Microaerophilic Biodegradation of Tallow-Based Anionic Detergents in River Water

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ABSTRACT

Nine anionic detergents from five general classes (alcohol sulfates, ether alcohol sulfates, sulfated alkanolamides, α-sulfo esters and alkylbenzenesulfonates) were rapidly screened for biodegradability under aerobic and microaerophilic conditions in river water at 25 and 35 C. In decreasing order, the ease of biodegradation under microaerophilic conditions at 35 C was as follows: alcohol sulfates, sulfated alkanolamides, α-sulfo fatty acid esters and ether alcohol sulfates. Linear alkylbenzenesulfonate did not degrade.

INTRODUCTION

In past studies this laboratory has reported on the biodegradation of some tallow-based surface active agents in river water (1), in activated sludge (2) and in a laboratory scale activated sludge system (3,4). One study (5) requiring 30 days' experimental time was conducted in anerobic digesters using primary sludge as the source of inoculum. Completely anaerobic conditions for biodegradation are seldom realized in practice but are approximated by relatively frequent microaerophilic conditions under which biodegradation occurs at a low oxygen level of about 1 ppm or less. This paper describes the adaptation of the river water test for rapidly screening anionic detergents under microaerophilic conditions.

Since approximately one third of the U.S. population relies for their sewage disposal on septic tanks, cesspools and lagoons that are anaerobic or nearly so, it is of interest to study the biodegradation of synthetic detergents under microaerophilic conditions using river water as the source of inoculum.

EXPERIMENTAL PROCEDURES

Materials

Previous publications by this laboratory have described the preparation of sodium hexadecyl sulfate (6), sulfated hydroxyethylpalmitamide and sulfated hydroxypropylstearamide (7), sodium hexadecyloxyethyl, -oxypropyl and -oxybutyl sulfates (8), and sodium methyl and isopropyl α-sulfostearates (9). The linear alkylbenzenesulfonate (LAS) used was the active ingredient extracted from a commercial sample with absolute ethanol.

Procedure

The apparatus used is shown in Figure 1. Nitrogen gas or air was passed into vented 3 liter aspirator bottles at the rate of 50-100 ml/min. The bottles were fitted with extra coarse spargers which dispersed the incoming gas and provided continuous agitation to the solutions. Aluminum foil was wrapped around the bottles to prevent or minimize growth of algae which release oxygen to the system in daylight. The effectiveness of a constant flow of nitrogen in removing disolved oxygen (DO) from the test solutions was easily determined by an oxygen meter (YSI Model 51) equipped with a combination probe for measuring temperature and oxygen.

Detergent solutions of 5 or 10 ppm were prepared by dissolving the test compounds in 4 liters of river water. Duplicate two-liter portions were tested simultaneously under aerobic and microaerophilic conditions at 25 C and,

[1]Presented at the AOCS Meeting, New Orleans, April 1970.

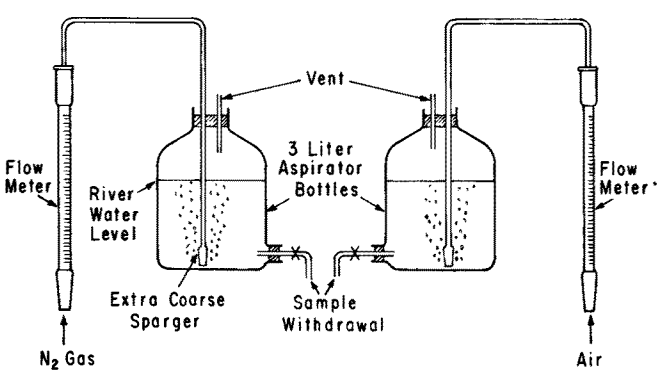

FIG. 1. Experimental apparatus used for simultaneous microaerophilic and aerobic tests.

