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Evaluation of Detergent Degradation Using Activated Sludge

R. L. HUDDLESTON and R. C. ALLRED, Continental Oil Company, Ponca City, Oklahoma

Abstract

Continuous feed activated sludge systems provide excellent facilities for evaluating detergent biodegradability only when the environmental conditions can be rigidly controlled. Degradation is rapid in such a system, and because of the microorganisms and environment used, the rate and extent should closely approximate detergent decomposition in many municipal waste disposal plants. The design and operation of such a continuous feed activated sludge unit are described, and observed detergent degradation patterns are reported.

Introduction

DURING THE 1950s, it became evident that tetrapropylene derived alkylbenzene sulfonates (ABS) were not eliminated by conventional methods of domestic waste disposal. As a result of this problem, numerous techniques were utilized for evaluating biodegradation characteristics of newly developed detergent surfactants. Some of the techniques; i.e. static bottle tests and shake flask tests, provided very useful comparative data. In addition to comparative test data it was also necessary to develop test procedures that would predict surfactant degradation in municipal waste disposal systems.

Although several types of sewage treatment are widely used, the activated sludge technique appeared most acceptable for laboratory studies. Biological reproducibility in laboratory models of other systems is more difficult to attain. Numerous designs of labora-
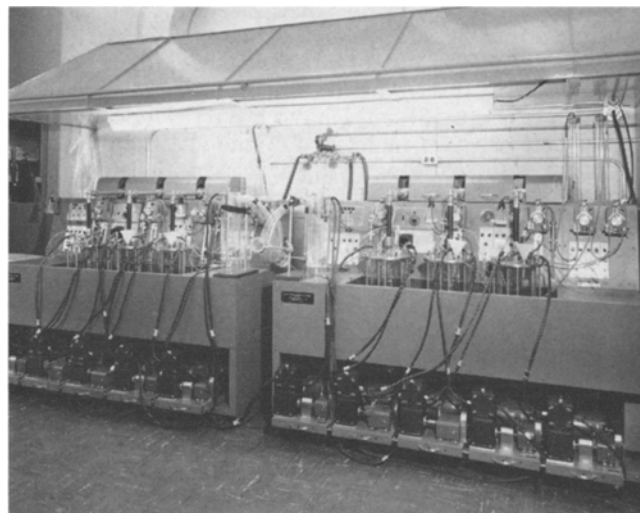

FIG. 1. Over-all system of three-stage continuous fermentors.

tory continuous flow activated sludge units were available, one of which has been adopted by the West German government (1) as their standard detergent degradation test system. Most of these units were either quite complex to construct and operate or they lacked adequate control features to insure reproducibility. Because of these problems, a somewhat different approach to unit design was undertaken.

Slight modification of commercially available continuous fermentation equipment provided a system that very nearly duplicated conventional activated
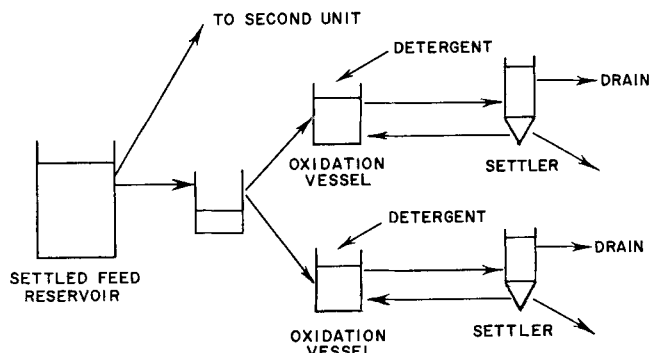
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FIG. 2. Flow pattern of laboratory continuous flow activated sludge system.
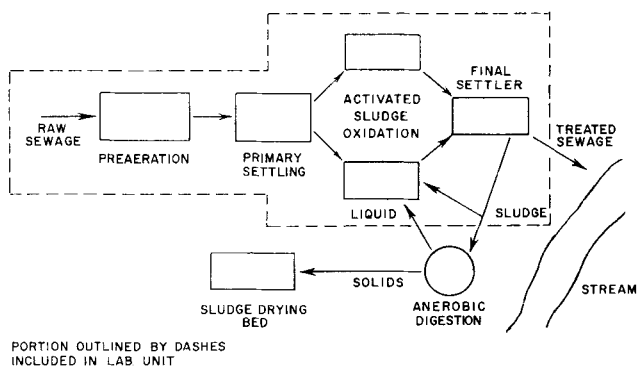
Fig. 3. Flow pattern of domestic activated sludge waste disposal plant.

sludge waste disposal. This system had enough capacity to overcome minor environmental changes that sometimes harass smaller systems, had accurate controllable devices for varying operating conditions, and could be operated continuously with minimum supervision.

