Field Study of the Removal of Linear Alkylate Sulfonate Detergents by the Activated Sludge Process

P. V. KNOPP, L. J. UHREN, G. A. ROHLICH and M. S. NICHOLS,
University of Wisconsin, Department of Civil Engineering, Madison, Wisconsin

Abstract

Field evaluation of the removal of linear alkylate sulfonate (LAS) detergents by the activated sludge process was carried out at the Kettle Moraine Boys' School near Plymouth, Wisconsin. The procedures and controls afforded by the school's central supply system along with its new and well-operated "extended aeration" activated sludge plant, provided an excellent arrangement for controlled field comparison of the removal of LAS and ABS (alkyl benzene sulfonate) material. In addition, the sewage treatment plant was operated intentionally to produce poor results in order to observe the effects of such conditions on removals.

Previous work showed that, with products containing ABS in use at the school, removals of methylene blue active substance could be expected to fall in the region of 75 to 85%. Removals with LAS material in use at the school were shown to be from 95 to 99% as long as the plant was operated satisfactorily. Further, the results showed that there was a strong correlation between LAS removal and BOD removal with a one to one slope.

The results support the conclusion that for biological treatment processes, the removal of LAS material corresponds to the removal of BOD.

Introduction

WITH THE DEVELOPMENT by the soap and detergent industry of detergents which do not have the biologically persistent properties of ABS (alkyl benzene sulfonate) surfactants, interest has focussed on the so-called LAS (linear alkylate sulfonate) surfactant. LAS differs from ABS in that the alkane chain which is attached to a sulfonated benzene ring is not branched; it is this property to which its biodegradable characteristic is attributed.

Field tests of the biodegradability of LAS have been reported by Renn, Kline and Orgel (1) and Klein et al. (2). An extensive study by Hanna et al. (3) has been reported recently in which they concluded among other things, that LAS has much improved biodegradability over ABS and that under good operating conditions LAS removal was comparable to soluble BOD (5-day biochemical oxygen demand) removal.

The field test reported herein, presents further information concerning the performance of the activated sludge process in the removal of LAS surfactants.

A. Purpose of Study

The purpose of this field study was twofold: first, the comparison of the removal of ABS and LAS by the activated sludge process under field conditions; and secondly, the measurement of the efficiency of LAS removal under so-called "good" and "poor" operating conditions.

The complex of buildings comprising the Kettle Moraine Boys School, the procedures and controls afforded by the central supply system, along with its new and well-operated sewage treatment plant, provided an excellent arrangement for controlled comparison of removal of LAS and ABS material for a field study of this nature.

The cooperation of the school personnel made it possible to assure that the conditions set forth during the field study were easily maintained.

B. Description of the School

The Kettle Moraine School for Boys is a state-operated "minimum security" institution for delinquent boys. It is located 6 miles southwest of Plymouth, Wisconsin, in the Kettle Moraine State Forest. The school consists of a complex of buildings made up of a control center (administrative offices), a food and supply center, a junior and senior high school, maintenance building, chapel, four staff residences, a motel for staff living on the grounds, and twelve cottages, each of which houses 25 to 30 boys. The number of boys at the school varies from 250 to 320 while the staff and employees number approximately 170.

Sewage treatment is provided by an activated sludge unit with the treated effluent being discharged into a pond. The pond has not outlet; thus evaporation and soil absorption balance the incoming flow.

C. The Sewage Treatment Plant

The treatment plant is an activated sludge plant of the extended aeration type. A plan view of the plant is shown in Figure 1. Although the plant is equipped with a primary settling tank, it was not used during these tests because previous data were collected with the primary tank out of service.

Sewage enters the plant approximately 20 ft below grade and is lifted by two pneumatic ejectors to a small grit removal chamber. The flow then discharges through a comminutor directly into the aeration tank. The aeration tank is equipped with swing diffusers and air diffusion is accomplished with 34 disc type air diffusers. The volume of the aeration tank is 57,600 gal.

The final settling tank is equipped with sludge collectors and an air lift pump for return sludge. The effluent discharges over V-notched weir troughs. A 90° V-notch weir is installed at the outlet for measuring waste flow. Finally, a chlorine contact tank is provided prior to discharge to the pond.

Air is supplied to the aeration tank by two "Sutorbilt" blowers. These belt-driven blowers are equipped with various size pulleys to permit flexibility of capacity. A separate air system supplies air to the pneumatic ejectors.

Materials and Methods

A. Methods of Analyses

All analytical techniques were in accordance with the 11th edition of *Standard Methods for the Examination of Water and Waste-water* (4) with the following exceptions.

