate in the plant effluent at steady state is obtained:

$$S_1 = \frac{Ks\,(1 + Kd\theta s)}{\theta s\,(\hat{u} - Kd) - 1}$$

Examination of this equation leads to the following conclusions.

(a) The effluent concentration is independent of the influent concentration, S_0, since this parameter does not appear in the expression.

(b) The only plant control parameter affecting the level of substrate in the effluent is the sludge retention time, and the variation of effluent substrate concentration with SRT will be as shown in Figure 2.

(c) For any given influent concentration there will be a critical sludge retention time $\theta_{sc} = \hat{u}So/(Ks + So) - Kd$, below which the competent microorganisms will be washed out of the plant and the rate of biodegradation will fall to zero.

(d) Since all other parameters in the equation are associated with the growth kinetics of the microorganisms degrading the substrate, then the temperature is likely to affect the effluent substrate level and the critical sludge age, i.e., if over the selected temperature range the biological coefficients vary appreciably with temperature, a shift in position of the curve shown in Figure 2 would be observed and the SRT required to obtain efficient treatment would increase with decreasing temperature.

The above considerations suggest that to assess the treatability of materials in the activated-sludge process it is necessary to control both the sludge retention time and the temperature and to determine how these factors affect the biodegradability of the material under test.

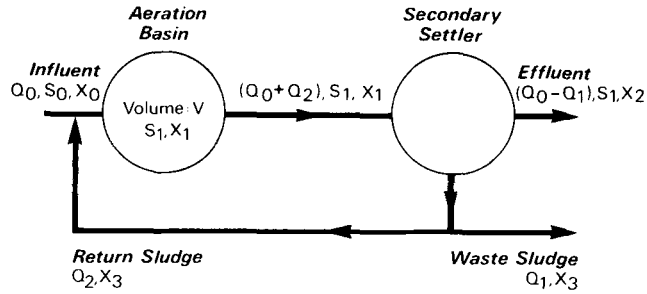

FIG. 1. Flow diagram of activated-sludge process. Q_0, Q_1 and Q_2 are the influent, waste sludge and return sludge flows in liters/day. S_0, S_1 are the substrate concentrations in the influent and effluent in mg/L. X_0, X_1, X_2 and X_3 are the concentrations of microorganisms in the influent, aeration basin, effluent and return sludge in mg/L.

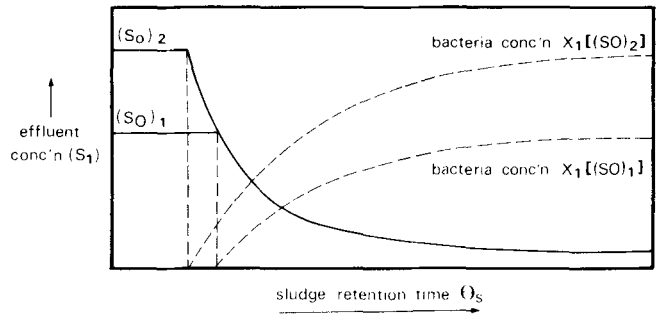

FIG. 2. Effect of SRT on effluent concentration.

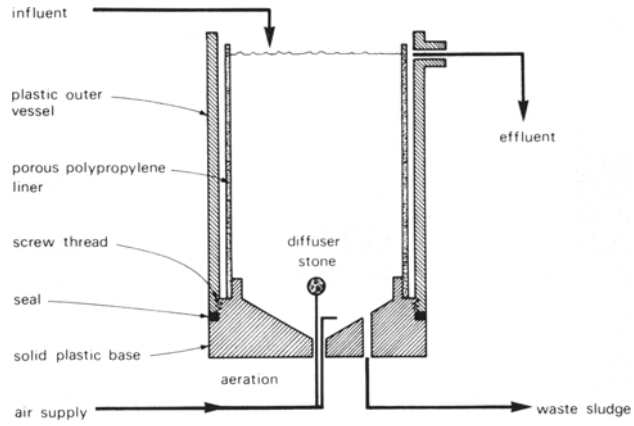

FIG. 3. "Porous pot" with SRT control.

EXPERIMENTAL SYSTEM

A laboratory-scale activated-sludge plant suitable for this purpose based on the Water Research Centre "porous pot" type plant is shown in Figure 3. The conical base of the porous inner vessel was replaced by a solid base to allow waste sludge to be drawn continuously from the aeration basin.

Since the level of microorganisms in the plant effluent, X_2, is very low and the SRT = $VX_1/[(Q_0-Q_1)\,X_2+Q_1\,X_1] \approx VX_1/Q_1X_1 = V/Q_1$, by controlling the sludge wastage rate the plants can be operated at any preselected SRT. The plants are used to process domestic sewage drawn from the municipal sewerage system and test compound is dosed

directly into the pot. The plant temperature is controlled and adjusted during the test and data are obtained at different temperatures within the desired range – usually between 5 and 20 C. The air supply is arranged to ensure complete mixing of the system. Plants are operated to give a range of SRT – usually 2,4,6,8 and 10 days. At each temperature and for each SRT, samples of effluents are analyzed to obtain a number of values for each set of conditions.