Biodegradation of various detergents was studied using this continuous system to establish degradation patterns for activated sludge systems. Intermediate static operation was also used to investigate actual rates of detergent biodegradation. Results of these studies are presented and discussed.

Experimental Methods

Two modified three-stage continuous fermentors (New Brunswick Scientific Corp., New Brunswick, N.J.) were arranged in parallel. A photograph of the overall system is shown in Figure 1. The flow pattern within the system is outlined in Figure 2 and may be compared to the arrangement found in a typical domestic activated sludge plant (Figure 3).

A detailed drawing of one of the six mixing vessels is shown in Figure 4. Each vessel contains a shaft which drives two impellers to provide adequate mixing of the vessel contents. The agitation is facilitated by two baffles located on the periphery of the vessel. An air supply line terminates directly beneath the lower impeller where the air is expelled in fine bubbles from a sparger. Located on the cover of the vessel are the medium influent line, a thermometer well, a liquid level control probe, an anti-foam control probe and inlet port, a substrate (detergent) inlet line, the effluent line, and a sample port. The vessel sits in a
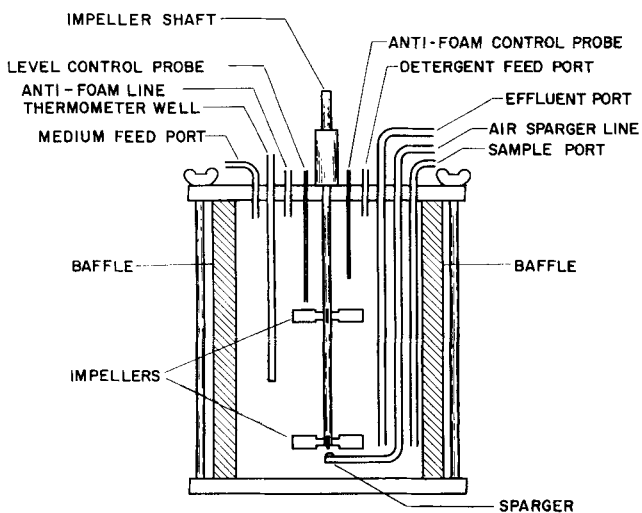

Fig. 4. Activated sludge oxidation vessel.

TABLE I
Composition of Synthetic Sewage Feed

Soy Peptone powder [a]	70 g
NaCl	60 g
K₂HPO₄	10 g
MgSO₄	2 g
Deionized water	180 liters
Filtered city raw sewage	20 liters

[a] Sheffield Chemical Co., Norwich, N.Y. Complete Composition available from the marketer.

water bath, the temp of which is controllable from room temp to 60C within ±0.5 degrees. The aeration system contains individual pressure and flow gages for each vessel.

All of the pumps that control medium flow through the system are operated by variable speed drives so that retention times, fluid levels, and sludge return rates can be independently varied for each vessel. Pumps used for detergent and anti-foam feeds to the oxidation vessels operate at fixed rates. Fluid levels in all six containers are controlled by automatic level sensing devices, and automatic foam sensers control the anti-foam pumps.

The medium used to feed the system is described in Table I. The relatively high sodium chloride content was necessary to activate the automatic sensing devices and the raw sewage was prefiltered through activated charcoal to remove ABS. The filtered sewage was then stored up to one week under refrigeration without a significant change in composition or microbial count.

Ten liters of activated sludge, obtained at a nearby municipal treatment plant, were added to each of the four oxidation vessels. The liquid levels in the two preaeration vessels were established and maintained at 3.3 liters. This produced a residence time one-sixth that in the oxidation containers. Continuous medium feeding was then initiated and continued for 72 hr with no detergent feed. This period allowed essentially complete removal of ABS associated with the sludge by degradation and dilution prior to the addition of test detergent.

Water bath temp was maintained at 30C, impeller speeds at 200 rpm, and aeration rates at 8,000 cc/min for each vessel. SAG 47 (Union Carbide Corp., New York, N.Y.) was used as antifoam agent.