TABLE I

Summary of Sample Analyses for 24-Hr Variation of Flow and Concentration

Time	Flow Cubic ft/sec	Influent						Effluent					
		mg/liter			lb/2 hr			mg/liter			lb/2 hr		
		MBAS	SS	BOD	MBAS	SS	BOD	MBAS	SS	BOD	MBAS	SS	BOD
Run 1, 6-18-64 (ABS in use)													
8–10 am	.0993	11.4	436	510	.255	9.75	11.40	1.54	24	23	.0345	.588	.515
10–12	.0821	10.8	196	405	.200	3.62	7.48	1.10	60	25	.0203	1.110	.462
12– 2	.1185	9.9	264	......	.264	7.05		.97	0	24	.0261		.640
2– 4 pm	.0993	7.6	164	423	.170	3.66	9.44	1.06	66	13	.0237	1.475	.291
4– 6	.0904	3.6	312	375	.073	6.35	7.63	.97	8	15	.0198	.163	.305
6– 8	.1086	3.6	224	120	.088	5.49	3.93	.88	40	17	.0215	.979	.415
8–10	.0904	1.02	52	......	.021	1.06	......	1.02	20	32	.0210	.406	.650
10–12	.0534	1.14	116	......	.014	1.39		1.02	24	11	.0122	.289	.132
12– 2 am	.0364	0.80	276	212	.006	2.26	1.73	1.10	108	24	.0090	.885	.196
2– 4	.0417	0.32	12	33	.003	.11	0.31	.84	72	28	.0079	.675	.263
4– 6	.0365	0.32	......	25	.003	......	0.21	.84	4	31	.0069	.033	.255
6– 8 am	.0904	3.0	260	715	.061	5.29	14.50	.97	96	41	.0197	1.950	.835
Run 2, 7-9-64 (LAS in use)													
8–10 am	.0782	11.0	508	741	.194	8.93	13.10	1.06	43	17	.0186	.758	.300
10–12	.0823	8.0	568	673	.148	10.50	12.50	.92	34	19	.0170	.630	.352
12– 2 pm	.0948	9.6	617	891	.205	13.10	19.00	1.28	61	22	.0273	1.300	.469
2– 4	.0821	8.1	321	469	.150	5.95	8.69	1.14	71	20	.0211	1.310	.370
4– 6	.0789	8.1	520	710	.144	9.23	12.60	1.54	79	43	.0273	1.400	.762
6– 8	.0419	5.5	377	369	.052	3.55	3.47	1.10	70	23	.0140	.660	.216
8–10	.0754	2.2	69	181	.037	1.17	3.07	1.23	2	21	.0208	.034	.357
10–12	.0240	1.75	43	99	.009	.23	0.53	.90	26	28	.0050	.140	.151
12– 2 am	.0163	1.58	196	102	.006	.72	.38	.92	66	17	.0034	.243	.063
2– 4	.0163	1.06	97	42	.004	.36	.15	1.40	77	12	.0051	.282	.044
4– 6	.0234	1.20	34	63	.006	.44	.33	1.19	78	8	.0063	.410	.042
6– 8	.0830	7.90	301	396	.148	5.62	7.40	.85	95	9	.0159	1.780	.168

1. *Methylene Blue Active Substance (MBAS, LAS and ABS).* This method was a modification of the Longwell-Maniece Method (5) in which a colored complex is formed between methylene blue chloride and the sodium salt of the anionic surfactant. This colored complex, which is soluble in chloroform obeys Beer's law at low concentrations. This modification was recommended because it minimizes interferences, shows greater recovery in the presence of solids, and has been shown to give better reproducibility than other methods. Absorbance values were measured with a Coleman model 11 Universal Spectrophotometer.

2. *Mixed Liquor and Return Sludge Suspended Solids* (MLSS and RSSS). This method consisted of filtering 100 ml of sample through an oven-dried (103C) tared No. 1 Whatman filter paper. The paper and solids were air dried, then dried at 103C for 2 hr and weighed. An analytical balance was used for weighing all suspended solids determinations. Determinations were made in duplicate.

B. Routine Laboratory Analyses by the Plant Operators

It has been the practice of the plant operators to carry out certain analyses daily, on grab samples. These samples were taken between 7:45 AM and 8:30 AM. Analyses include aeration tank temperature, settleable solids, relative stability, oxygen demand of the aeration tank solids, and dissolved oxygen of the aeration tank and final effluent.

C. Sampling Procedures

1. *Influent Waste.* During Phase 1 of the study, samples were collected with a commercial effluent sampler. This sampler proved to be inadequate because it plugged frequently with solids and it did not collect the sample in proportion to flow. The influent waste sampler shown in Figure 2 was then developed and installed. The data for Phase 1 have been included along with all other data but have not been used for comparison in this report. The sampler was installed so that each time the pneumatic ejectors discharged, a small portion (200 to 300 ml) of waste was discharged into a sample barrel. The pipe on the sampler had an inside diameter of 0.5 in. which allowed for passage of solids in the waste. The sample collected was approximately in proportion to flow. After the specified period a representative sample of the barrel contents was collected for analysis.

2. *Effluent.* The effluent was sampled using a submersible pump set in the effluent weir trough. This pump discharged into a dip-type sampler which collected approximately 5 gal of sample in 24 hr. The 5-gal sample was stirred and a one-liter aliquot was removed and saved for analysis. This sample was not composited according to flow.

3. *Mixed Liquor and Return Sludge.* Grab samples of mixed liquor were taken at the point of maximum turbulence just above the air diffusers at the effluent end of the aeration tank.

