

CHAPTER 1

Biodegradation of Esters of α -Sulfo Fatty Acids in Activated Sludge

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Six detergents and wetting agents derived from animal fats were tested for biodegradability in a laboratory scale activated sludge unit. A branched chain alkylbenzenesulfonate, a linear alkylbenzenesulfonate, and a salt of a branched chain α -sulfo fatty acid were included for comparison.

Sodium oleyl sulfate showed greater than 95% degradation throughout a month and a half of operation with an average effluent analysis of less than 0.1 ppm. Tallow alcohol sulfates, sodium methyl α -sulfostearate, sodium isopropyl α -sulfostearate, and disodium 2-sulfoethyl α -sulfostearate all showed greater than 95% degradation most of the time with an average effluent analysis below 1 ppm. Sodium hexyl α -sulfo-pelargonate and disodium α, α -dioctyl sulfoacetate showed 95% degradation only part of the time and average effluent analyses of 5.7 and 1.6 ppm respectively. All of the above named compounds were more easily degraded than linear or branched chain alkylbenzenesulfonates which had average effluent analyses of 7 and 11 ppm respectively.

The degradation of those compounds in activated sludge was compared also with their degradation in river water.

The development of all-purpose synthetic detergents reached commercial proportions about the end of World War II. Since that time the use of these materials has grown to such an extent that, by 1962, they constituted over 75% of all the cleansers used and about 90% of those used for household dishwashing and laundering (Orsanco Detergent Subcommittee, 1963). During the same period new problems developed in sanitary engineering that were ascribed more and more to these detergents. The frothing in sewage disposal plants, streams, and even at faucets is well-known. By far the most commonly used of the synthetic detergents is a mixture of alkylbenzenesulfonate isomers (ABS). Isomers containing branched alkyl groups in the ABS molecules are relatively resistant (hard) compared with those consisting primarily of linear alkyl groups (soft). Obviously, compounds may and do exist with varying degrees of degradability.

Whether or not ABS is responsible for all the problems attributed to it, a great deal of opposition has developed to the use of this material both in this country and abroad. Under the threat of legislation it appears that the detergent industry will be making a marked shift away from the less degradable products.

The replacement of soap by synthetic detergents has resulted in the accumulation of large amounts of inedible animal fats formerly used for making soap. As part of a research program to find new uses for these fats, this laboratory has synthesized a large number of detergents based on animal fat. Although it might be expected that these compounds would be easily degraded by virtue of their straight chain structure, it is of value to demonstrate this under simulated sewage disposal conditions.

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The compounds tested were sodium methyl α -sulfostearate, sodium isopropyl α -sulfostearate, disodium 2-sulfoethyl α -sulfostearate, (Stirton, 1962), disodium α,α -dioctyl sulfoacetate, (Ault, Micich, Stirton, and Bistline, in press), hydrogenated tallow alcohol sulfate, (Weil, Stirton, Bistline, and Maurer, 1959), sodium hexyl α -sulfopelargonate, sodium oleyl sulfate, disodium 9,10-dichlorooctadecyl sulfate (Weil, Stirton, and Maurer, 1955), and sodium oleate. Two samples of linear alkylbenzenesulfonate (LBS), one commercial (LBS I) and one prepared in the laboratory by the AlCl_3 catalyzed reaction of 1-dodecene and benzene, followed by sulfonation with concentrated sulfuric acid (LBS II), and a standard branched chain (ABS) obtained from the Soap and Detergent Association were included for comparative purposes. Results of the biodegradation of these compounds in river water (Weil and Stirton, 1964) and in activated sludge are reported in this paper.

River Water Tests

The river water used in these tests came from the Schuylkill River at Fairmount Park in Philadelphia. Solutions containing 5 ppm detergent in river water were stored in

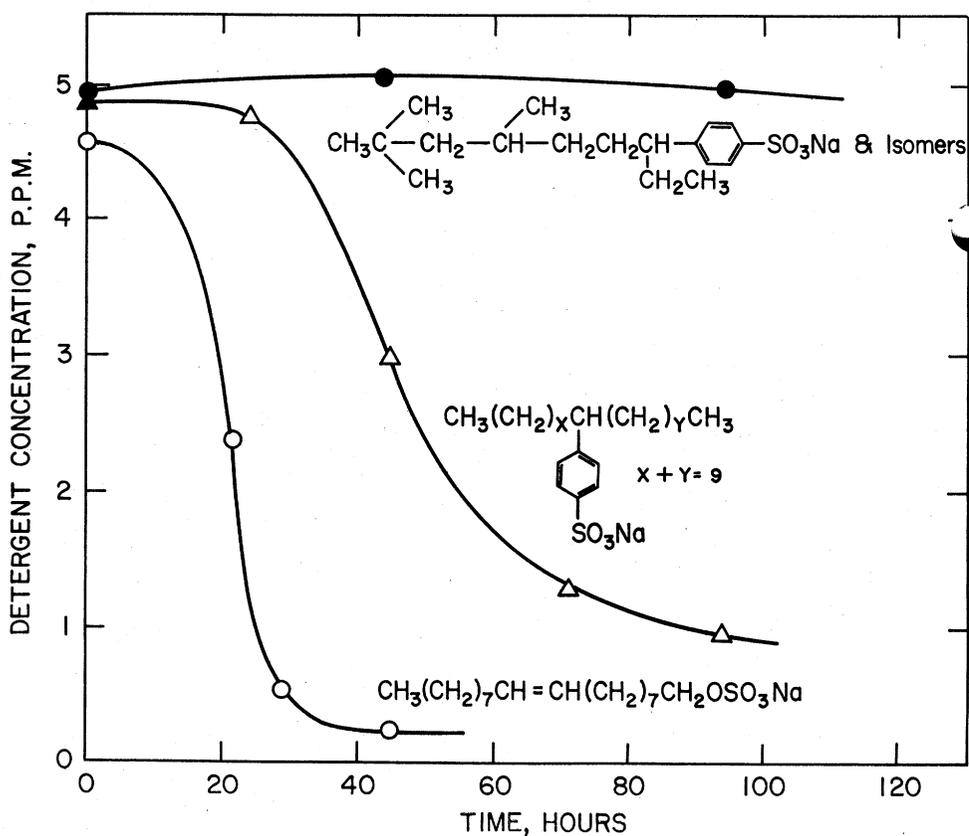


FIG. 1. Degradation of sodium oleyl sulfate, linear alkylbenzenesulfonate I (commercial sample), and branched chain alkylbenzenesulfonate in river water.