Following the 72-hr sludge ABS removal period, 200 mg of test surfactant were added to each oxidation vessel and continuous surfactant addition (equivalent to 20 mg/liter in the medium feed) started. Effluent samples, usually daily, were taken from the final settlers for surfactant measurements. Concurrent samples from the preaeration vessel served as analytical blanks.

Analysis for anionic surfactants was made using AutoAnalyzer technology. Precision and reproducibility are not sacrificed using this technique (5) instead of the Standard Methylene blue test (2). Acid

TABLE II
Biodegradation of LAS Made from Dodecene-1

	Average steady state degradation levels					
	Vessel A		Vessel B		Vessel C	
	mg/liter	% Degraded	mg/liter	% Degraded	mg/liter	% Degraded
Run No. 1	0.70	96.9	0.63	96.9	0.73	96.4
Run No. 2	0.75	96.3	0.78	96.1	0.85	95.8

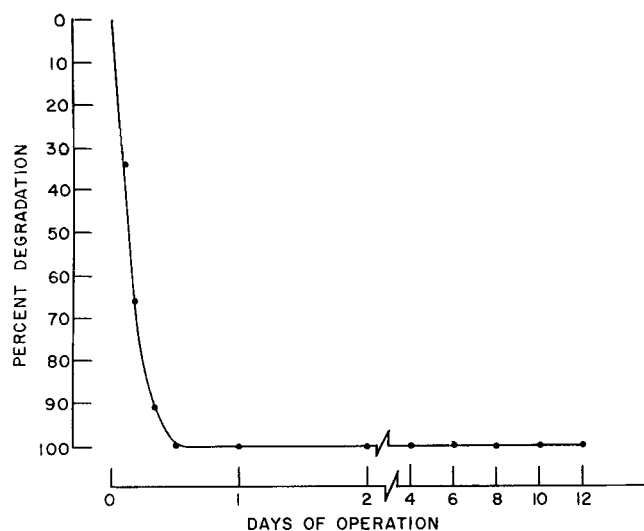|	Standard deviation—mg/liter		
	Vessel A	Vessel B	Vessel C
Run No. 1	0.20	0.38	0.16
Run No. 2	0.18	0.33	0.30

FIG. 5. Biodegradation of "Alfol" 12 alcohol sulfate with a four-hr retention time.

hydrolysis (4-hr reflux in $1N$ H_2SO_4) of samples to decompose sludge was performed on periodic mixed liquor samples to determine adsorbed surfactant. A cobaltothiocyanate colorimetric test (3) was used for determinations of nonionic surfactants.

Static detergent degradation studies, used to measure rates of surfactant degradation, were initiated by interrupting a continuous feed experiment following establishment of steady state degradation. Interruption included cessation of detergent and medium feeds. Immediately, 200 mg of surfactant were added to the oxidation vessel and samples of the mixed contents taken over a 3–4 hr period. All of these samples were subjected to acid hydrolysis.

Results

Reliability of degradation data between oxidation vessels within an experimental run and between different experiments (starting with fresh activated sludge) was determined. Linear alkylate sulfonate (LAS) made from dodecene-1 was used as the surfactant. After operating three oxidation vessels for five days to establish steady-state surfactant degradation, surfactant degradation was followed over a two-week period. Average steady-state degradation values, as well as standard deviation figures determined for each of three vessels in two such experiments, are shown in Table II. The data indicated close agreement
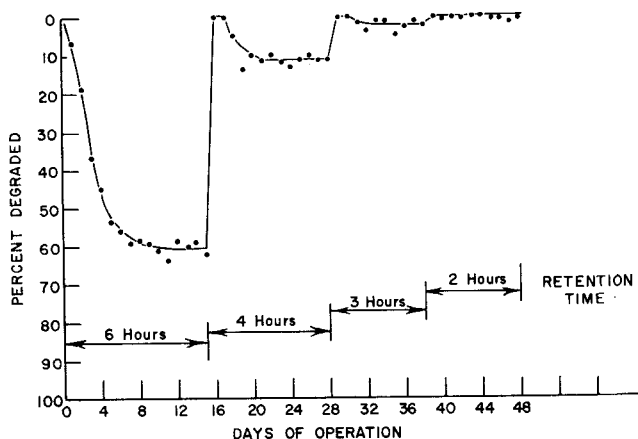