TABLE II

Summary of Efficiency and Operating Conditions for Phases 1 Through 6

Phase	Detergent product in use	Flow Gallons/day	Mixed liquor Susp. solids	Return sludge Susp. solids	Mixed liquor dissolved oxygen	Aeration rate SCFM	Recirc. flow Gallons/day	% Removal		
								MBAS[a]	Susp. solids	BOD
1	ABS	......	......	......	...	.....	......	73.6	.....	.....
2	ABS	39,700	8,430	12,388	0.5	788	122,000	89.9	94.5	97.2
3	LAS	41,630	2,087	5,261	1.2	646	70,000	82.4	77.0	87.8
4	LAS	39,373	3,535	5,248	0.8	788	122,000	87.0	85.2	91.5
4-A	LAS	33,541	3,134	4,600	0.8	788	122,000	75.2	77.0	80.1
4-B	LAS	47,534	3,937	5,896	0.8	788	122,000	96.5	91.9	97.2
5	LAS	40,044	3,413	4,360	0.0	450	122,000	50.0	—03.0[b]	48.7
6	ABS	35,126	2,578	3,506	1.2	788	122,000	65.2	37.6	81.8

[a] Samples collected with commercial sampler during this phase.
[b] Effluent suspended solids greater in effluent than in influent.
[c] Average of phases 4A and 4B.
[d] Standard cubic feet/minute.
Note: Volume of aeration tank = 57,000 gal.

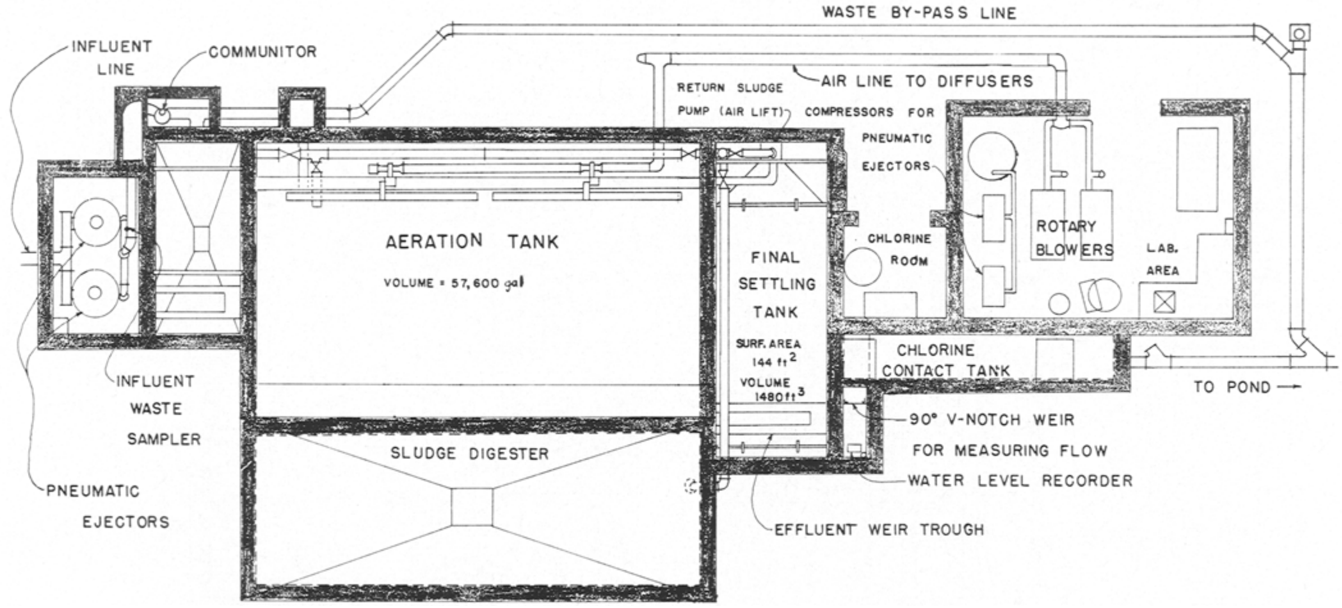

FIG. 1. Plan view of sewage treatment plant at Kettle Moraine Boys School.

Return sludge was sampled immediately after discharge over the 90° V-notch weir which was used to measure recirculation flow.

D. Flow Measurement and Control

1. *Waste Flow.* The waste flow was measured with a 90° V-notch weir located at the effluent end of the plant (see Fig. 1). Water level was recorded with a Friez model F-1 water level recorder. Estimates of waste flow were then made by averaging the water levels over 1-hr intervals for the 24-hr period and converting these average levels to average hourly flow rates. These average hourly flow rates were then averaged over the desired intervals.

2. *Return Sludge.* A weir box with a 90° V-notch weir was installed for measuring return sludge flow. Water levels were recorded with a Friez model F-1 water level recorder.

3. *Air Flow.* No suitable means was available for measuring air flow. It was necessary to make estimates by considering the displacement of the blower and the pulley size used. Reasonable deductions were made for air used by the sludge recirculation air lift pump. Air flow to the aeration tank was kept constant by controlling the air pressure on the air diffusers. The air pressure was measured with a "test" bourdon gage, located just above the liquid surface of the aeration tank. Although slight variations in pressure occurred, it was felt that these steps permitted suiable control of the aeration rates and allowed a reasonable estimate of its magnitude.

E. Sewage Flow Variation

During the study, two 24-hr sampling runs were made (June 18 and July 9, 1964) in order to determine the variation in flow and concentration throughout the day. These runs consisted in collecting 2-hr composite samples of the influent and effluent. These samples were analyzed for MBAS, BOD and suspended solids.

The results of these runs are tabulated in Table I and are plotted in Figures 3 and 4. (Note the 10:1 scale difference between influent and effluent values.)