RESULTS

To test the validity of the rather simplified model used and the assumptions made in arriving at the above conclusions, a material known to be less efficiently treated during the winter months was examined. Plants operating at 2,4,6,8 and 10 days SRT were dosed with the test compound to give an influent concentration of 10 mg/L and effluent concentrations were determined at 3 temperatures. Results are shown in Figure 4.

At 14-17 C, it is apparent that there is no significant increase in the effluent concentration as the SRT decreases. At 7-10 C, a small increase is apparent at an SRT of 4 days and at 2 days almost 70% of the material passes through the plant unchanged. At 5-7 C, the material can only be efficiently treated in plants operating with an SRT of greater than 6 days.

Throughout the study, the overall plant performance was monitored by measurement of dissolved organic carbon in the effluent which under all conditions remained acceptable. The nitrification of ammonia, which is also known to be greatly affected by temperature and to require an SRT of 3-4 days even at 15 C for efficient treatment, showed a similar pattern to that observed for the test compound.

The implications of these results are, of course, that in those plants where the SRT is below ca. 6 days the material will be inefficiently removed during winter, although during the summer months efficient treatment will be possible over the whole range of plant SRT likely to occur.

A similar study was made on an oxo-alcohol based nonionic having an ethoxylate chain length of ca. 8 units. The results obtained for this material are shown in Table III and presented graphically in Figure 5.

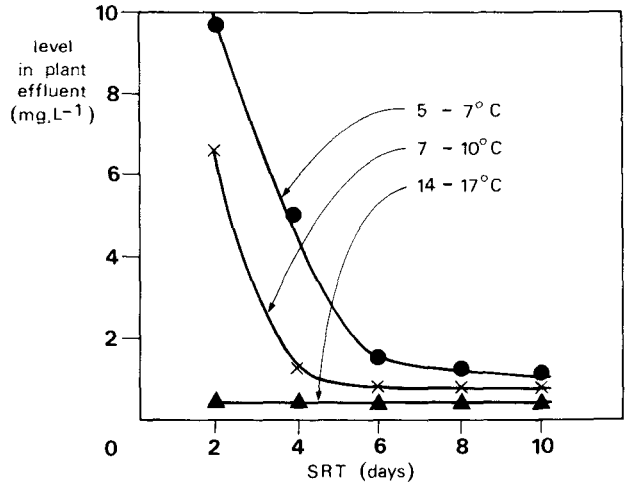

FIG. 4. Observed effect of SRT and temperature on effluent concentration.

TABLE III

Median Levels of Alcohol Ethoxylate 8EO in Plant Effluents (Influent Concentration = 5 mg/L)

SRT	Temperature 9 C	12 C	15 C
2	0.96	0.51	0.47
4	0.58	0.39	0.30
6	0.56	0.36	0.28
8	0.41	0.26	0.22
10	0.32	0.25	0.16

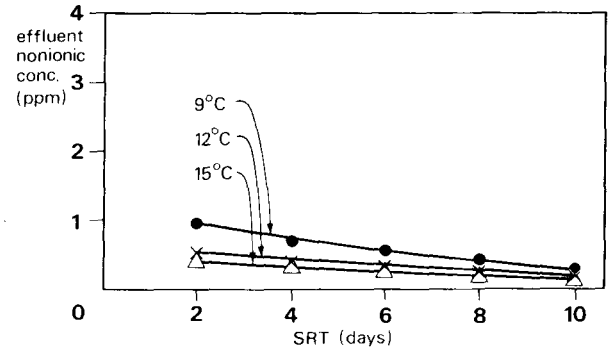

FIG. 5. Effect of temperature and SRT on biodegradation of alcohol ethoxylate 8 EO.

The values plotted are the median values of 7 analyses at each temperature/SRT combination. The results suggest that the biodegradability of alcohol ethoxylates is only slightly reduced by the lower temperatures which may occur during the winter months and that they will be efficiently removed throughout the range of SRT normally encountered in practice.

In a separate study to test the premise that, at steady state, the effluent concentration is independent of the influent concentration, a series of 4 activated-sludge plants was acclimatized to oxo-alcohol based nonionics containing 7, 11, 15 and 20 EO units at a concentration of 5 mg/L in the influent sewage. After several weeks, the level of nonionic in the influent sewage was increased to 25 mg/L and the plant again allowed to attain steady state. Throughout the test the plants were operated at an SRT of 6 days and a temperature of 15 C. The levels of intact nonionic in the plant effluents at each influent level are given in Table IV.