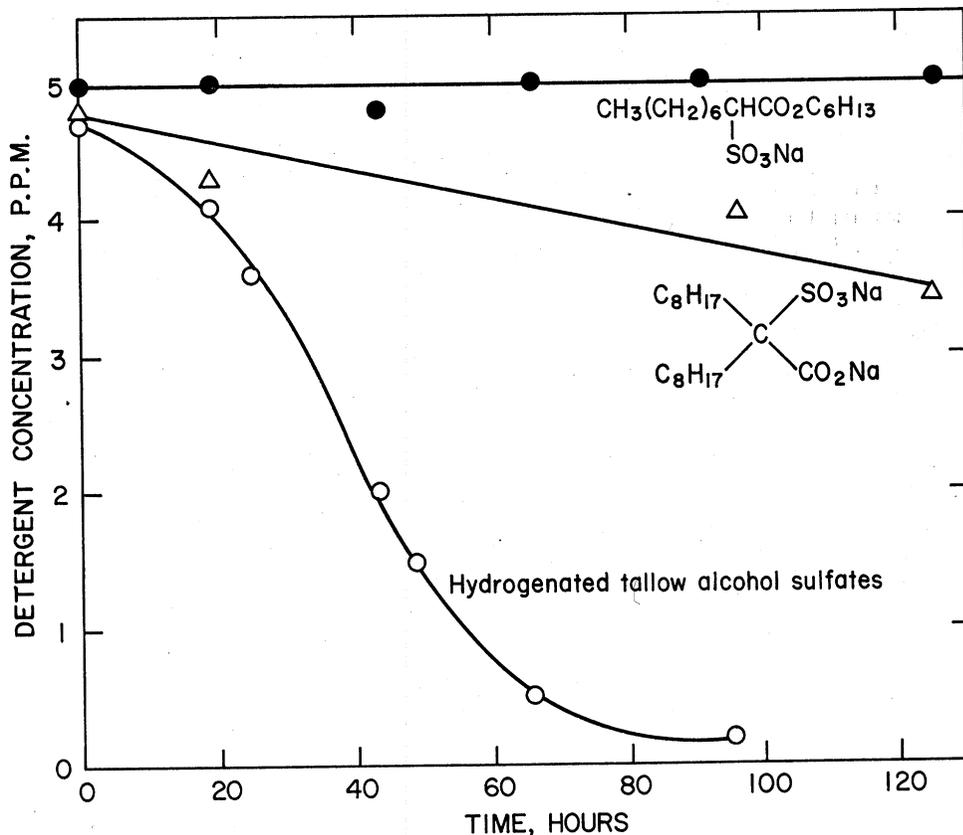


FIG. 2. Degradation of sodium hexyl α -sulfopelargonate, disodium α,α -dioctyl sulfoacetate, and hydrogenated tallow alcohol sulfates in river water.

the dark at 20 C, and aliquots were analyzed regularly for detergent content by the methylene blue method of Degens et al. (1953).

Ten ml of the stored test solutions were added to 100 ml of distilled water and treated with 5 ml of 0.035% methylene blue solution, made acid with 1.2% sulfuric acid. The salt that formed in the reaction of detergent and methylene blue was removed by extraction with three 10 ml portions of chloroform. Absorbance of the chloroform extract was measured in a Coleman Universal Spectrophotometer¹ at 650 m μ .

Analysis of dilutions of 5 ppm sodium dodecanesulfonate solutions showed the straight line relationship between absorbency and concentration predicted by Beer's Law. This curve for sodium dodecanesulfonate was used to convert absorbency values to concentration as sodium dodecanesulfonate. Concentration as sodium dodecanesulfonate was in turn converted to ppm of each detergent by appropriate molecular weight

¹ Reference to specific manufactured items does not constitute recommendation by the U. S. Department of Agriculture over similar articles not mentioned.