The relative importance of proper compositing of influent and effluent samples is illustrated in the following tabulation in which time composites were estimated from the two 24-hr runs by averaging the concentrations found in the 2-hr composite samples and flow composites were estimated by weighting the concentrations with the respective flows for the 2-hr intervals:

	Influent		Effluent	
	Run 1	Run 2	Run 1	Run 2
Time composite mg/liter, MBAS	4.46	5.50	1.02	1.13
Flow composite mg/liter, MBAS	5.43	7.05	1.05	1.16
Per cent error	18.	20.	3.	3.

These data supported the conclusion that on the one hand, influent waste samples should be collected in proportion to flow; while on the other hand the effluent samples could be straight composites without introducing significant error.

F. Control of Detergents Used by the School

In order to assure control over the use of detergents in the school all LAS (linear alkylate sulfonate) material was dispensed from "Central" stores. Residents of the four staff houses and the motel were requested to obtain detergents from the school stores during the study. On the designated day of switchover to LAS material, all commercial products containing ABS material were picked up by a member of the research staff along with a representative of the school. These materials and the commercial prod-

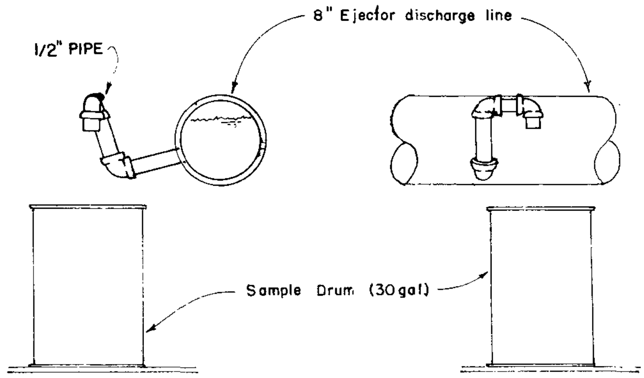

FIG. 2. Raw waste sampler.

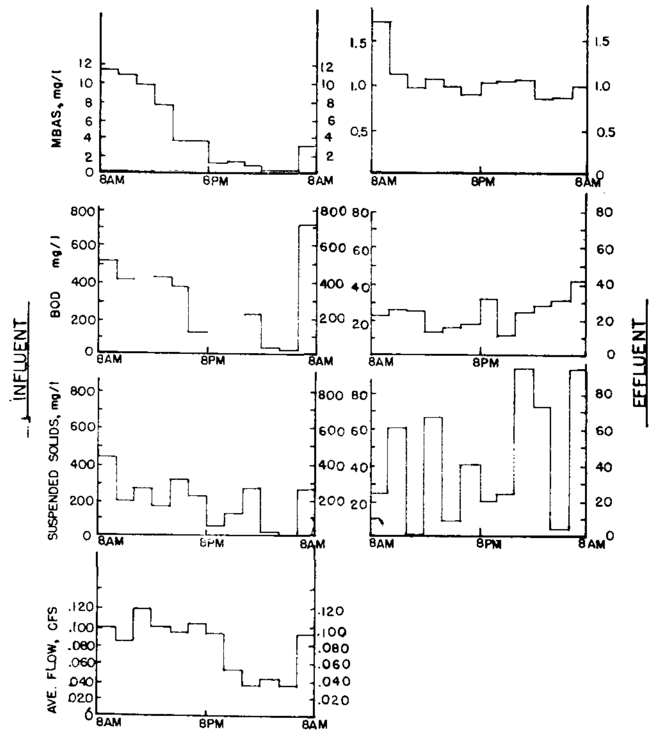

FIG. 3. Variation of MBAS, BOD, suspended solids, and flow over 24 hr period, June 18 to June 19, 1964.

ucts containing ABS that were on hand in the storeroom were then stored in a separate locked room for the duration of use of LAS material. Similar products specially formulated and containing LAS were substituted for the ABS products.

Those containers which could be confused with the ABS material were clearly marked with a "B" (indicating biodegradable) as they were dispensed to make possible identification at the time of change back to the ABS material. After completion of the

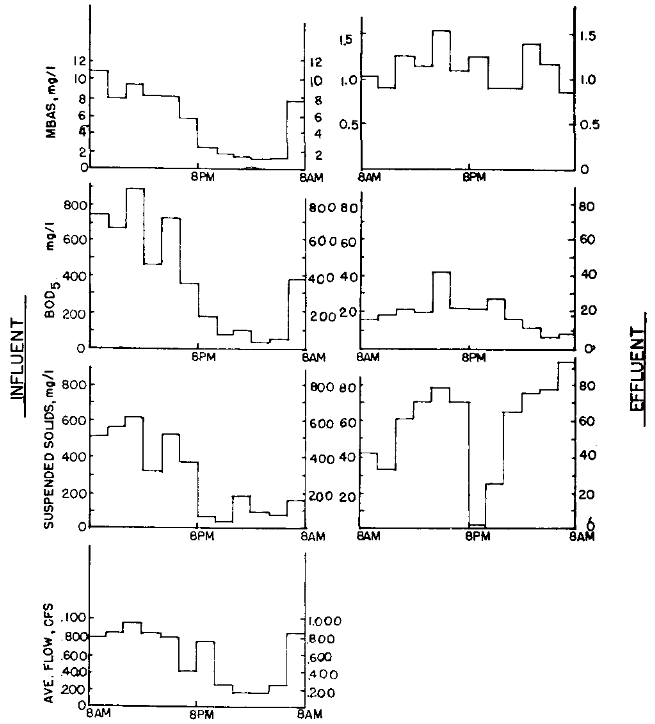

FIG. 4. Variation of MBAS, BOD, suspended solids and flow over 24 hr period, July 9 to July 10, 1964.