Given the inherent variation in sewage strength and the background level of nonionic in the sewage, the differences observed are not considered significant and the predictions of the model were upheld since the effuent concentration remained essentially unchanged despite a 5-fold increase in influent level.

During the course of the study it was observed that activated sludge rapidly adsorbed alcohol ethoxylates and this raised the possibility that adsorption may play a significant role in the treatment process. To establish if this were the case, the activated sludges were analyzed for nonionic and the results obtained are given in Table V.

The sludge production rate for the plants varied between 650 and 1000 mg/day, hence the percentage nonionic removed from the system by adsorption was between 0.5 and 1.0%. Ca. 2% of the influent nonionic passed through the plant unchanged, suggesting that the fraction removed by biodegradation was better than 97%.

TABLE IV

Effect of Influent Concentration on Effluent Level

Nonionic	Level in plant effluent Influent: 5 mg/L	Influent: 25 mg/L
7 EO	0.14	0.15
11 EO	0.15	0.10
15 EO	0.21	0.31
20 EO	0.34	0.62
Control plant (sewage only)	0.33	0.11

TABLE V

Levels of Nonionic on Activated Sludge (Influent Concentration = 25 mg/L)

Nonionic	% Nonionic on dried solids
7 EO	0.28
11 EO	0.29
15 EO	0.24
20 EO	0.25
Control plant	0.29

TABLE VI

Polyethylene Glycol Levels in Plant Effluents

Nonionic	Influent "PEG" (mg/L)	Effluent "PEG" (mg/L)	% Removal
11 EO	19.8	0.77	96.0
15 EO	20.9	2.61	88.0
20 EO	21.8	2.45	89.0

The above discussion refers only to the levels of primary biodegradation since, throughout, the analysis was made using the Wickbold method which only measures intact nonionic. To obtain some indication of the level of ultimate biodegradation, the polyglycol intermediates in the plant effluents were determined by the HBr fission method described by Tobin et al. (3). This technique determines the total $-OCH_2 \cdot CH_2-$ functional groups present in the sample. The results obtained are given in Table VI.

The results clearly demonstrate that a large proportion of the PEG-like intermediates are removed during treatment and show that alcohol ethoxylates undergo extensive ultimate biodegradation during sewage treatment.

In contrast, Tobin et al. (3) found only ca. 25% 'PEG' degradation when testing Dobanol 9E0 in the OECD confirmatory test. The rather low activity of sludges grown on synthetic wastes compared with the highly active biomass produced from domestic sewage is the most probable explanation for the discrepancy.

ACKNOWLEDGMENTS

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Manufacture of Fatty Alcohols Based on Natural Fats and Oils

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ABSTRACT

The present worldwide capacity of fatty alcohols is ca. 1.0 million metric tons per year. About 60% of this capacity is based on petrochemical feedstocks, 40% on natural fats and oils. Three basic dominating commercial-scale processes are used to manufacture fatty alcohols: the Ziegler process and the Oxo synthesis starting from petrochemical feedstocks, and the high-pressure hydrogenation of natural fatty acids and esters. Basically, the high-pressure hydrogenation can be used with triglycerides, fatty acids or fatty acid esters as feedstock. The direct hydrogenation of fats and oils has not been developed to a commercial-scale process, mainly because it was not possible to prevent decomposition of the valuable byproduct glycerol. Conversion of fatty acids into fatty alcohols by catalytic hydrogenation without preesterification requires corrosion-resistant materials of construction and acid-resistant catalysts. Required reaction temperatures are higher, resulting in a higher hydrocarbon content. The majority of fatty alcohol plants based on natural fats and oils use methyl esters as feedstock. These can be made either by esterification of fatty acids or by-transesterification of triglycerides. For catalytic high-pressure hydrogenation of methyl esters to fatty alcohols, several process options have been developed. The bawic distinguishing feature is the catalyst application either in a fixed bed arrangement or suspended in the methyl ester feed.

INTRODUCTION

Fatty alcohols, particularly the detergent range C_{12} and higher alcohols, have become an important basic material for a host of derivatives and applications.

Today, in the Western hemisphere, the commercial production of fatty alcohols is based on three different process alternatives: the high-pressure hydrogenation of fatty acids and esters, the Ziegler synthesis, and the Oxo synthesis.

The Ziegler and Oxo processes start from petrochemical feedstocks producing synthetic alcohols, whereas natural fats and oils are the raw materials for the hydrogenation of fatty acids and esters to natural alcohols (1).

The present world capacity of natural and synthetic fatty alcohols is ca. 1.0 million metric tons/year (Table I). A regional breakdown of the world capacity into natural and synthetic fatty alcohols shows that in the USA the bulk of fatty alcohols is of petrochemical origin, whereas in Europe more than 60% of the total volume is made from natural fats and oils. Worldwide, ca. 60% of the fatty alcohol capacity is based on petrochemical feedstocks and