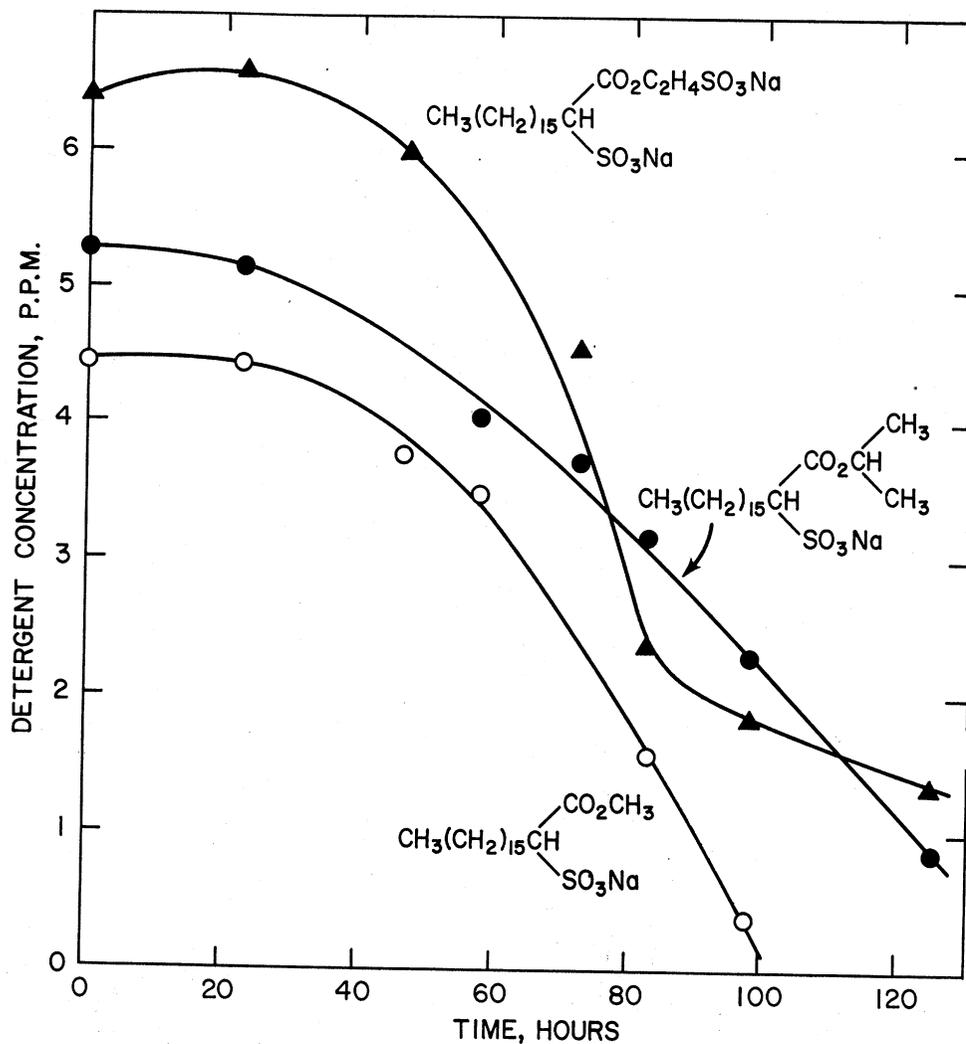


FIG. 3. Degradation of sodium methyl-, sodium isopropyl-, and disodium 2-sulfoethyl α -sulfostearate in river water.

correction, assuming a 1:1 stoichiometric relationship between dye molecule and surface active agent.

The curves in Figure 1 show that sodium oleyl sulfate disappeared almost completely in about 40 hours. LBS I was not attacked until after 24 hours but only 20% remained at 100 hours. This commercial sample of LBS was selected for use in this study because it was the most easily degraded of several samples tried in the river water tests. The residue of undegraded material probably consists of resistant isomers. Ruschenburg and Hirsch (1964) have found that isomers in which the benzene ring is at the

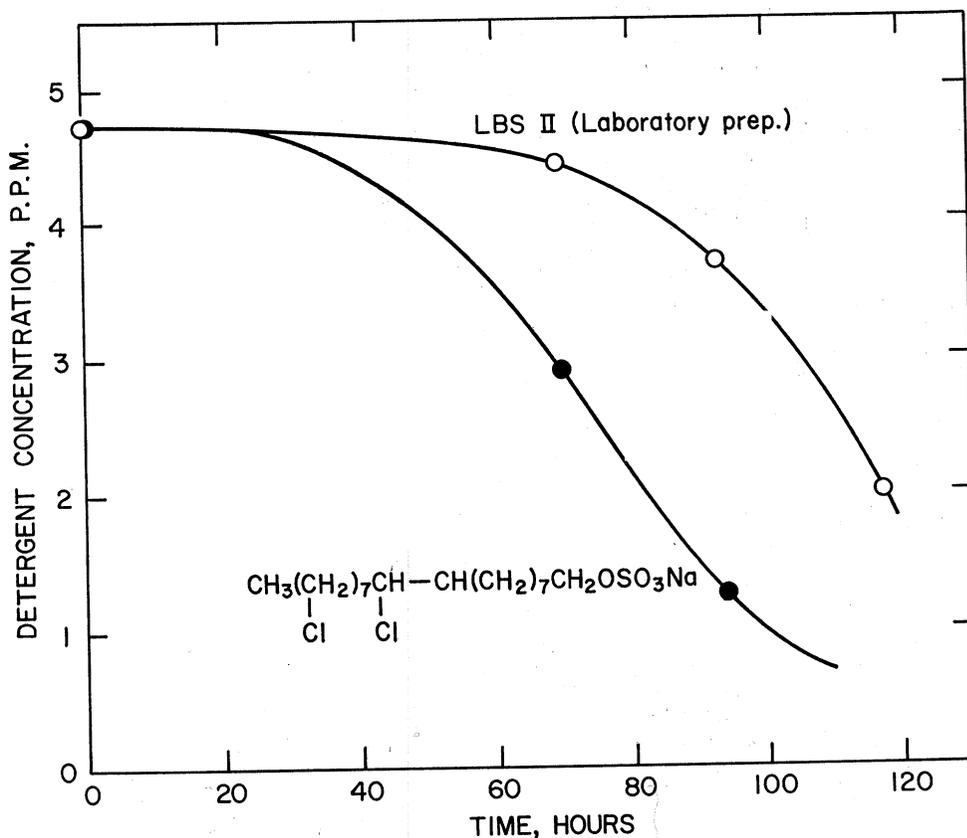


FIG. 4. Degradation of linear alkylbenzenesulfonate II (laboratory preparation) and sodium 9,10-dichlorooctadecyl sulfate in river water.

center of the chain were much more resistant to biodegradation than those with the ring near the end of the chain and that midchain isomers of C_8 and C_{16} did not degrade. Sweeney (1964) has reported similar results. ABS was not degraded significantly in 100 hours.

