REMOVAL OF SURFACE ACTIVE AGENTS FROM WASTEWATERS WITH OZONE

by

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Introduction

The destructive oxidation of the anionic surfactant alkylbenzene-sulfonate (ABS) has been reported, but research about surfactant removal by frothing with oxidation is new. To effectively utilize the surfactants present in sewage for frothing, knowledge concerning surfactant destruction and removal from the liquid phase must be considered. This article discusses the reactivity and frothing of ABS and/or the linear alkylate sulfonate (LAS) with ozone.

Evans and Ryckman[1] stated that ozonization of secondary sewage effluent achieved reduction in the concentration of the anionic surfactant alkylbenzene-sulfonate (ABS), but frothing information was not reported. Buesher and Ryckman[2] stated that ozone is economical as a treatment method for removing ABS.

Sawyer[3] showed that commercial alkyl benzene sulfonates were not readily degradable by the activated sludge process. The commercial variations of ABS (such as the new soft linear alkylate sulfonate – LAS) are rated with a higher value of biodegradability than ABS.

A series of experiments were performed to determine the removal process of ABS and/or LAS from the liquid phase of sewage. Experiments 2, 3, 4, 5, and 6 were compared with the Control Run-Experiment 1. Experiments 2, 3, 5, and 6 were performed to test the oxidation of biodegraded or partially oxidized LAS and/or ABS by ozone. The Experimental Methods section lists a description of each experiment.

The ozone reactor was a semibatch unit in which a gas passes continuously through the liquid contained in the reactor.

Experimental Methods

1. Reactions were run in the ozone reactor with only LAS solutions (the stock sample was an Interim Reference Sample from the American Soap and Detergent Association, Oct. 20, 1964). The LAS analysis was as follows: (a) LAS–60.8%, (b) Na_2SO_4–36.1%, (c) free oil–0.4%, and (d) water–2.7%. The equivalent weight of the material was 348. The Infrared Method (IR) listed in Standard Methods was the test procedure for ABS and LAS, and the reactant for derivative preparation was 1-methyl heptyl amine. A very high concentration of

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LAS (1g/1) was added to the 3-liter glass reactor. A Welsbach Model T-23 ozone generator with oxygen feed having a capacity of 6 g/hour of ozone served as an ozone source. Approximately 45 mg of ferrous sulfate and manganous sulfate were added to the reactor.

2. An experiment was performed using effluent from the laboratory activated sludge system fed by a 5:1 ratio of glucose to yeast extract mixture and LAS (6mg/1). The predominant organisms in the biological reactor were paramecium, fillamentous bacteria of the sphaerotilus-Leptothrix group (*Sphaerotilus Natans*), and nematodes.

3. An experiment was performed using concentrated sewage effluent from the Robert A. Taft Pilot Plant. The sewage effluent was concentrated by a factor of at least 5 by vacuum distillation. The ozonization period was seven hours.

4. An experiment was performed using a commercial detergent. The foam was not allowed to evolve from the vessel.

5. An experiment was performed using effluent from the laboratory activated sludge system fed by a 5:1 ratio of glucose to yeast extract with added detergent. The reactant was ozonated for 1 hour, *re-seeded* with fresh sewage and aerated for a longer period.

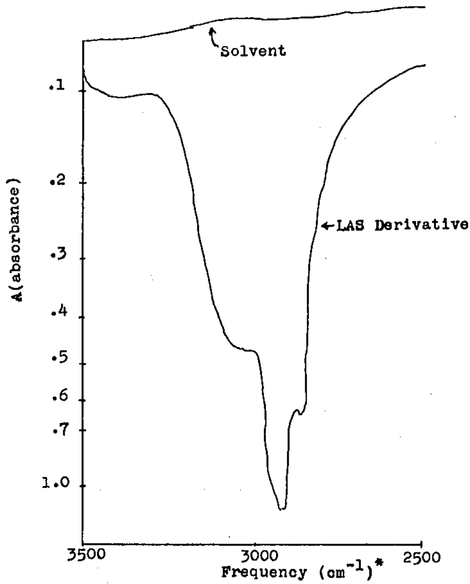
6. An experiment was performed using secondary sewage effluent. A part of the initial sample was filtered and evaporated to dryness. The material was redissolved in distilled water, filtered, and reevaporated to dryness. The ozone reaction froth was separated from the particulate material by centrifuging at 10,000 rpm and filtering through 0.47 micron millipore filter paper. The froth was evaporated to dryness, redissolved in distilled water, and reevaporated to dryness. Surface tension measurements were determined for the initial surfactant present and the surfactant present after ozonization.

