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Decomposition of *t*-Butanol in Water by γ-Irradiation Combined with Ozone; Cupric Ion Effect

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When *t*-butanol in aqueous system was decomposed by simultaneous application of γ-rays and ozone treatment, the addition of the cupric ion (Cu^{2+}) drastically improved the efficiency of the removal of organic substances from water. The major reason for the remarkable decrement of total organic substances is the positive catalytic effect of Cu^{2+} on the oxidation of carboxylic acids.

t-Butanol, when it is oxidized in water by ozone, has been known to disturb chain oxidation of organic compounds because it acts as a scavenger for OH radicals and does not produce O_2^- radical which acts as a chain carrier in the system.[1] It is also difficult for *t*-butanol to be oxidized effectively by ozonization alone. On the other hand, some of the heavy metal ions had been studied to promote the decomposition of organic compounds by ozone as catalyst when organic compounds were oxidized in the presence of heavy metal ions.[2, 3] This communication is a preliminary report on the effect of cupric ion upon decomposition of *t*-butanol in water with ionizing radiation combined with ozone ($\gamma/O_3/Cu^{2+}$).

Four experimental systems studied were as follows: (1) γ-irradiation with oxygen (γ/O_2), (2) γ-irradiation with oxygen and Cu^{2+} ($\gamma/O_2/Cu^{2+}$), (3) γ-irradiation with O_3 (γ/O_3), and (4) γ-irradiation with O_3 and Cu^{2+} ($\gamma/O_3/Cu^{2+}$). The concentration of Cu^{2+} ion was 1 m mol L^{-1}. About 200 ml of the aqueous *t*-butanol solution (2.5 m mol L^{-1}) with or without Cu^{2+} ion ($CuSO_4$) was placed in a 5 x 16 cm pyrex reaction vessel and was irradiated with Co-60 γ-rays at room temperature. During the irradiation, oxygen or ozonized oxygen gas from an ozone generator Model OT 31-2 (Nippon Ozone Co. Ltd) was bubbled through a porous ball at the bottom of the vessel. The dose rate was 4.1 kGy/h. The flow rate of gas was 190 ml/min and ozone concentration was 1.7 wt% in O_2. The irradiated solution with ozone was purged by high-purity nitrogen gas to remove the remaining ozone. After treatment, total organic carbon (TOC), the concentration of remaining *t*-butanol and by-products were measured. A Dohman model DC80 TOC analyzer, a Shimadzu GC9AM gas chromarograph with PEG 1000 25% coated Uniport R 60/80 columns and a HPLC with the column of KC-811 (8 mm dia. x 300 mm) made by Showa Denko K.K. were used to determine the TOC, concentrations of remaining *t*-butanol and by-products, respectively.

The TOC reduction rate with γ-irradiation combined with ozone in the presence of Cu^{2+} ion ($\gamma/O_3/Cu^{2+}$) was increased effectively as compared to that of γ-irradiation combined with ozone in the absence of Cu^{2+} ion (γ/O_3) as seen in Fig.1. This means that the TOC reduction rate can be increased by addition of Cu^{2+} ion when it is oxidized with γ-irradiation combined with ozone. This can be supported from the analysis of the by-pro-

ducts from oxidation of *t*-butanol. With the gas chromatograph and HPLC, acetone, formic, acetic, lactic and pyruvic acids were detected as by-products, and their concentrations at the irradiation time of 60 min were tabulated in Table 1. The presence of Cu^{2+} ion in the system of γ/O_3 had an important effect on decreasing acid concentrations, especially lactic and pyruvic acids. On the other hand, when Cu^{2+} ion was added to the γ/O_3 treated solution, the concentration of pyruvic acid drastically decreased, while the concentrations of lactic and formic acids did not change. In this case, the concentration of acetic acid increased slightly. However, pyruvic and lactic acids in water were hardly oxidized only by Cu^{2+} ion. From these results, we suppose that Cu^{2+} plays two roles, that is, (1) acceleration of decomposition of pyruvic acid with the aid of peroxides which are thought to be produced by irradiation, and (2) decomposition of precursors of lactic acid. These effects may accelerate the decarboxylation of organic acids leading to the remarkable decrement of total organic carbon. In order to clarify the mechanisms, a further work is now progress.

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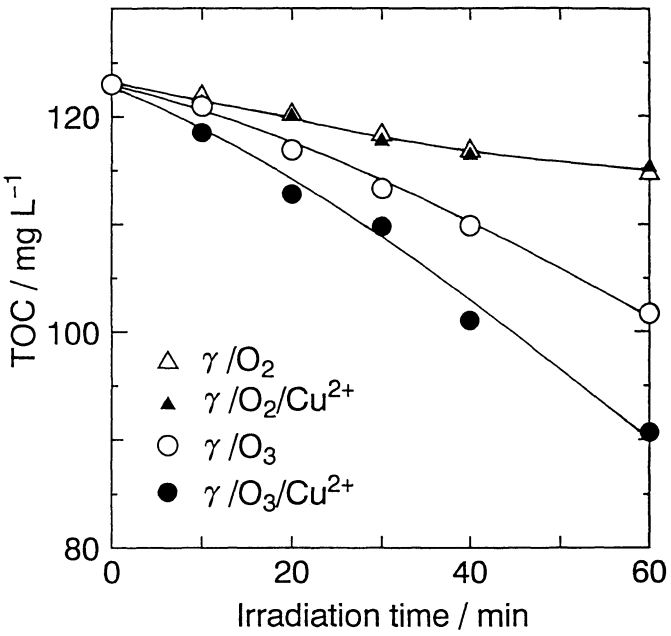

Fig. 1. The effect of Cu^{2+} on the decrement of total organic carbon by the combined action of γ-irradiation and ozone.

Table 1. The effect of treating methods on the residual amount of *t*-butanol and its decomposition products after 60 min

System	Concentration (m mol L^{-1})					
	t-butanol[a)]	acetone	formic	acetic	lactic	pyruvic acid
γ/O_2	1.68	0.40	0.075	0.015	0.065	nd
$\gamma/O_2/Cu^{2+}$	1.79	0.55	0.12	0.015	0.01	<0.001
γ/O_3	0.35	0.99	0.15	0.18	0.81	0.16
$\gamma/O_3/Cu^{2+}$	0.53	1.26	0.03	0.19	<0.01	<0.001

a)the remaining concentration. nd: not detected.

References

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