



Sonocatalytic facilitation of hydroxyl radical generation in the presence of TiO₂

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ABSTRACT

The generation of hydroxyl (OH) radicals was investigated during ultrasonic irradiation and in the presence of TiO₂. The effect of TiO₂ on an ultrasonic system's oxidation power was evaluated by examining the oxidation of salicylic acid. The generation of the salicylic acid derivatives, 2,3-dihydroxybenzoic acid (DHBA) and 2,5-DHBA, was measured by high-performance liquid chromatography coupled with electrochemical detection under different experimental conditions. The presence of TiO₂ enhanced the generation of DHBA during ultrasonic irradiation, thus indicating a higher oxidation power in the ultrasonic system. Al₂O₃ also increased the generation of DHBA during irradiation; however, the effect of TiO₂ was found to be higher than that of Al₂O₃. The addition of OH radical scavengers such as dimethylsulfoxide (DMSO), methanol and mannitol significantly suppressed the production of DHBA, and DMSO was found to have the highest suppressive effect among all scavengers. The effects of dissolved gases on the generation of OH radicals were further studied, and their power was found to be in the order Xe > Ar > O₂ > N₂. The degassing of the irradiation solution completely suppressed the generation of OH radicals. These results indicate that the presence of TiO₂ accelerates the generation of OH radicals during ultrasonic irradiation, and that the process may be mediated through the induction of cavitation bubbles in irradiating solutions.

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1. Introduction

Considerable interest has grown recently around the application of ultrasound as an advanced oxidation process for the treatment of hazardous contaminants in water [1]. Sonochemical degradation of pollutants in the aqueous phase generally results from acoustic cavitation created by the growth and implosion of bubbles in the liquid. Extreme temperature and pressure are generated at the center of these collapsed bubbles, creating several reaction pathways and zones in the bubble–liquid interface as well as inside the bubble or in the bulk of the liquid [2,3]. The generation of hydroxyl (OH) radicals due to the pyrolysis of water molecules has been reported as one of the main factors in the oxidation pathways of several compounds [4]. However, the oxidation efficiency of OH radicals is usually limited by the rates of their generation and the short lifespans of these reactants after generation. Therefore, increasing the generation of OH radicals and keeping their concentrations at high levels are the main factors in controlling the degradation efficiency of the pollutants.

Several attempts have been devoted to improve the oxidation power of the ultrasonic system. The application of titanium dioxide (TiO₂) seemed to be an efficient method for enhancing the degra-

dation of chemicals in this system [5–8]. The TiO₂-photocatalyst has been used in the degradation of different chemicals under UV light illumination since the first report of Fujishima et al. on the application of semiconductors to oxidation processes [9]. Those findings indicated that TiO₂ can catalyze the production of OH radicals and other oxidizing agents on its surface in photochemical reactions [10–12]. Based on these specific characteristics of TiO₂, considerable attention has been focused on the application of TiO₂ in the ultrasonic system to extend its biocidal power in the absence of UV light illumination [13–16]. While the detailed mechanisms have not been clarified yet, the possible roles of OH radicals in the ultrasound/TiO₂-induced degradation of methylene blue or in the disinfection of *Escherichia coli* and *Legionella pneumophila* were proposed using several OH radical scavenging agents. These agents significantly suppressed degradation or disinfection, possibly due to the quenching of the OH radicals. While these results may indicate the possibility that OH radicals play important roles in degradation or disinfection mechanisms, the successful application of TiO₂ in the ultrasonic system first requires the clarification of the augmentation of OH radical generation in this system.

Because the detailed mechanisms underlying the sonocatalytic degradation of environmental pollutants remain a controversial issue, we have introduced a method of high-performance liquid chromatography coupled with electrochemical detection (HPLC–ECD) to analyze the generation of OH radicals on the TiO₂ surface during

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ultrasonic irradiation. The present study demonstrates that OH radicals are formed at much higher levels in ultrasound/ TiO_2 conditions than in controls. Furthermore, the generation of OH radicals in the presence of TiO_2 was compared with that in the presence of Al_2O_3 to elucidate the characteristics of the sonocatalytic effects of TiO_2 .

2. Experimental

2.1. Materials

TiO_2 pellets in rutile form (99% by X-ray diffraction) were obtained from Nissin Chemco, Ltd. (Osaka, Japan) and were used as ceramic-based pellets (diameter, 2.0 mm). Al_2O_3 pellets (diameter, 2.0 mm) were obtained from As One Corp. (Osaka, Japan). The densities of the TiO_2 and Al_2O_3 pellets were 4.0 g/cm^3 and 3.8 g/cm^3 , respectively. The pellets were washed with distilled water and dried before their use in the experiments. Milli-Q pure water (Millipore, Bedford, MA, USA) was used to prepare the chemical solutions. Sodium salicylate was purchased from Nacalai Tesque, Ltd. (Kyoto, Japan). 2,3-dihydroxybenzoic acid (DHBA) and 2,5-DHBA were purchased from Wako Pure Chemical Industries (Osaka, Japan). 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Labotec Co., Ltd. (Tokyo, Japan). Other chemicals used in this study were of analytical-reagent grade and used without further purification. All special grades of Xe, Ar, O_2 and N_2 in cylinders were purchased from Japan Fine Products Co., Ltd. (Kanagawa, Japan). The purity of each was more than 99.99%.