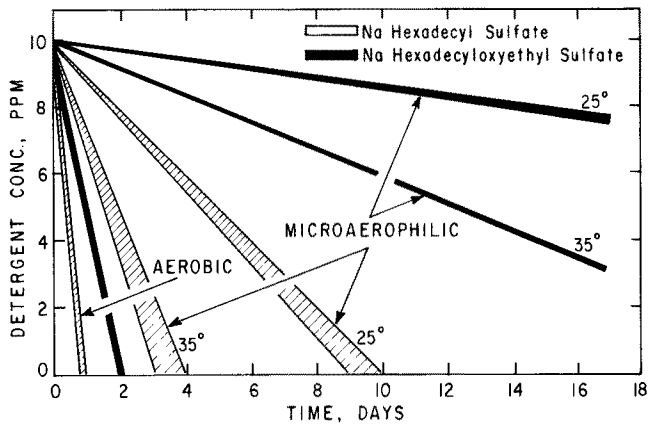

FIG. 2. Effect of oxyethyl group on biodegradation time.

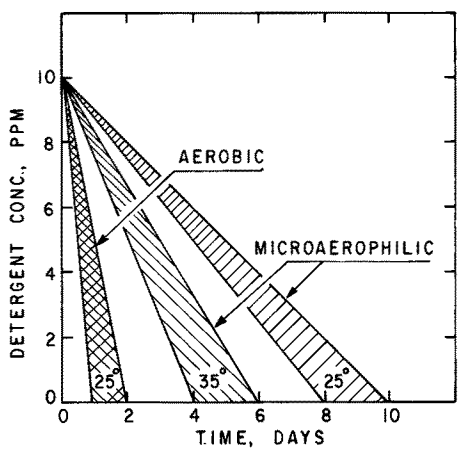

FIG. 3. Biodegradation range of sulfated hydroxyethylpalmitamide.

TABLE I

Per Cent Methylene Blue Active Substance[a] Reduction in Days

Compound	5 ppm				10 ppm			
	Aerobic[b]		Microaerophilic		Microaerophilic			
	25 C		25 C		25 C		35 C	
	%	Days	%	Days	%	Days	%	Days
Na hexadecyl sulfate $C_{16}H_{33}OSO_3Na$	100	1	100	3-6	100	9-10	100	3-4
Sulfated hydroxyethyl palmitamide $CH_3(CH_2)_{14}CONHCH_2CH_2OSO_3Na$	100	2	100	3	100	8-10	100	5-6
Sulfated hydroxypropyl stearamide $CH_3(CH_2)_{16}CONHCH_2CH(CH_3)OSO_3Na$	100	2	100	14	100	11-15	100	9-11
Na hexadecyloxyethyl sulfate $C_{16}H_{33}OCH_2CH_2OSO_3Na$	100	2	25	11	25	17	70	17
Na hexadecyloxypropyl sulfate $C_{16}H_{33}OCH_2CH(CH_3)OSO_3Na$	100	2	0	11	0	17	23	17
Na hexadecyloxybutyl sulfate $C_{16}H_{33}OCH_2CH(C_2H_5)OSO_3Na$	100	3	0	11	0	11	20	11
Na methyl α-sulfostearate $C_{16}H_{33}CH(SO_3Na)CO_2CH_3$	100	3	0	11	0	11	100	11
Na isopropyl α-sulfostearate $C_{16}H_{33}CH(SO_3Na)CO_2CH(CH_3)_2$	100	3[c]	0	11	0	14	100	7-9
Linear alkylbenzenesulfonate[d]	100	7[e]	0	10	0	18	0	18

[a]100% reduction = zero MBAS.
[b]No difference in time at 10 ppm.
[c]Six days at 10 ppm.
[d]Isolated active ingredient from a commercial linear alkylbenzenesulfonate.
[e]Nine days at 10 ppm.

similarly, under microaerophilic conditions at 25 and 35 C. An incubator was used to maintain the solutions at 35 C; the 25 C experiments were subject to fluctuations in room temperature.

Each test series was accompanied by a blank consisting of river water with no added detergent and by a control consisting of sodium hexadecyl sulfate in river water. Although the dispersed flow of gas effectively agitated the solutions, it was found to be necessary to shake each solution thoroughly before removing a sample for analysis; otherwise, low results were obtained because of solubility or foam fractionation problems. The dispersed flow of gas sometimes caused excessive foaming, which was controlled effectively by an inert silicone antifoam spray.

Before use, the river water, obtained from the Schuylkill River at Fairmount Park, Philadelphia, was allowed to stand overnight, then filtered through glass wool. The course of biodegradation was followed by analysis for methylene blue active substance (MBAS) using a Technicon Autoanalyzer.