Figure 2 shows that disodium α,α -dioctyl sulfoacetate and sodium hexyl α -sulfo-pelargonate were quite resistant in this test. The sulfoacetate was only about 25% degraded, and the pelargonate was not degraded at all in 120 hours. The curve shows 96% disappearance of the tallow alcohol sulfate in 80 hours. The esters graphed in Figure 3 were all quite easily degraded. The high initial value for disodium 2-sulfo-ethyl α -sulfo-stearate is attributed to its diionic nature which makes the molecular weight correction based on a 1:1 stoichiometry invalid.

With the laboratory preparation of LBS, graphed in Figure 4, about 80 hours elapsed before significant degradation occurred and 130 hours were required for 80% degradation. The fact that sodium 9,10-dichlorooctadecyl sulfate also required a rather long induction time (Fig. 4) would indicate that the organisms in this river water sample required time for acclimatization as postulated by Sweeney (1964).

Activated Sludge Tests

The activated sludge unit devised by Ludzack (1960) was used with only slight modification. Figure 5 is a photograph of some units in operation. Instead of using a gravity system for delivering the feed solution to the digesters, Sigmamotor pumps (Model TS, Middleport, N. Y.) with peristaltic action were used. Silicone tubing (Ronthor Reiss, Little Falls, N. J.) was found to be very resistant to the action of the pumps. No failures were experienced even after using the same tubing for several weeks.

Activated sludge was obtained from a local sewage disposal plant and the content of total and volatile solids was determined. Enough sludge was placed in each aerobic digester so that the concentration of volatile solid was 1.0 to 1.2 g per liter when the digester was filled. The feed used was trout feed (Purina Trout Chow) as recommended by Ludzack (1960). The load ratio of feed was 0.5 to 1.0 g COD per gram of sludge

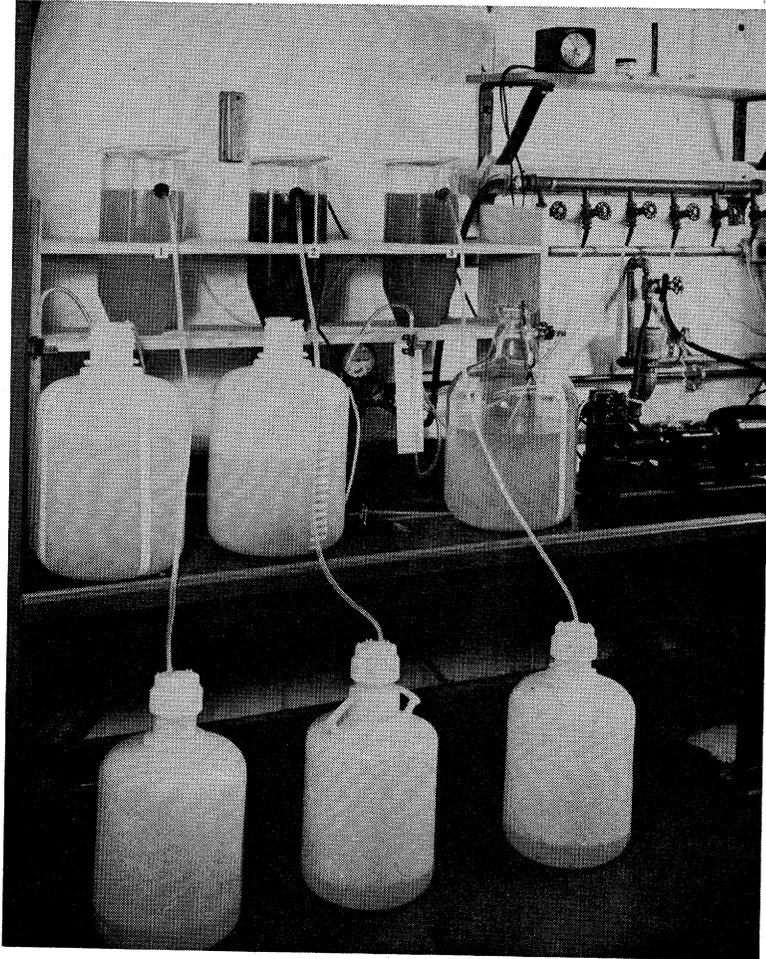


FIG. 5. Laboratory activated sludge unit.

volatile solids per day. The trout chow had a COD of about 1.4 g per gram, moisture free basis, and the digester held about 5.5 liters. The amount of feed was therefore about 3.0 to 3.5 g of air-dry material per digester, per 24 hours. The trout chow pellets were weighed out, placed in 200-300 ml of water and autoclaved. One week's supply was usually prepared at a time. The pellets could also be soaked overnight and mixed in a Waring blender. The quantity of feed solution was 17 to 18 liters per day so that the holdup time in the digesters was 3 to 3½ hours.

Air was supplied through a fritted glass sparger at 500 ml per minute. With this aeration rate, the oxygen content of the effluents was of the order of 7 to 9 ppm and the sludges were kept in suspension. Aeration was continuous but no feed was added on Saturdays or Sundays.

The quantity of solids in the digesters was controlled by discarding 250 to 300 ml of mixed liquor when necessary. Determination of total and volatile sludge solids was made once per week and the sludge contents of the digesters were adjusted accordingly. In the few instances where foaming became a problem it was controlled by an anti-foaming agent on the glass cover of the digester.

Detergents were added to the feed at 5 ppm for about 1 week and then increased to 20 ppm. In most cases, after 40 days, 50 ppm per day was added for about 1 week to determine how the system would respond. The effect on detergent loss of varying the feed rate over wide limits was also determined for some detergents.

Sludges were analyzed for total solids, volatile solids and settleability, and effluents for BOD, COD, and filterable solids, once each week according to the Standard Methods for the Examination of Water and Wastewater (1960). Detergent concentration in the effluents was determined daily by the methylene blue method as described above. Ten milligrams per liter of mercuric chloride were placed in the effluent receivers to prevent microbial growth. This did not interfere with detergent analysis.