2.2. Ultrasonic irradiation

The generation of OH radicals during ultrasonic irradiation was studied by measuring the oxidation products of salicylic acid, which is thought to be a highly selective OH radical trapping reagent. An ultrasonic bath (UO 300 FB-P; Kokusai Electric Alpha Co., Ltd., Toyama, Japan; working volume: 5.8 L), operating at a frequency of 36 kHz and with a rated output power of 200 W, was

used as the ultrasonic source. Two milliliters of $10 \mu\text{M}$ salicylic acid solution was added to a Pyrex glass reaction vessel containing 2 g of TiO_2 pellets. The volume of the reaction vessel was 50 ml. The reaction vessel was fixed in the center of the sonication bath and was sonicated for various periods of time. The reaction vessels were covered with aluminum foil before and after irradiation to eliminate the effects of illumination. Ultrasonic irradiation was performed in the dark by covering the bath. To control the temperature, a circulator was connected to the ultrasonic bath and the temperature was kept at $20 \pm 0.5 \text{ }^\circ\text{C}$.

After ultrasonic irradiation, each sample (1 ml) was withdrawn from the reaction vessel and was centrifuged at 10,000 rpm for 10 min to remove the suspended TiO_2 particles. The supernatant (0.2 ml) was withdrawn carefully and used for the further analysis of OH radicals.

2.3. Deaeration and gas saturation of salicylate solution containing TiO_2 pellets

For the deaeration experiment, the salicylate solution containing TiO_2 pellets was continuously degassed by the application of the negative pressure of 96 kPa, starting at 5 min prior to sonication and continuing to its end.

To saturate the salicylate solution with either Xe, Ar, O_2 or N_2 , the solution was initially degassed by the application of negative pressure of 96 kPa for 5 min, after then each gas was passed through Teflon tubing to bubble the solution for 15 s at a flow rate of 80 ml/min. Immediately after the gas bubbling, the reaction vessel was capped tightly and sonicated.

2.4. Assay for OH radicals

2.4.1. HPLC measurement of hydroxylated products of salicylic acid

The HPLC technique was utilized to measure the hydroxylated products of salicylic acid. 2,3-DHBA and 2,5-DHBA can be directly measured by the HPLC system coupled with amperometric detection. The HPLC-ECD system (Model HITEC-500; Eicom, Kyoto,

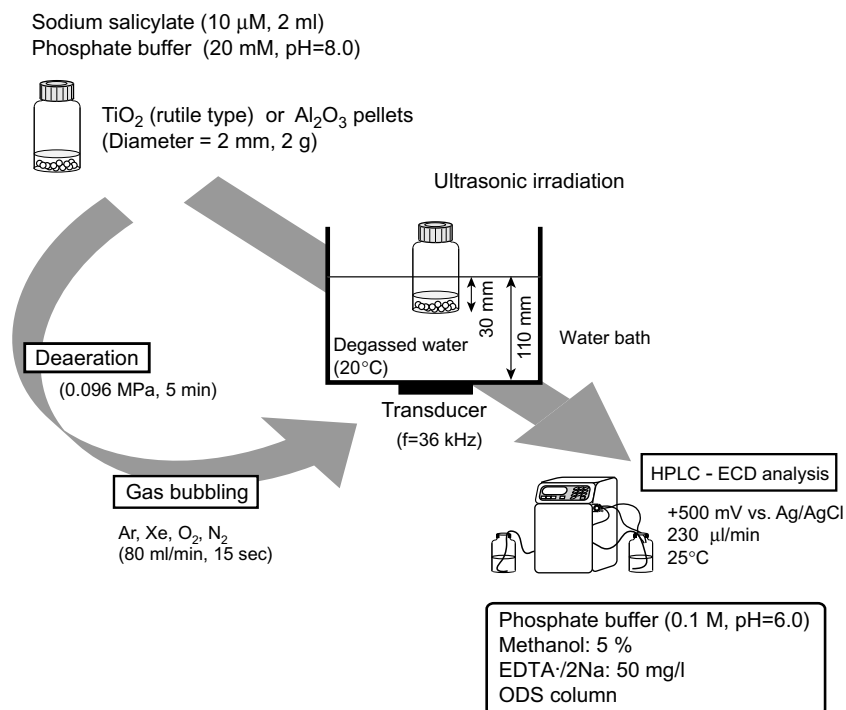


Fig. 1. Schematic illustration of the experimental procedures.

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