test period, all LAS material was picked up and returned to "stores" for inventory. The change over from ABS to LAS material was completed in one day as was the change back to ABS material. An inventory of LAS material showed that for the period from June 17 to August 14 the following quantities were used:

1.	General purpose household detergent	25 lb
2.	Scouring powder	52
3.	Hand dishwashing (powder)	506
4.	Hand dishwashing (liquid)	277
5.	Floor cleaner	566
6.	General purpose cleaner	246
	Total	1,702 lb

Analysis of the influent sewage accounted for 123.7 lb of MBAS material during the period from June 17 to August 14. Based on the inventory of LAS material used during this same period and the quantity of MBAS material contained in the products used (approximately 7.8% MBAS), the total MBAS material used was calculated to be 133 lb.

Results of Study

A. Procedure and Experimental Plan

The schedule of operation for the duration of the study was as follows:

Phase 1: May 21 to June 6. Operation under set conditions with local supervision. Composite samples were collected daily and sent to the University of Wisconsin Hydraulics and Sanitary Lab for MBAS analysis. Routine analyses were made by the plant operator. The main purpose of this phase was to set operating conditions so that reasonably steady conditions prevailed at the time of starting Phase 2.

Phase 2: June 9 to June 17. Operation during this period was under supervision of the research staff. Operating conditions which had been set in Phase 1 were continued in order to establish removal efficiency of ABS under closely controlled conditions. Daily samples were analysed and flow measurements were made.

Phase 3: June 18 to July 7. The use of LAS material was initiated at the school on June 18. The aeration tank was emptied of both sludge and waste at the beginning of this period, and refilled with raw waste. Solids in the aeration tank were allowed to build up under lower aeration rates. Routine analyses on a daily basis were continued.

Phase 4: July 7 to July 29. Operating conditions were set to get maximum removal of LAS by increasing the aeration rate and sludge recirculation rate to those prevailing during Phase 2.

Phase 5: July 30 to August 14. The aeration rate was cut back during this period to simulate "poor" operating conditions for the system.

Phase 6: August 15 to September 4. Use of LAS material ceased on August 14; all LAS material was picked up and replaced with ABS material previously in use. Operation conditions were set at approximately those of Phase 4 and Phase 2.

B. Summary of Results

Table II summarizes the percent removal of MBAS, suspended solids and BOD, for the various phases of the field study. In addition the DO (dissolved oxygen), mixed liquor and return sludge suspended solids, average daily flow, recirculation flow, and aera-