RESULTS AND DISCUSSION

Dissolved Oxygen

Usually after 1 hr of sparging nitrogen through the solutions the dissolved oxygen content was less than 0.5 ppm and, after 2 hr, about 0.2 ppm. The reliability of the sensor readings was checked by comparing with results obtained by the time consuming standard Winkler Azide method (10). Results obtained by the Winkler method were invariably less than those obtained by the oxygen meter, indicating that the meter readings tended to be high at low concentrations. Reynolds (11) has substantiated the reliability of the oxygen sensor as an analytical tool.

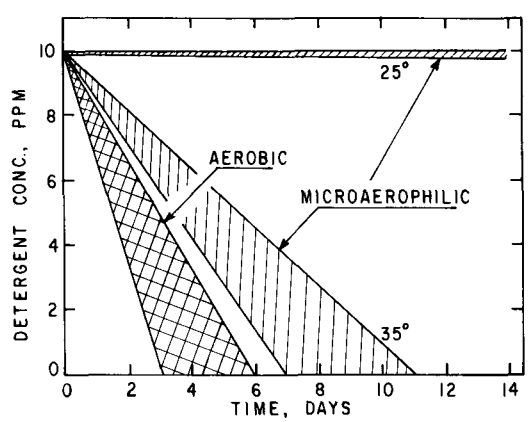

FIG. 4. Biodegradation range of sodium methyl and isopropyl α-sulfo-stearates.

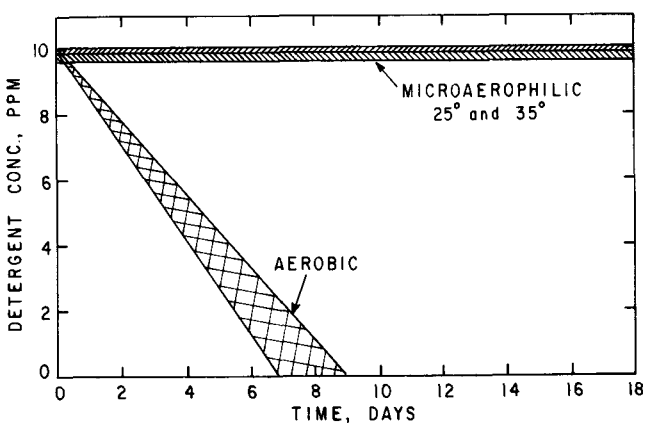

FIG. 5. Biodegradation range of LAS.

Aerobic Biodegradation

All of the tallow-based detergents degraded to zero MBAS (100% reduction) in 1 to 3 days at 5 and 10 ppm, except sodium isopropyl α-sulfostearate which required 6 days at 10 ppm. The results are shown in Table I. Sodium hexadecyl sulfate had the fastest biodegradation time. The aerobic data correlate well with previous work (4) but show little difference between detergents except the much greater time required by LAS.

Microaerophilic Biodegradation

Microaerophilic conditions at 25 and 35 C revealed in finer detail the effect of structural differences on biodegradation (Table I). The straight chain alcohol sulfate had the fastest biodegradation time under all conditions.

Sodium hexadecyloxyethyl, -oxypropyl and -oxybutyl sulfates degraded only partially; the branched chain compounds degraded least. The effect of substitution is illustrated in Figure 2 which compares the range of biodegradation for sodium hexadecyl sulfate and sodium hexadecyloxyethyl sulfate at 10 ppm.

The sulfated alkanolamides nearly equalled sodium hexadecyl sulfate in ease of biodegradation; however, the brached chain hydroxypropylstearamide took the longest time to degrade. The effect of conditions is illustrated in Figure 3 which shows the biodegradation range for sulfated hydroxyethylpalmitamide.

Surprisingly, sodium isopropyl α-sulfostearate degraded faster than the methyl ester at 35 C. The biodegradation range for these esters is illustrated in Figure 4.

LAS did not degrade under any of the microaerophilic conditions. Figure 5 illustrates the biodegradation range for LAS.

Biodegradation times for the surfactants reported in this paper show the relationship between molecular structure and ease of biodegradation under aerobic and microaerophilic conditions. The present method is much shorter, just as reproducible and possibly more realistic than existing methods.

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