Decomposition of Aromatic Compounds by Active Oxygen Generator

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An active oxygen generator system using UV irradiation and ozone aeration was developed. The purpose of this study was to decompose benzoic acid using the active oxygen generator. The product of decomposition reaction was measured by UV absorption spectrum, and was analyzed by FT-IR. This active oxygen generator was confirmed to decompose benzoic acid effectively.

Today, the campaign to protect the environment spreads worldwide. In particular, pollution with aromatic organic compounds harms organisms in various forms. Advanced waste water treatment methods using ozone,[1,2] Fenton reaction,[3] activated sludge, titanium using photochemical and photocatalytic reaction,[4–7] etc,[8] have already been reported. However, decomposition of aromatic compounds is not easy and takes time because of its resonance structure. Then, efficient and cost-effective water treatment method for aromatic organic compounds is required.

An aqueous 10 ppm benzoic acid solution (50 mL) was placed in a quartz test tube (30 cm long by 2.1 cm inside diameter) and aerated with ozone (300 ppm) at 2.0 L/min flow rate. Then, it was irradiated from both sides by changing the combination of two 6 W low-pressure mercury lamps (UV lamps) having $\lambda = 245$ nm and $\lambda = 312$ nm.

Light quantity was determined to be 0.131×10^{-5} mol s^{-1} using iron(III) oxalate method.[9] The ultraviolet light intensity measured with a silicon photodiode was 7280 μW/cm^2. The progress of the decomposition reaction as a function of time was measured at near 225 nm of the absorption spectrum of aromatic π–π^*. Furthermore, the products in the decomposition reaction were analyzed by FT-IR. A trace amount of products produced by decomposition reaction of aqueous 10 ppm benzoic acid solution (50 mL) was too small to be analyzed with FT-IR. Therefore, an aqueous 0.218 mol dm^{-3} benzoic acid solution (150 mL) was used only for FT-IR measurement, and treated for 5 h. The decomposition products were extracted with benzene and diethyl ether. The water soluble product was freeze-dried and analyzed by FT-IR. The hydroxyl radical generated in the active oxygen generator was trapped with a spin trap agent DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) and identified by ESR.

Figure 1 shows changes in the absorption spectrum of benzoic acid caused by ozone aeration and UV irradiation with two UV lamps (254 nm); the absorption peak of aromatic π–π^* of benzoic acid gradually decreased and disappeared after 20 min treatment.

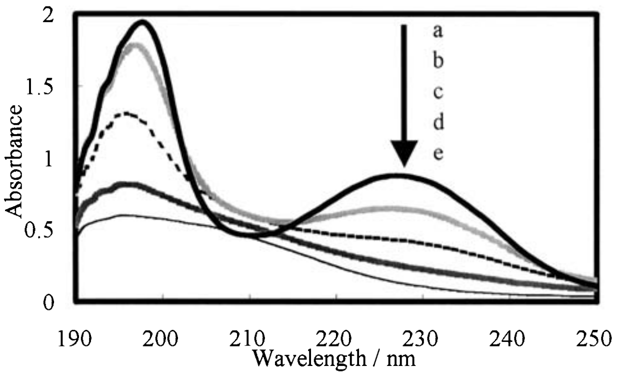

Figure 1. Changes in the UV spectrum of benzoic acid (initial concentration, 10 ppm) as a function of treatment time; (a) before treatment, (b) after 5 min treatment, (c) after 10 min treatment, (d) after 15 min treatment, (e) after 20 min treatment.

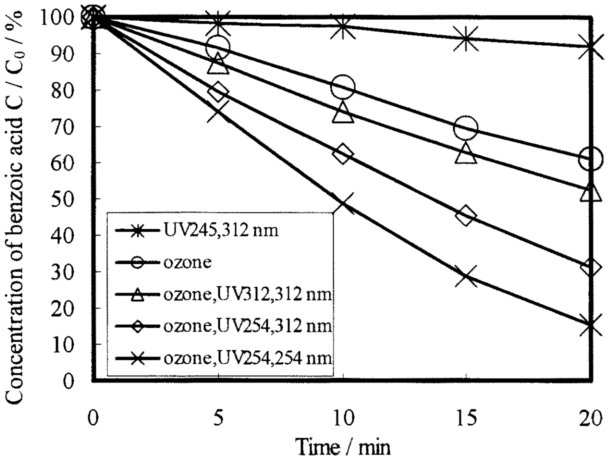

Figure 2. Change in the decomposition efficiency of benzoic acid by irradiation of UV lamps with different wavelength.
C_0: Initial concentration (10 ppm). C: Concentration after treatment.

Figure 2 shows that the aromatic ring of benzoic acid resists decomposition by either UV irradiation alone or ozone aeration, however, the decomposition reaction is allowed to proceed efficiently with the combination of ozone aeration and UV irradiation in water. In this experiment, the combination of ozone aeration and irradiation with two UV lamps (254 nm) showed the highest efficiency in the decomposition reaction; that is, more than 85% of benzoic acid decomposed after 20 min treatment.