In general the sludge analyses were within the limits usually found in full scale plants. The pH values were between 5.7 and 7.2. With some detergents, namely, ABS, LBS, disodium α,α -dioctyl sulfoacetate, hydrogenated tallow alcohol sulfate, and sodium oleyl sulfate, sludge densities were sometimes rather high. Qualitative differences in sludges were evident when certain detergents were present. No attempt was made to study the microbiota systematically but in several cases the sludges became dark red because of the abundance of a red-colored ciliate, and in some cases, bristle worms and aquatic earthworms became very abundant. The presence or absence of filamentous forms appeared to have a marked effect on sludge settleability and may be related to density and to the quantity of effluent solids.

The nature of the sludges changed most dramatically by increasing the feed rates several fold. In an extreme case, the sludge density index was 0.08 compared to usual values of 1.0 to 2.5. However, even such drastic changes in the physical condition of the sludge did not appear to affect the degradation of the detergents; no relationship was found between the physical condition of the sludges and the extent of detergent degradation.

The results of the analyses of effluents given in Table 1 show that the digesters operated satisfactorily. The median decrease in BOD ranged between 80 and 93%. Usual sewage disposal plant values for BOD are about 3 to 20 ppm, with a decrease of 85-90%. The values reported for effluent solids are mostly within the limits found in plant practice and are not significantly different from the control.

The quantities of detergent in the effluents were determined by the methylene blue method. The digesters were run for a few days without adding detergent until residual

TABLE 1. Analysis of effluents from laboratory activated sludge

Detergent	BOD, ppm			Solids, ppm		
	Min.	Median	Max.	Min.	Median	Max.
Control.....	9	13	18	25	26	33
Branched Alkylbenzenesulfonate, ABS.....	10	13	18	5	14	15
Linear Alkylbenzenesulfonate LBS I (com- mercial).....	5	18	38	4	33	38
Sodium Dodecylbenzenesulfonate, LBS II.....	9	21	35	8	15	30
Sodium Methyl α -Sulfostearate.....	7	9	16	7	17	30
Sodium Isopropyl α -Sulfostearate.....	4	9	11	5	18	28
Disodium 2-Sulfoethyl α -Sulfostearate.....	6	7	21	9	17	46
Disodium α , α -Dioctyl Sulfoacetate.....	13	16	28	10	21	26
Sodium Hexyl α -Sulfopelargonate.....	16	18	25	8	16	19
Tallow Alcohol Sulfates.....	5	9	17	5	18	32
Sodium 9, 10-Dichlorooctadecyl Sulfate.....	7	18	28	8	14	58
Sodium Oleyl Sulfate.....	15	19	23	18	28	45
Sodium Oleate.....	13	18	24	22	27	29

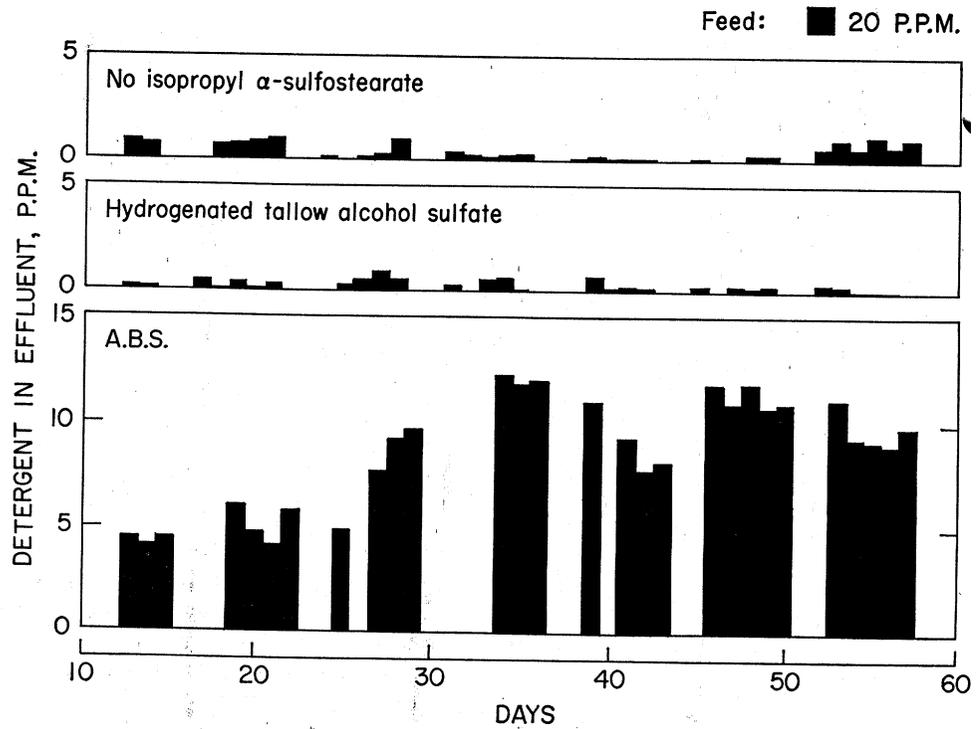


FIG. 6. Degradation of sodium isopropyl α -sulfostearate, hydrogenated tallow alcohol sulfates, and ABS in activated sludge.

