Decomposition of Dodecylbenzenesulfonate in River Water by Simultaneous Treatment with Ozone and UV Irradiation

KAZUYA MURAKAMI,^{1),a,b} TAKEMI KINOCHI,^b SHIGERU AKIMOTO,^b YOSHINARI OHNISHI^b and HISAO MATSUMOTO^a

Faculty of Pharmaceutical Sciences, Tokushima Bunri University,^a Yamashiro-cho, Tokushima, 770, Japan, and School of Medicine, The University of Tokushima,^b Kuramoto-cho, Tokushima, 770, Japan

(Received March 20, 1990)

A procedure for decomposition of contaminants in environmental water by simultaneous treatment with ozone and UV irradiation (ozone/UV treatment) was applied to linear dodecylbenzenesulfonate (DBS) in river water. Total organic carbon in the river water was decreased by this, though the reduction was not total and some persistent substances remained. When various river waters supplemented with DBS were treated with both ozone and UV, DBS was completely decomposed into inorganic carbons, while the decomposition was incomplete with ozone treatment alone. These results suggest that ozone/UV treatment is an effective procedure for purifying wastewater containing DBS.

Keywords — decomposition; alkylbenzenesulfonate; dodecylbenzenesulfonate; ozone; ozone-UV irradiation; river water

Introduction

Linear alkylbenzenesulfonates (LAS) have been generally used as synthetic detergents and discharged into untreated domestic sewage and factory effluents. Although these detergents are known to be assimilated easily by bacteria in an aqueous environment, they have been detected in various bodies of environmental water and sediments.^{2,3)} Ozone has been widely used for the purification of drinking water, however, it is difficult to decompose organic materials completely by ozone treatment alone.⁴⁾

We earlier reported a method for the decomposition of synthetic detergent by simultaneous treatment with ozone and UV irradiation (ozone/UV treatment); by this method, alkylbenzenesulfonates dissolved in distilled water were completely decomposed.⁵⁾ We also reported that ozone/UV treatment decomposed the mutagens formed from linear

dodecylbenzenesulfonate (DBS), one of the LAS, more rapidly than did ozone treatment alone.⁶⁾

In the present study, we applied our method of ozone/UV treatment to DBS dissolved in polluted river waters which had various degrees of biochemical oxygen demand (BOD).

Materials and Methods

Materials — A standard substance of sodium linear dodecylbenzenesulfonate (DBS) with purity of more than 99% was purchased from Wako Pure Chemical Industries, Ltd. All other materials were of reagent grade.

Reaction Apparatus and Procedure — DBS was added to samples of various river water at a concentration of 1×10^{-4} M and these sample solutions were treated by either ozone/UV or ozone alone. Ozone was generated from dry air using a Nippon Ozon O-1-2 ozonizer and bubbled into the bottom of a reactor as described

previously.⁵⁾ UV was irradiated by a 15W low pressure mercury lamp to 200 ml of various samples from the interior of the vessel. Ozone production was adjusted to 2.5 mg/min at a flow rate of 200 ml/min. Other procedures and methods were the same as described previously.⁵⁾

Analytical Methods—Total organic carbon (TOC) in decomposed samples and river waters was determined using a Shimadzu TOC-10B analyzer. The residual amount of DBS was determined by high performance liquid chromatography (HPLC) as described previously.⁵⁾ The BOD of river waters was determined by an Erument Kogyo BOD determination apparatus (EBG-33C) placed in an incubator (IS-1600E, Toyo Co. Ltd.) at a temperature of 20°C for 5 d. Chlorine ions in river waters were measured by the Mohr method.⁷⁾