Therefore, the aromatic ring was verified to disappear in the product for which the K absorption band could not be observed in the FT-IR measurements. As shown in Figure 3,

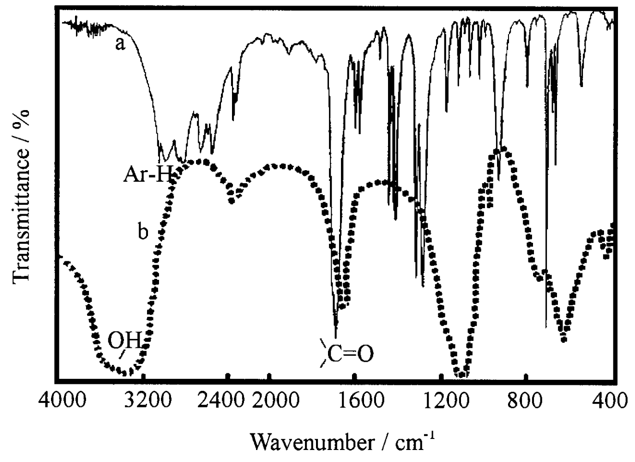

Figure 3. Infrared absorption spectra of (a) benzoic acid and (b) 0.218 mol dm^{-3} benzoic acid treated for 5 hours by a combination of ozone aeration and UV irradiation (two UV lamps, wavelength: 254 nm).

the ozone aeration and the irradiation with two 254 nm lamps made the decomposition of benzoic acid most efficient. After treatment, the infrared spectrum had no peak in the region from 3100 to 3000 cm^{-1} assigned to C–H stretching in aromatic compounds, while the peak near 3600 cm^{-1} assigned to O–H stretching increased. Consequently, the aromatic ring of benzoic acid evidently decomposed to form a nonaromatic compound containing OH groups.

Furthermore, decomposition of phenol was tested to check whether the active oxygen generator can decompose higher concentration of aromatic compounds. The absorption band near 270 nm would be due to a red shift of the B absorption band (the π–π* band observed at 256 nm for benzene) caused by auxochromic action of OH group. As shown in the Figure 4, the B absorption peak increased during the first 30 min of treatment, and decreased afterwards. As the peak of the B absorption band increased by addition of OH group to phenol, the addition of OH group to phenol was occurred after the treatment for 30 min, then the benzene ring of phenol was likely to decompose through a high energy state of the OH or O adduct of phenol.

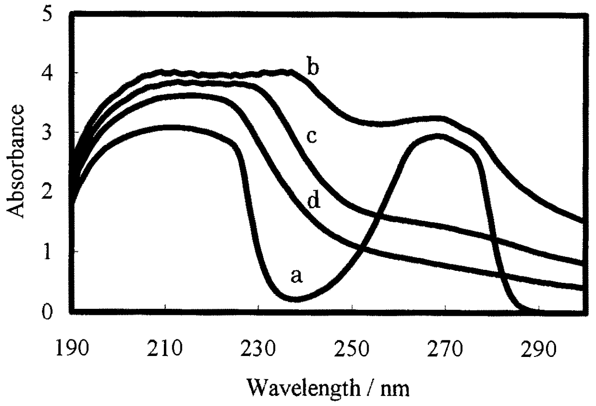

Figure 4. Changes in the spectrum of phenol (initial concentration, 204 ppm) as a function of treatment time; (a) before treatment, (b) after 90 min treatment, (c) after 150 min treatment, (d) after 180 min treatment.

The existence of hydroxyl radical was confirmed by an observation of the DMPO–OH adduct after 10 s treatment (Figure 5). Furthermore, the DMPO–OH adduct peak disappeared after 20 s treatment, and a DMPO=O peak appeared after 40 s treatment. Since OH radicals have a hydrogen drawing action, the hydrogen atom in the DMPO–OH would be drawn by OH radical leaving DMPO=O. Although the DMPO=O adduct peak was not observed after treatment for 20 s, this would correspond to the transition state of DMPO–O.

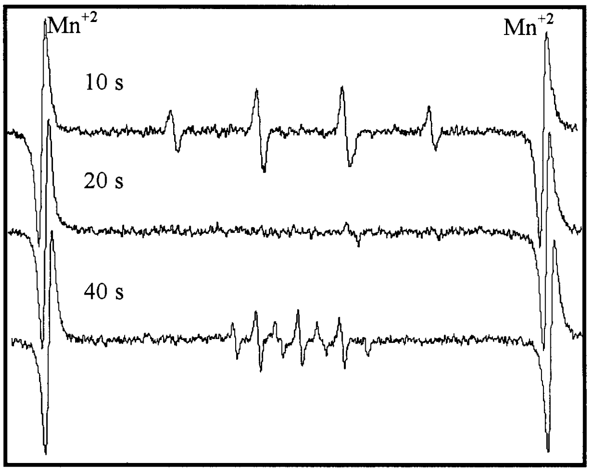

Figure.5. ESR spectra of DMPO aqueous solution by ozone aeration and irradiation with two UV lamps (254 nm) for 10 s, 20 s, and 40 s.

Ozone aeration and UV irradiation is considered to cause photolysis of ozone. Large amounts of high oxidation potential species such as •OH, •O, and •O_2H would be produced continuously by the photolysis of ozone in water. As these chemical species play an important role in the decomposition of aromatic compounds, the combination of ozone aeration and UV irradiation would accelerate this decomposition reaction. Although active oxygen species such as •OH and •O_2H are produced only by ozone aeration, the rate of their formation would be slow compared to that in the combination of ozone aeration and UV irradiation.

References and Notes

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