Experimental Results

IR spectra of the LAS (1-methyl heptyl amine) derivative are shown in Figures 1 and 2. Figures, 3, 4, and 5 show the IR spectra of the detergent products from the ozonization reactions.

All of the tested extraction solutions showed the following phenomena: (a) the solutions were initially a dark orange-brown color, (b) the solutions sampled from the ozone reactor became light-yellow or clear as a function of the ozonization time, and (c) the recovered foamate extractions were a dark-orange brown color.

The IR spectra were identical (as a function of frequency of absorption) for all the samples. The IR spectra also indicated that the concentration of LAS in the foamate was greater than the concentration of LAS in the ozone reactor.



* traced from Perkin-Elmer paper (Part No. 337-1207)

Figure 1. Spectrum of LAS (1-methyl heptyl amine) Derivative

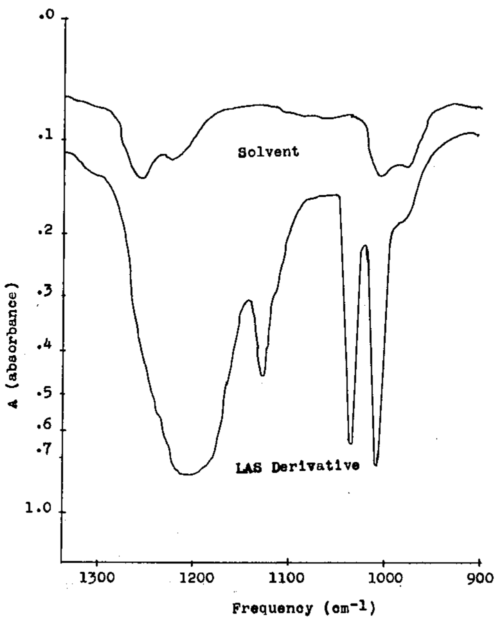


Figure 2. Spectrum of LAS (1-methyl heptyl amine) Derivative

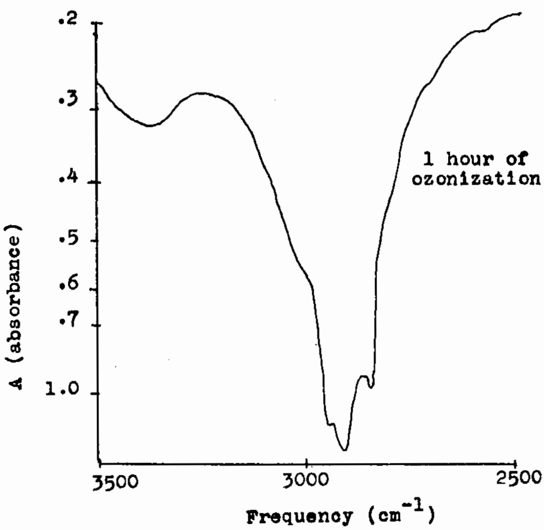


Figure 3. Spectrum of LAS (1-methyl heptyl amine) Derivative

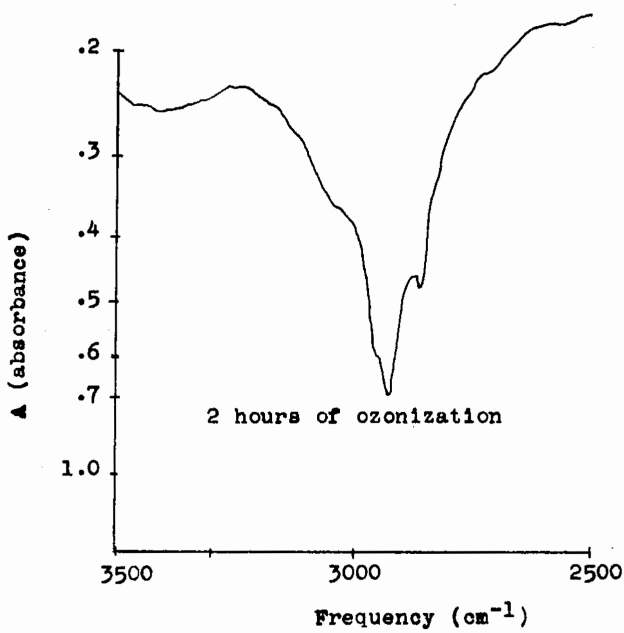


Figure 4. Spectrum of LAS (1-methyl heptyl amine) Derivative

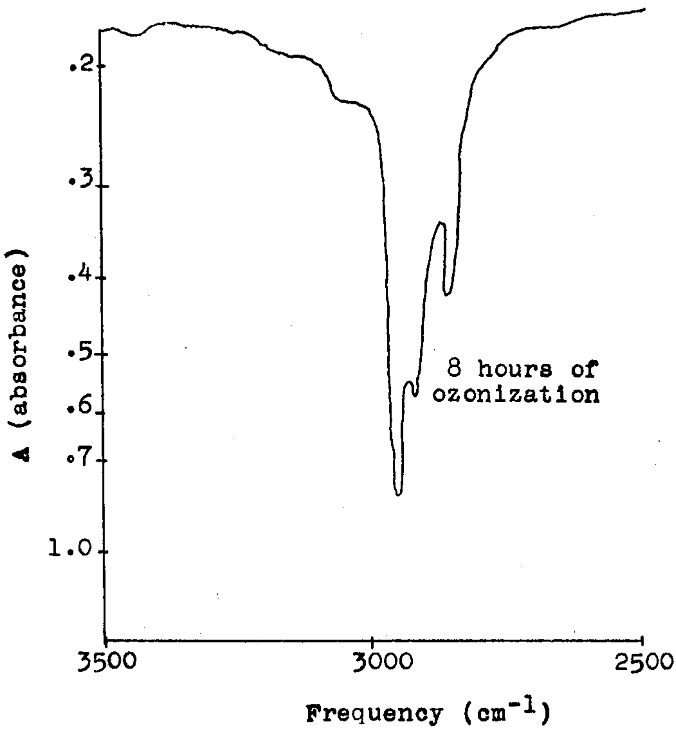


Figure 5. Spectrum of LAS (1-methyl heptyl amine) Derivative

In the ozone semibatch reaction, a froth was produced within a short period of reaction time. The reaction gases, however, were in contact with the collapsed phase of foamate. The reactor was pre-aerated with oxygen for 30 minutes before the start of a reaction to determine if a froth would rise from the reactor. A slight frothing action was noticed, but the froth did not rise. The ozone stream was introduced into the reactor solution, which contained manganous and ferrous ions. These metal ions reacted with ozone.