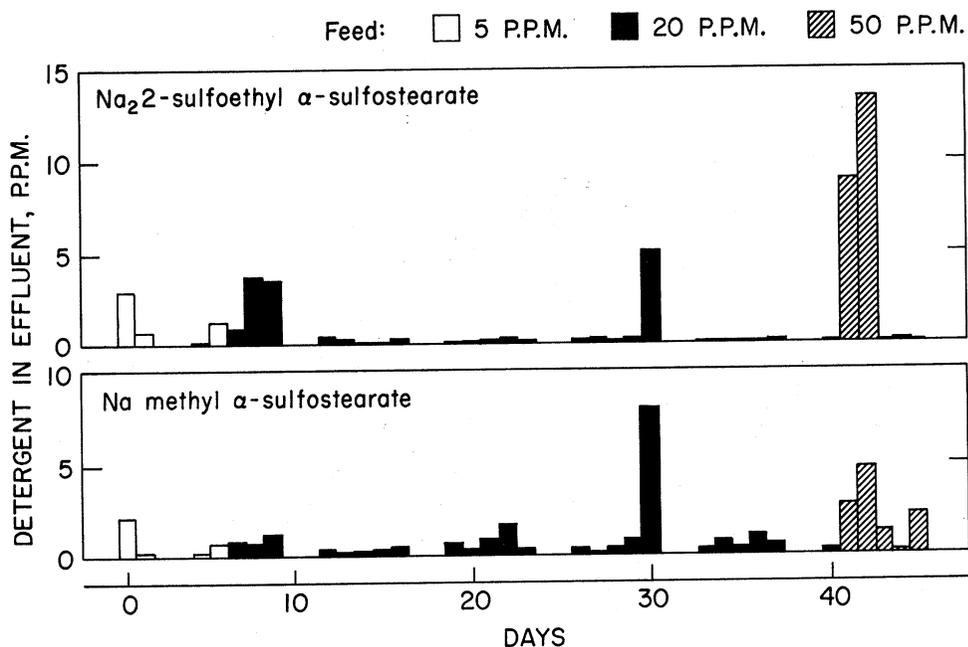


FIG. 7. Degradation of sodium methyl- and disodium 2-sulfoethyl α -sulfostearate in activated sludge.

detergent disappeared. Sodium isopropyl α -sulfostearate, hydrogenated tallow alcohol sulfate, and ABS (Fig. 6) were run for 60 to 80 days. With the first two compounds the detergent concentration was often zero and never went above about 1 ppm. The over-all amount of undegraded ABS gradually increased over a period of 72 days, although there was considerable variation in day to day values. At the end of this period about 75 to 90% of that added was found in the effluent. Sodium methyl α -sulfostearate and disodium 2-sulfoethyl α -sulfostearate (Fig. 7) were run for 45 days. They were easily degraded. The 4 ppm values in the early stages with the sulfoethyl ester may be due to the need for acclimatization of the sewage microorganisms to this compound. We have no explanation for the 5-8 ppm values present at the 30 day sampling. The addition of 50 ppm of detergent after 40 days resulted in relatively high values in the effluents which were only temporary and quickly dropped to low values again. The effluent from the digester fed sodium oleyl sulfate (Fig. 8) was almost completely devoid of detectable detergent. The addition of 50 ppm caused only a temporary increase up to about 1 ppm. Disodium α,α -dioctyl sulfoacetate was not as well degraded as the tallow-based compounds discussed previously. The level of detergent in the effluent reached about 4 ppm several times during the 20 ppm feed period. Fifty ppm in the feed caused an increase in effluent detergent to 4-6 ppm that persisted throughout the duration of the test.

The behavior of sodium hexyl α -sulfopelargonate (Fig. 8) was unique among the compounds tested. During the first few days when 5 ppm were fed, the level in the

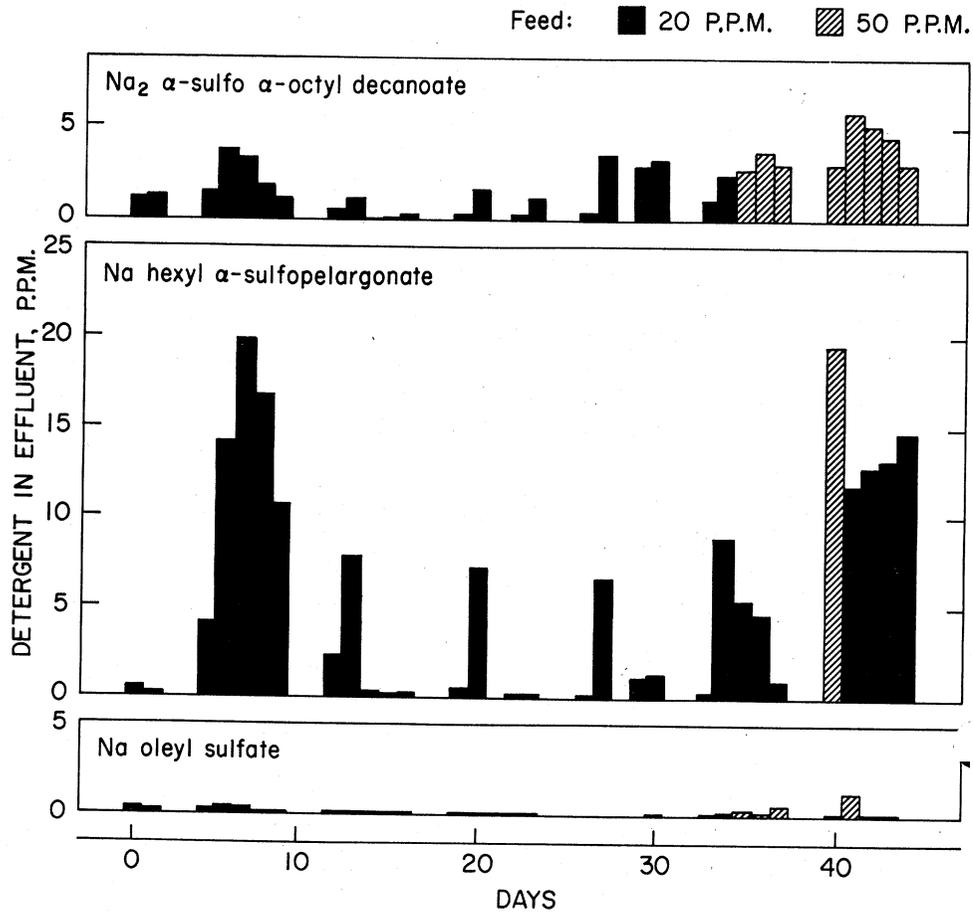


FIG. 8. Degradation of disodium α,α -dioctyl sulfoacetate, sodium hexyl α -sulfopelargonate, and sodium oleyl sulfate in activated sludge.