FIG. 6. Biodegradation of tetraproplylene ABS at various retention times.
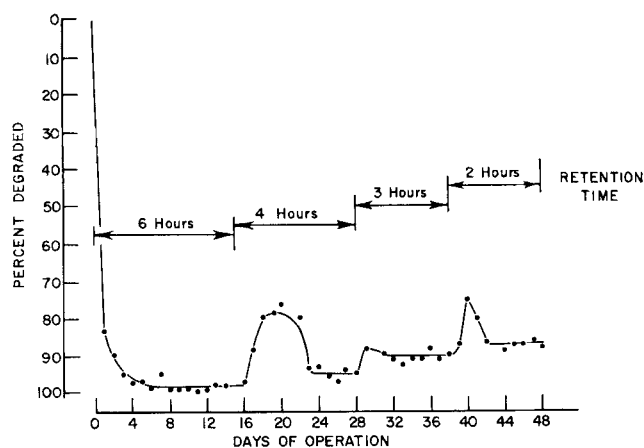

FIG. 7. Biodegradation of LAS (Nalkylene) at various retention times.

between vessels within a single run and between vessels in separate experiments.

The degradation pattern of ALFOL 12 (Continental Oil Co. straight-chain normal alcohol. The "12" denotes carbon chain length) sulfate in the continuous system is shown in Figure 5. The initial 20 mg/liter in the oxidation vessel was quickly decomposed, and the steady-state level in the effluent was below analytical resolution (<0.02 mg/liter).

When the system was fed ABS, the degradation patterns shown in Figure 6 were observed. Currently in this country the usual residence time in domestic activated sludge disposal plants is about six hr, but there is a definite trend towards shorter retention time. Thus, steady-state degradation levels were determined for several different residence times; six hr, four hr, three hr and two hr. Sixty per cent of the influent ABS was decomposed when the microorganisms had six hr contact time, but with a four hr residence period the organisms could degrade only 12%.

The biodegradation of linear alkylate sulfonate (LAS) ("NALKYLENE" derived; Continental Oil Co. straight chain detergent alkylate made from normal paraffins) was studied under the same conditions as was the ABS. These findings are shown in Figure 7. The influent LAS was 98% decomposed with a six hr retention time, and 87% was degraded with only a two hr residence time.
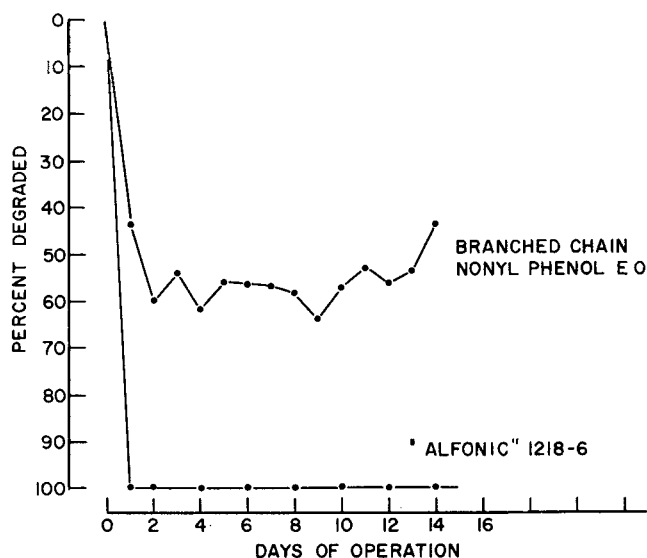

FIG. 8. Biodegradation of nonionic surfactants using a four-hr retention time.
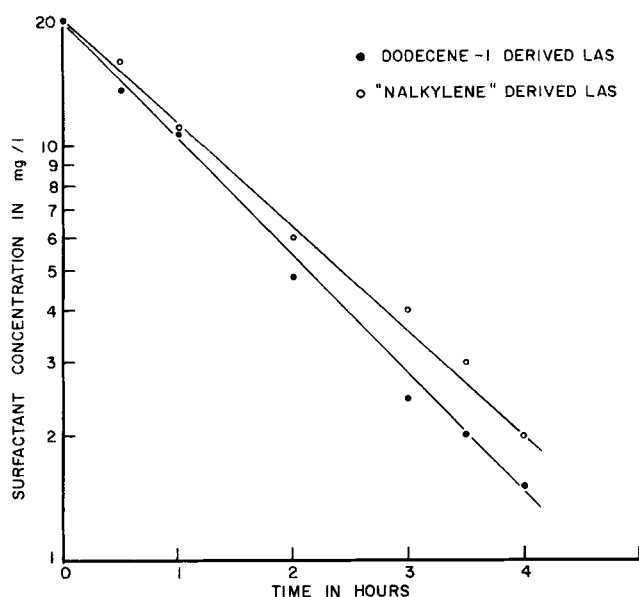
FIG. 9. Biodegradation rates of two LAS detergents.