Results and Discussion

Three samples of river water were taken from the middle of the Katsuura river (A), the lower reaches of the Sonose river (B) and a small stream (C), all in Tokushima city. Sample pH, concentration of chlorine ions, BOD and TOC are compared in Table I. DBS and other alkylbenzenesulfonates were not detected in any samples by HPLC analysis (detection limit of DBS: 3×10^{-6} M). Judging from the BOD of classes I—VI in the standard of water quality in Japanese rivers,⁸⁾ samples A and B belong to classes II (lightly polluted water) and IV (moderately polluted water), respectively. Sample C showed higher BOD than that of river water in class VI (heavily polluted water). DBS was added to these water samples at a concentration of 1×10^{-4} M, and the solutions were treated with ozone/UV or ozone alone. Figure 1 (A, B and C) shows the time course of TOC of the river waters with and without the addition of DBS after ozone/UV or ozone treatment alone. Although TOC in the river water itself decreased after ozone/UV treatment, persistent substances remained. With the addition of DBS to the water, TOC decreased rapidly

after the ozone/UV treatment for over 60 min, but this decrease ceased at the level of TOC contained in the persistent substances in the original waters. Although similar results were obtained by ozone treatment alone, each level of remaining TOC in samples A and B after the treatment was larger than that after ozone/UV treatment. Sample C, the most polluted water, was treated with ozone alone but TOC was not measured because of continuous foaming of the sample.

Figure 1 (D, E and F) shows the degradation of DBS added to the river water after ozone/UV or ozone treatment alone. DBS was degraded more rapidly after the ozone/UV treatment, and, even in heavily polluted water, was completely decomposed within 30 min.

LAS has been detected in environmental waters^{2,3,9,10)}: Nakae *et al.* reported that LAS concentration in the Tama river (Naruko Bridge, Tokyo) was 0.37 mg/l,⁹⁾ and Utsunomiya *et al.* recently reported that concentration of LAS in influent sewage and river water in Kanagawa prefecture ranged from 0.46 to 4.5 mg/l.¹⁰⁾ In the present study, the concentration of DBS added to the river water was about 34.8 mg/l (1×10^{-4} M). Even at this high concentration, DBS was completely decomposed in both the sea water-containing water (sample B) and in the heavily polluted water (sample C) following ozone/UV treatment.

These results suggest that ozone/UV treatment is a useful procedure for purifying not only drinking water but wastewater containing DBS.

TABLE I. Chemical Analysis of River Water

River sample	pH	Cl ⁻ (mg/l)	BOD (mg/l)	TOC (mg/l)
A	7.1	7.1	1.4	2.9
B	7.8	1255.0	4.3	5.9
C	7.1	19.6	14.5	14.7

A: The Katsuura River, B: The Sonose River, C: A stream in Tokushima city.

Fig. 1. Decrease of TOC and DBS in River Water by Ozone/UV or Ozone Treatment Alone

A and D: Katsuura River water,
 B and E: Sonose River water,
 C and F: Stream water in Tokushima city.
 —●—: TOC (A, B and C) or DBS (D, E and F) in DBS-added river water after ozone/UV treatment,
 —○—: TOC (A, B and C) or DBS (D, E and F) in DBS-added river water after ozone treatment alone,
 —▲—: TOC (A, B and C) in the river water after ozone/UV treatment.

References and Notes

- 1) Present address: Department of Bacteriology, School of Medicine, The University of Tokushima, Kuramoto-cho, Tokushima, 770, Japan
- 2) M. Kikuchi, A. Tokai and T. Yoshida, *Water Res.*, **20**, 643 (1986).
- 3) J. McEvoy and W. Giger, *Environ. Sci. Technol.*, **20**, 376 (1986).
- 4) Y. Kawazu and I. Ohkago, *Journal of Water and Waste*, **6**, 643 (1964).
- 5) H. Matsumoto, K. Murakami and R. Matsumoto, *Eisei Kagaku*, **35**, 408 (1989).
- 6) K. Murakami, H. Matsumoto, T. Kinouchi and Y. Ohnishi, *Environmental Mutagen Research Communications* (EMS Japan), **11**, 123 (1989).
- 7) Pharmaceutical Society of Japan (ed.), "Standard Method of Analysis for Hygienic Chemists—with Commentary—1980," Kanehara Publish. Co., Tokyo, 1981, pp.753—754.
- 8) H. Utsumi, *Eisei Kagaku*, **34**(3), iv (1986).
- 9) A. Nakae, K. Tsuji and M. Yamanaka, *Anal. Chem.*, **52**, 2275 (1980).
- 10) A. Utsunomiya, S. Naitou and I. Tomita, *Eisei Kagaku*, **35**, 152 (1989).