A plot of surface tension versus concentration is shown in Figure 6. The curve is similar in appearance to the curve for ABS.

Figure 7 shows the region on the curves where COD/COD_O plots as a horizontal line, demonstrating the first-order region of the curve. The initial COD reduction is rapid. With additional ozonization, reduction in COD of the tested sewage resulted at a slower rate.

Figure 8 shows that an ozonated sewage can be oxidized further by aerobic action. This result is of *great* concern to everyone concerned about toxicity in a water supply.

The importance of the frothing action in the COD reduction of wastewaters possessing detergents is shown in Figure 9. A very good mathematical description is summarized by Lemlich[4].

Conclusions

No chemical oxygen demand (COD) reduction of LAS and/or ABS was detected in the series of experiments, and each experiment was replicable.

The infrared spectral analysis tests indicated that the surface active agent and/or agents in sewage during ozonization were replicable. All IR spectra were run from 4,000 to 1,500 cm^{-1} and from 1,300 to 400 cm^{-1}. Since product-spectra were identical to parent-structure-spectra, chemical oxidation is not suggested.

The significance of the testing is that a significant COD reduction of many domestic sewages is possible by oxidation and frothing with ozone[5]. It should be emphasized that the central treatment goal at a sewage treatment plant is separation and conversion by some process.

The fact that the LAS and/or ABS were not oxidized in the semibatch reaction system means that it could be recycled in a continuous ozone-frothing-reactor system, having added ferrous salts to stabilize the froth.