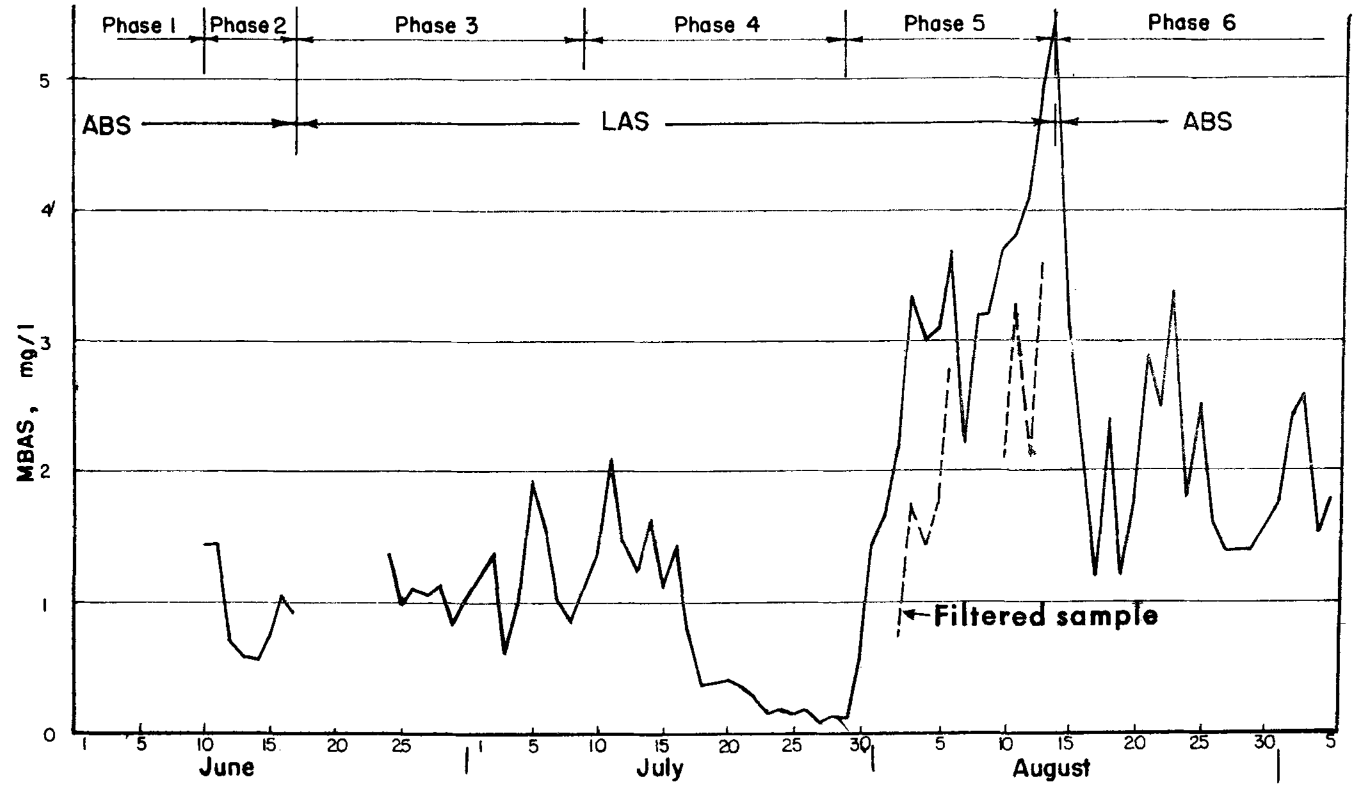

FIG. 5. Effluent MBAS concentration, Kettle Moraine Field Study.

tion rate, are shown. A summary of the field study is shown graphically in Figures 5, 6 and 7. In Figure 5 are shown the daily MBAS analyses of the plant effluent for the 6 phases of the study. Corresponding flows and MBAS removal efficiencies are shown in Figures 6 and 7, respectively. Figure 7 is a plot of per cent removal of MBAS and BOD for the duration of the study. Phase 2, as outlined earlier, was a period of controlled operation of the plant under supervision of the research staff. Detergents containing ABS were in use at this time. Operation during this period was characterized by the high (approx. 8,000 mg/liter) mixed liquor suspended solids concentration in the aeration tank, and high aeration and recirculation rates. Average effluent MBAS concentration during this period was approximately 1.0 mg/liter, and the average MBAS removal was 89.9% while the average BOD removal was 97.2%. Note the high MBAS removal efficiency during this period even though ABS material was in use. This may be accounted for by the high suspended solids and the long detention time.

At the beginning of Phase 3 (June 18), the school was converted over to the use of LAS material, the aeration tank was emptied, refilled with raw waste, and the aeration rate and recirculation rate were reduced. Three days were required to completely empty and refill the system with sewage. During Phase 3, the mixed liquor suspended solids increased from essentially that of the raw waste to approximately 3,000 mg/liter. The average effluent MBAS concentration for Phase 3 was 1.14 mg/liter, while the average MBAS removal was 82.4%, the average BOD removal was 87.7%. At the beginning of Phase 4 (July 7), the aeration rate and recirculation rate were increased to correspond with those of Phase 2. The MLSS, however, were 3,500 mg/liter as compared with 8,400 mg/liter during Phase 2. After ap-

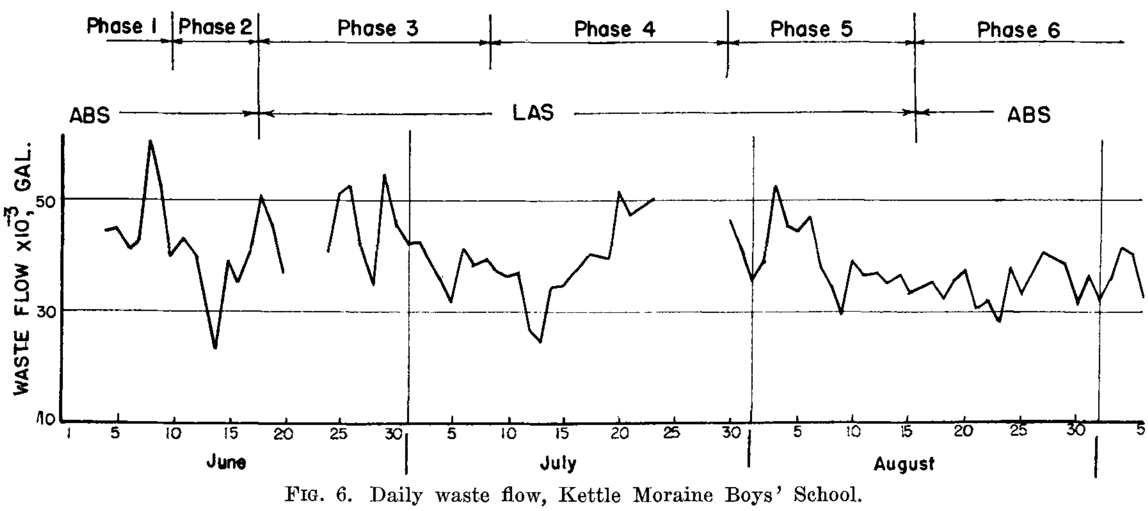

FIG. 6. Daily waste flow, Kettle Moraine Boys' School.