TABLE IV
Biodegradation of LAS by Activated Sludge Waste Disposal

Influent		mg/liter Detergent sewage plant effluent—different residence times			
		2 hr	4 hr	6 hr	8 hr
Dodecene-1 derived LAS	— 2 mg/liter	0.6	0.15	0.01	0.01
	— 5 mg/liter	1.5	0.4	0.1	0.03
	—10 mg/liter	2.8	0.8	0.2	0.06
Commercial LAS	— 2 mg/liter	0.6	0.2	0.06	0.02
	— 5 mg/liter	1.7	0.5	0.17	0.05
	—10 mg/liter	3.2	1.0	0.3	0.1

Degradation characteristics of two nonionic surfactants, ethoxylated nonyl phenol (65% EO) and AL-FONIC 1218-6 (Continental Oil Co. ethylene oxide adducts made from ALFOL alcohols. The 1218 denotes that the product was made from a mixture of C-12, C-14, C-16 and C-18 "ALFOL" alcohols. The "-6" denotes 60% ethylene oxide), as determined in the continuous systems, are shown in Figure 8. Within the four hr residence time used, the straight alkyl chain ALFONIC product was completely biodegraded, but the branched chain alkyl phenol adduct was only 56% degraded.

The relationship in a continuous feed system between residence time and effluent substrate concentration is directly dependent upon the biodegradation rate of the substrate. By varying the retention time in the oxidation vessel and noting subsequently developed steady-state surfactant effluent levels, the degradation rate of the substrate can be plotted. However, this method requires several experiments and considerable time. Detergent degradation rates were more easily determined by interrupting the continuous feed for a brief time. Biodegradation rates of two LAS surfactants determined in this manner are shown in Figure 9.

Discussion

The degradation data found in this continuous activated sludge were remarkably uniform and reproducible for this type of operation indicating the importance of utilizing an experimental system in which rigid control over environmental conditions can be maintained. The operational aspects of this study so closely resembled those usually found in domestic activated sludge disposal systems, that the detergent

TABLE III
Operational Characteristics of the Laboratory Continuous Activated Sludge Unit and a Domestic Activated Sludge Disposal Plant

	Laboratory unit	Domestic plant (4,6,7)
Feed		
Total organic	355 ppm	200–400 ppm
Organic nitrogen	32 ppm	15–30 ppm
Bod	260 ppm	100–400 ppm
Aeration period	2–6 hr	4–16 hr
Bod removal	90%	80–95%
Suspended solids	2000–3000 ppm	2000–3000 ppm
Sludge volume index	50–100	50–100
Return solids	25%	Avg. 30%

degradation characteristics found should be applicable to municipal plants. Some of these operational aspects are shown in Table III.

It should be noted that sludge wasting was not necessary to maintain desired solids levels in the oxidation vessels, and that detergent did not build up to significant levels on the sludge during operation. Thus, detergent removal was entirely by microbial decomposition. Detergent removal in domestic activated sludge systems is normally the product of two functions; microbial decomposition and adsorption on sludge, which is removed to anaerobic digestors and then dried. Although adsorption on sludge eliminates detergent from the waste water cycle, the detergent may re-enter the cycle directly from the anaerobic digestor or later if the dried sludge is used as fertilizer and the detergent is leached from the sludge. Thus, detergent may be removed more rapidly and to a greater extent in domestic waste treatment than observed in this laboratory study.

The normal procedure for measuring biodegradation characteristics of a substrate in a continuous flow system is to determine the steady-state effluent level of the substrate under specific operating conditions. By inserting a very short static degradation rate study immediately following adaptation, degradation characteristics of detergents were determined in a much shorter time. The interruption was so short that the continuous feed environment remained in effect. The detergent degradation rates were then used to calculate detergent concn levels in continuous operation levels at various residence times (Table IV).

Final demonstration of how well newly developed detergent surfactants will be decomposed by municiwaste disposal systems will, of course, come after larger-scale domestic tests similar to Colgate-Palmolive Company's recent study (8). However, it appears from the data presented that biodegradable detergents will be readily decomposed in waste treatment facilities and alleviate, if not eliminate, problems which can properly be attributed to detergents. Obviously, other problems caused by inadequate treatment or by other contaminants will not be corrected by the change to biodegradable detergents.

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