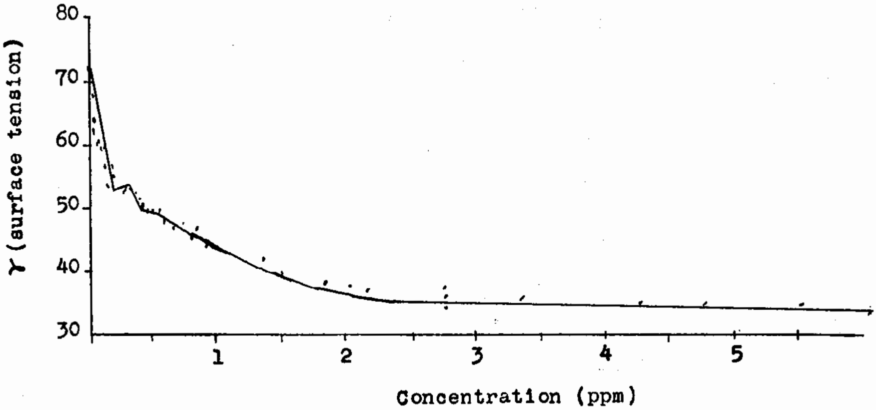


Figure 6. Plot of Surface Tension vs. Concentration

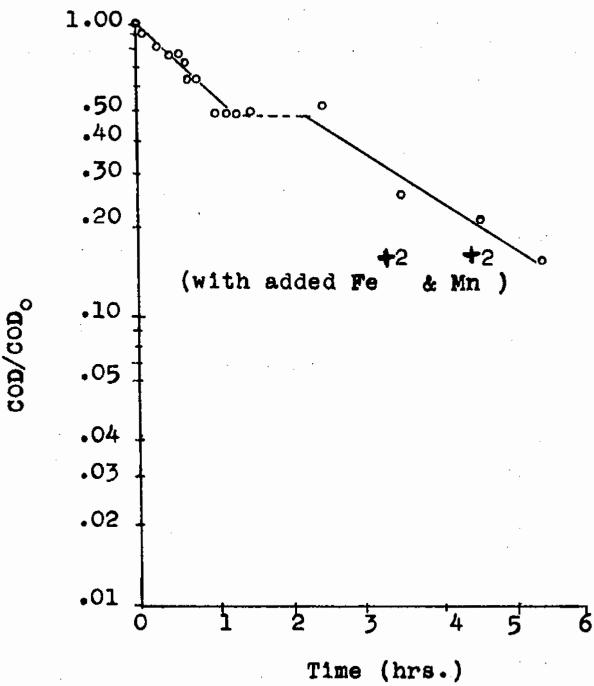


Figure 7. Laboratory Activated Sludge Effluent Feed (5:1 ratio of glucose to yeast extract with added detergent)

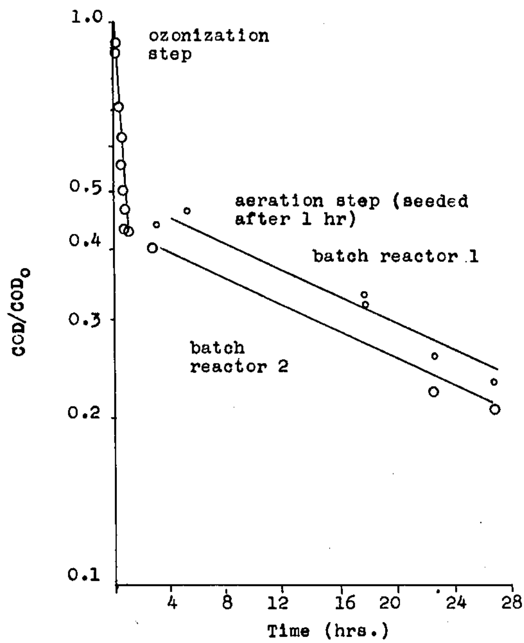


Figure 8. Laboratory Activated Sludge Effluent Feed (5:1 ratio of glucose to yeast extract with added detergent)

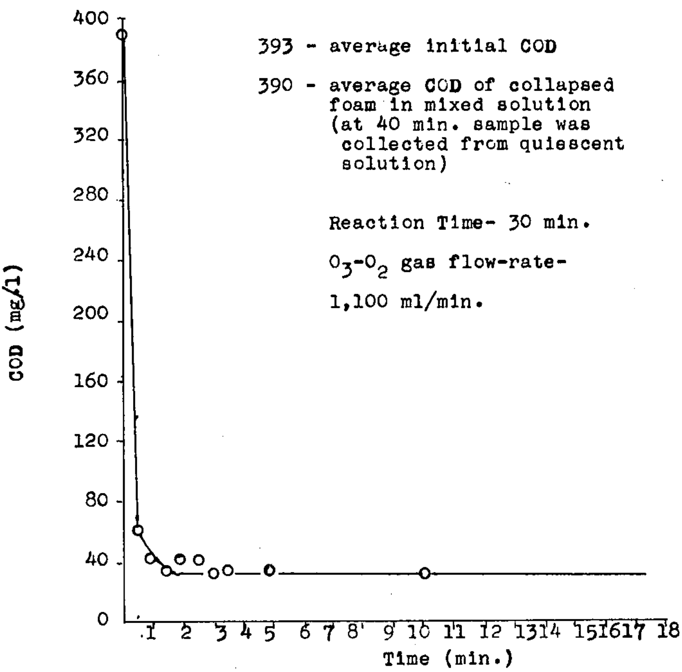


Figure 9. Detergent Behavior In Semibatch Reactor System

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