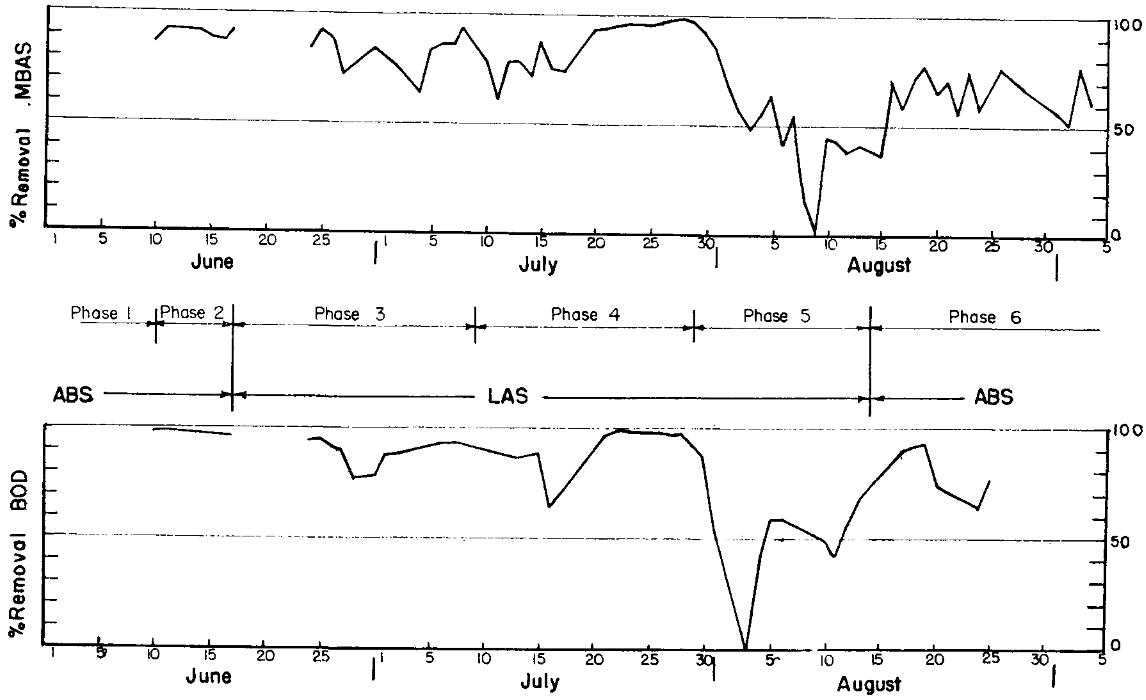

FIG. 7. Per cent removal of BOD and MBAS.

proximately 7 days, the effluent MBAS concentration dropped substantially to values less than 0.5 mg/liter and appeared to level off at near 0.1 mg/liter.

During this period, the plant performance (as measured in BOD and suspended solids removals) was excellent, with effluent BOD values less than 25 mg/liter. As a matter of fact, performance was so good that the concentration of MBAS, suspended solids, and BOD were reduced to levels below accurate detection levels. This was particularly true for the MBAS and BOD analysis for the period from July 17 to July 29. With the MBAS analytical procedure, it was necessary to extract 500 ml of sample in two separatory funnels in order to obtain enough MBAS to be above the recommended 0.02 mg. With the BOD analysis, the improvement occurred so rapidly that the dilution ranges chosen were not within the range

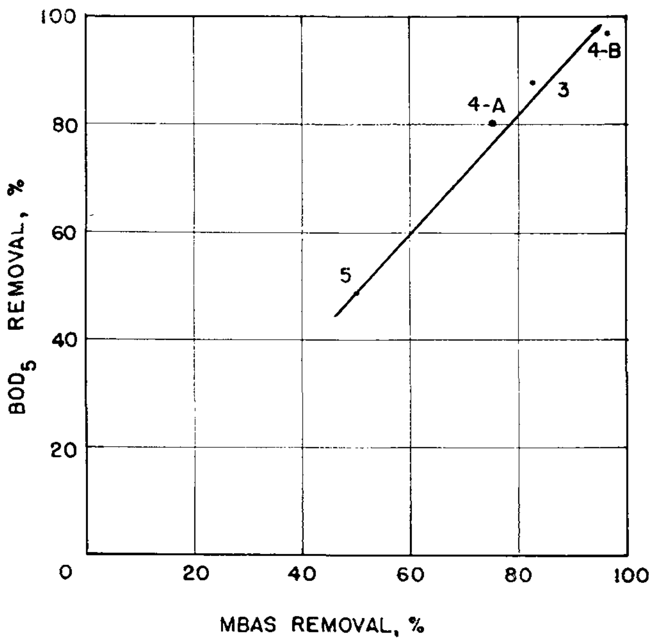

FIG. 8. BOD_5 vs LAS removal for phases 3, 4-A, 4-B and 5.

for good accuracy, but were recorded as best values.

It was further observed and verified by microscopic analysis that during the first few days (July 7 to July 15) of Phase 4, a filamentous growth developed in the sludge. The cause of this was not known. The poor settling characteristics resulted in a carry-over of solids into the effluent between July 10 and July 15. The filamentous growth cleared up just prior to the sudden drop in effluent MBAS concentration suggesting the possibility that lower effluent MBAS concentrations might have occurred earlier in Phase 4 if the poor settling characteristics had not developed. For this reason, Phase 4 was divided into two periods, 4-A (July 7 to July 15) and 4-B (July 16 to July 29), for the purposes of comparing the MBAS and BOD removals. During phase 4-B the average MBAS removal was 96.5% while the average BOD removal was 97.2%. At the beginning of Phase 5 (July 30), the aeration rate was reduced while the recirculation rate was maintained at the same rate as during Phases 2 and 4. The immediate response of effluent MBAS concentration is evident in Figure 5. During this period, the mixed-liquor dissolved oxygen decreased to zero and solids were soon lost in the effluent. BOD and MBAS determinations were run on both the total sample and on the filtrate of the sample passed through No. 1 Whatman filter paper. This was done because of the sludge present in the sample.