effluent was very low possibly due to absorption on the sludge particles. When 20 ppm were added to the feed the detergent content of the effluent increased to 20 ppm in 3 days then decreased to about 2 ppm. On Mondays when 20 ppm detergent was added, after no addition on Saturdays and Sundays, the quantity in the effluent decreased to 7-9 ppm (Tuesday sample) and then dropped abruptly to almost zero. This pattern continued for about 4 weeks. When 50 ppm were added the effluent value increased to 20 ppm and although the quantity in the feed was dropped back to 20 ppm, the effluent values remained high at about 15 ppm.

The degradation of LBS I (Fig. 9) varied from about 85 to 50% of that added while the digester was being fed at the rate of 20 ppm. When 50 ppm were fed, the amount degraded decreased to about 34%. LBS II was somewhat more easily degraded than LBS I (Fig. 10), but there were 12 days when the level was 5 ppm or higher. Sodium 9,10-dichlorooctadecyl sulfate (Fig. 10) was almost completely degraded. The

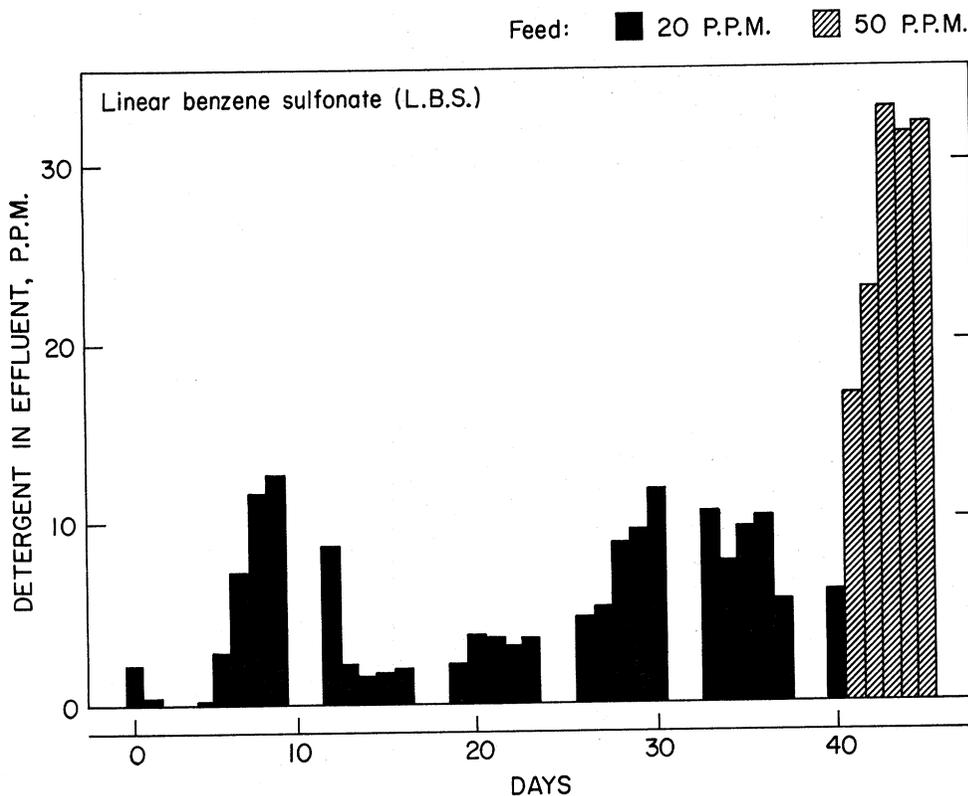


FIG. 9. Degradation of LBS I (commercial sample) in activated sludge.

concentration in the effluent never exceeded 1 ppm and reached this level on only 3 days.

The summary of the detergent degradation data given in Table II shows that six of the eight fat-based compounds were very easily degraded in river water and in activated sludge. Most of the time the effluents from the activated sludge contained less than 1 ppm of detergent. The other two experimental compounds, sodium hexyl α -sulfopepargonate and disodium α, α -dioctyl sulfoacetate were more resistant, confirming the river water tests. This resistance to degradation seems to be associated with branching in the hydrophobic chain or location of the hydrophilic groups near the middle of the hydrophobic chain. Both of the samples of LBS were much more easily degraded than ABS but the effluent from the digester fed 20 ppm of LBS I always contained over 1 ppm of detergent and the average value was 7.3 ppm. The effluent from the digester fed 20 ppm of LBS II contained 1 ppm or more 74% of the time, and the average analysis was 3.5 ppm. In an attempt to account for the difference in degradability of the two samples of LBS, infrared curves were run by the method of Frazee and Crisler (1964). These curves showed the two LBS samples to be identical in the 1450-1350 cm^{-1} region. Comparison with a synthetic mixture (95% LBS II, 5% ABS)