The following summarizes the amount of BOD and MBAS associated with the solids:

	Effluent Analysis	
	BOD	MBAS
Total sample mg/liter	229	3.10
Filtrate mg/liter	45	2.17
% associated in solids	80.3	30.0

It is interesting to note that even though 80% of the organics (as measured by BOD) in the effluent was associated with the solids, only 30% of the MBAS present was associated with these solids.

Conditions during Phase 5 (July 30 to August 14) did not appear to reach a steady state. Continued loss of solids occurred and it was noted that the mixed liquor dissolved oxygen remained at zero until August 10, when trace concentrations were found. It may have been advantageous to continue under these operating conditions until a steady state had been reached; however, the schedule made it necessary to terminate the use of LAS at this point, in order to acquire additional information on ABS removal at mixed liquor solids conditions similar to those prevailing during Period 4.

Removal of MBAS during Phase 6 (August 15 to September 4) returned to levels poorer than previously experienced during Phase 2. The average mixed liquor suspended solids during Phase 6 was 2,578 mg/liter as compared with 8,430 mg/liter during Phase 2. Per cent removal of MBAS during Phase 6 was 65.2% as compared with 89.9% during Phase 2. This difference could have been due to the higher solids levels present during Phase 2 or it is possible that further acclimation of the sludge and continued operation at these conditions would have resulted in improved removals of the ABS materials.

C. Correlation Between BOD and LAS Removal

Phases 3, 4-A, 4-B, and 5 provided results for comparing BOD removal with LAS removal. The BOD and MBAS average removals for these periods are plotted in Figure 8. The data indicate that a good relationship exists between the two with a slope of approximately 45 degrees.

Although the few points suggest a good one-to-one relationship, it would, of course, be necessary to verify these data before any firm conclusion could be made, recalling that the conditions during Phase 5 were essentially anaerobic, and that solids were being lost in the effluent during this phase. However, the data in Figure 8 do lend support to the hypothesis that LAS removal is correlated with BOD removal with a slope of approximately 1.

ACKNOWLEDGMENTS

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The Soap and Detergent Association and its cooperating members furnished the LAS products used during the test.

REFERENCES

1. Renn, C. E., W. A. Kline, G. Orgel, W.P.C.F. Journ. *36*(7), 864 (1964).
2. Klein, S. A., and P. H. McGauhey, "The Fate of Detergents in Septic Tank Systems and Oxidation Ponds," University of California SERL Report No. 64-1.
3. Hanna, G. P., P. J. Weaver, W. D. Sheets and R. M. Gerhold, "A Field Study of LAS Biodegradation," Water Sewage Works *111* (11), 478 (1964).
4. "Standard Method for the Examination of Water, Sewage and Wastewater," 11th Ed., A.P.H.A. New York (1960).
5. Longwell, J, and W. D. Maniece, "Determination of Anionic Detergents in Sewage, Sewage Effluents and River Water," Analyst *80*, 167 (1955).

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Sulfonation of Hexadecene-1 and Octadecene-1[1]

J. K. WEIL, A. J. STIRTON and F. D. SMITH, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

Abstract

The reaction of dioxane-sulfur trioxide with hexadecene-1 and octadecene-1 carried out below 10C gave difficultly soluble sodium 2-hydroxy-1-alkanesulfonates containing smaller amounts of other vicinal position isomers.

Sulfonation of the olefins at 50C gave a mixture of isomeric vicinal sodium alkenesulfonates containing also small amounts of hydroxyalkanesulfonates, sulfo-sulfates and sultones. This higher temperature reaction product was readily soluble with good foaming and detergent properties.

Introduction

Fat-based α-olefins of 16 and 18 carbon atoms, from the dehydration of hexadecanol and octadecanol, are possible intermediates for detergents and surface active agents. The sulfonation of the olefins and properties of the reaction products was therefore explored.

Products which are mixtures of hydroxyalkanesulfonates and alkenesulfonates have been reported in similar investigations (1,7), the former favored by lower and the latter by higher reaction temperatures.

$$RCH{=}CH_2 \xrightarrow[0\text{–}10C]{\text{Dioxane } SO_3} RCHOHCH_2SO_3Na$$

$$RCH{=}CH_2 \xrightarrow[50C]{\text{Dioxane } SO_3} RCH{=}CHSO_3Na$$

Dioxane-sulfur trioxide was selected as the sulfonating agent, since it appeared to have the right degree of reactivity, was convenient to work with, and dioxane was easily removed from the product. Markownikoff addition of sulfur trioxide or a sulfur trioxide adduct to an α-olefin would be expected to give products hydrolyzable to 2-hydroxy-1-alkanesulfonates. Comparison of these with 1-hydroxy-2-alkanesulfonates from the sodium borohydride reduction of methyl esters of α-sulfo esters (8), showed that, in contrast to the alkenesulfonates, both the 1-hydroxy and 2-hydroxy sulfonates were difficultly soluble, probably due to hydrogen bonding. Sulfosulfates from 1-hydroxy-2-alkanesulfonates, however, are readily soluble detergents and lime soap dispersing agents (6).

Experimental

α-Olefins. The commercial high purity α-olefins from Archer-Daniels-Midland Co. were further purified by crystallization from acetone at −20C, and

[1] Presented at the AOCS Meeting in Houston, 1965.
[2] E. Utiliz. Res. Devel. Div., ARS, USDA.