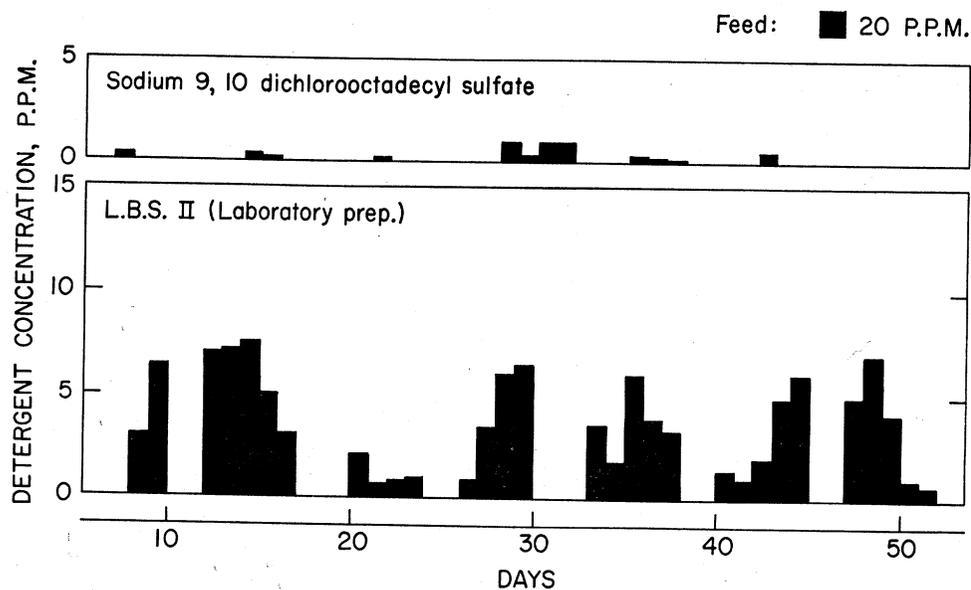


FIG. 10. Degradation of sodium 9,10-dichlorooctadecyl sulfate and LBS II (laboratory preparation) in activated sludge.

TABLE 2. Summary of detergent degradation in activated sludge and river water

Detergent	Activated Sludge			River Water
	Average Analyses ppm	High Value ppm	% of Time Over 1 ppm	Time for 80% Degradation Hours
Sodium Oleyl Sulfate	0.03	0.3	0	26
Tallow Alcohol Sulfates	0.4	1.3	3	56
Sodium 9,10-Dichlorooctadecyl Sulfate	0.2	1.0	0	82
Sodium Methyl α -Sulfostearate	0.3	1.8	10	93
Sodium isopropyl α -sulfostearate	0.5	1.4	6	117
Disodium 2-Sulfoethyl α -Sulfostearate	0.7	5.1	17	123
Sodium Hexyl α -Sulfopelargonate	5.7	19.8	77	265
Disodium α,α -Dioctyl Sulfoacetate	1.6	3.6	65	408
Linear Dodecylbenzenesulfonate, LBS I (commercial)	7.3	12.2	100	88
Sodium Dodecylbenzenesulfonate, LBS II	3.5	7.4	74	130
Branched Alkylbenzenesulfonate, ABS	11.0	17.0	100	>700

showed less than 5% branched chain isomer absorbing at 1367 cm^{-1} for the commercial linear alkylbenzenesulfonate, LBS I.

The finding of incomplete degradation of LBS I in contrast to the results of other investigators may be attributed to the use of different systems for determining biodegradability. The final answer must await actual use.

In conclusion three tallow alcohol sulfates and three esters of α -sulfo stearic acid have been found to be very easily degraded in a laboratory activated sludge sewage system. Two other tallow-based compounds, sodium hexyl α -sulfo pelargonate and disodium α,α -dioctyl sulfoacetate were less easily degraded. These latter two compounds were of about the same hardness as linear alkylbenzenesulfonate.

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REFERENCES

- American Public Health Association. 1960. *Standard Methods for the Examination of Water and Wastewater*. 11th Ed.
- Ault, W. C., T. J. Micich, A. J. Stirton, and R. G. Bistline, Jr. Branched chain fatty acids and sulfonated derivatives. To be published in *J. Am. Oil Chemists' Soc.*
- Degens, P. N., Jr., H. C. Evans, J. D. Kommer, and P. A. Winsor. 1953. Determination of sulphate and sulphonate anion-active detergents in sewage. *J. Appl. Chem.* **3**: 54-61.
- Frazer, C. D., and R. O. Crisler. 1964. Infrared determination of alkyl branching in detergent ABS. *J. Am. Oil Chemists' Soc.* **41**: 334-335.
- Ludzack, F. J. 1960. Laboratory model activated sludge unit. *J. Water Pollution Control Federation* **32**: 605-609.
- Orsanco Detergent Subcommittee. 1963. Components of household synthetic detergents in water and sewage. *J. Am. Water Works Assoc.* **55**: 369-399.
- Ruschenburg, Ernst, and Erich Hirsch. 1963. From a Staff report in *Chem. Eng. News* **41** (22): 70-71.
- Stirton, A. J. 1962. α -Sulfo fatty acids and derivatives. Synthesis, properties and use. *J. Am. Oil Chemists' Soc.* **39**: 490-496.
- Sweeney, W. A. 1964. Aerobic biodegradability of linear alkylbenzene sulfonate. *Soap and Chem. Specialties* **40** (3): 45-47, 190.
- Weil, J. K., A. J. Stirton, R. G. Bistline, Jr., and E. W. Maurer. 1959. Tallow alcohol sulfates. Properties in relation to chemical modification. *J. Am. Oil Chemists' Soc.* **36**: 241-244.
- Weil, J. K., and A. J. Stirton. 1964. Biodegradation of some tallow-based surface active agents in river water. *J. Am. Oil Chemists' Soc.* **41**: 355-358.
- Weil, J. K., A. J. Stirton, and E. W. Maurer. 1955. Synthetic detergents from animal fats. IV. Sodium 9,10-dichlorooctadecyl sulfates. *J. Am. Oil Chemists' Soc.* **32**: 148-151.