# Comparison of OH Radical Concentration Generated by Underwater Discharge Using Two Methods

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Abstract—Underwater discharges are an effective sources of radicals and active species, UV radiation, and shock waves. In particular, hydroxyl radicals (OH radicals, OH  $\cdot$ ) have a very strong oxidizing potential and may play an important role in the degradation of organic compounds. In this study, we attempted to quantify reactive species such as OH radicals and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) produced by underwater discharge. The OH radical concentration was determined by a chemical probe method. The H<sub>2</sub>O<sub>2</sub> concentration was colorimetrically determined through the reaction of H<sub>2</sub>O<sub>2</sub> with titanyl ions. In typical non-oxygenated solutions, the major pathway for hydrogen peroxide generation is a hydroxyl radical recombination reaction. We compared the OH radical concentration obtained by the chemical probe method with the estimated OH radical concentration inferred from the H<sub>2</sub>O<sub>2</sub> concentration and evaluated the absolute amount of OH radicals to investigate the accuracy of the chemical probe method.

Keywords—OH radical, hydrogen peroxide, underwater discharge, chemical probe method

# I. INTRODUCTION

The discharge of high-voltage electrical pulses directly into water has been of great interest for many years because of discharge phenomena and their various applications [1]-[4]. More recently, pulsed electrical discharge in water has been investigated for environmental applications, including drinking water and wastewater treatment [5]. Underwater discharges are known to be effective sources of radicals and active species, UV radiation, and shock waves [6]. In particular, the hydroxyl radical (OH radical,  $OH \cdot$ ) has a very strong oxidizing potential and may play an important role in the degradation of organic compounds. However, the quantification of OH radicals is difficult since the OH radical has a very short lifetime, on the order of a  $\mu$ s or less. Various techniques have been applied for OH radical detection. For example, optical emission spectroscopy (OES) [7], laser-induced fluorescence (LIF) [8], [9], and electron spin resonance (ESR) [10] have been studied for the identification of OH radicals in liquid and gas phases over or near the gas liquid interface. To develop knowledge of the fundamental chemical and physical processes occurring in an electrical discharge reactor, it is necessary to obtain precise measurements of the OH radicals in water.

In this study, we attempted to measure the reactive oxygen species such as OH radicals and hydrogen peroxide  $(H_2O_2)$  produced by underwater discharge. The OH radicals were measured by the chemical probe method [11], while the amount of  $H_2O_2$  was determined calorimetrically using the reaction of  $H_2O_2$  with titanyl ions [12]. In typical non-oxygenated solutions, the major path for  $H_2O_2$  generation is the OH radical recombination reaction as follows [13]:

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$$OH \cdot + OH \cdot \longrightarrow H_2O_2$$
 (1)

In this study, we compared the amount of OH radicals measured by the chemical probe method with that estimated from  $H_2O_2$  recombination and evaluated the absolute amount of OH radicals to investigate the accuracy of the chemical probe method.

## II. EXPERIMENTAL

# A. Underwater discharge system

A schematic of the experimental setup is shown in Fig. 1. A pulsed high-voltage circuit with a self-triggered spark gap switch was used to generate streamers in the liquid. A needle-to-sphere discharge electrode system was inserted into a terephthalic acid (TA) solution, filling a cylindrical silicaglass tube reactor (20 mm in inner diameter and 24 mm in outer diameter, 200 mm in length). A stainless-steel needle (0.14 mm in inner diameter and 0.32 mm in outer diameter) with an insulating cover was used as the stressed electrode, while a stainless-steel sphere (15 mm in diameter) was used as the grounded electrode. The gap distance between the needle and sphere electrodes was 20 mm, and the volume of the solution was 30 ml. The voltage pulses and the current were recorded on a digital oscilloscope (Tektronix, TDS 5104) using a high-voltage probe (Iwamatsu, HV-P30) and a current probe (Pearson Electronics, 2877), respectively.

### B. Chemical probe method

The OH radicals were measured indirectly by chemical dosimetry based on a solution of terephthalic acid (TA) at pH 10-11 or on a solution of disodium terephthalate (NaTA) at pH 6-7. Since TA (Aldrich) does not dissolve in acidic/neutral liquids, the TA solution was prepared by dissolving the TA in distilled water containing NaOH (Wako). The solubility of TA is a major concern in pulsed electrical discharge systems, since a substantial amount of NaOH is usually required to

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Fig. 1. Schematic of the experimental apparatus.



Fig. 2. Formation of HTA from (a) TA and (b) NaTA.

dissolve the TA, this NaOH addition results in a substantial increase in the solution conductivity. To resolve this problem, we used NaTA, which has a higher solubility than TA and does not substantially increase the conductivity of the experimental solutions [14]. The initial conductivities of the TA and NaTA solutions were 360 and 250  $\mu$ S/cm, respectively. The same initial concentration of 2 mM was used in each case. TA and NaTA are well-known OH scavengers that do not react with other radicals such as O2-, HO2, and H2O2. As shown in Fig. 2, TA and NaTA react with OH radicals to form 2hydroxyterephthalicacid (HTA). The yield of HTA-scavenging OH was assumed to be only 35% [15]. An LED lamp (UVIX,  $\lambda = 310$  nm, FWHM = 10 nm, power = 400  $\mu$ W) was used as a light source to excite the HTA. The fluorescence of HTA ( $\lambda = 425$  nm, center wavelength) was observed by an ICCD camera (Andor, i-star) and measured by a spectrometer (Ocean Optics, USB2000) as a function of treatment time. To quantify the OH radical concentration in the liquid, a calibration curve for known OH radicals concentrations was prepared using an HTA (Atlantic Research) standard solution. A typical calibration curve is shown in Fig. 3.

# C. Colorimetric method

Measurement of the  $H_2O_2$  generated in solution was conducted using a titanium sulfate colorimetric assay method by the following reaction:



Fig. 3. Calibration curve of HTA.



Fig. 4. Calibration curve for colorimetric determination of  $H_2O_2$ .

$$\operatorname{Ti}_{4}^{+} + \operatorname{H}_{2}\operatorname{O}_{2} + 2\operatorname{H}_{2}\operatorname{O} \longrightarrow \operatorname{Ti}_{2}\operatorname{H}_{2}\operatorname{O}_{2} + 4\operatorname{H}^{+} \quad (2)$$

The absorbance of the yellow peroxotitanium (IV) complex at wavelength  $\lambda = 410$  nm was measured. The solution conductivity was adjusted to the desired initial value by the addition of potassium chloride (Wako). The calibration curve relating the H<sub>2</sub>O<sub>2</sub> and tianyl ions is shown in Fig. 4. In typical non-oxygenated solutions, the major path for H<sub>2</sub>O<sub>2</sub> generation is the hydroxyl radical recombination reaction. We compared the amount of OH obtained by the probe method with that estimated from the H<sub>2</sub>O<sub>2</sub> content, determining the absolute amount of OH to evaluate our chemical probe method.

#### **III. RESULTS AND DISCUSSION**

Typical voltage and current waveforms for the discharge in a TA solution and the appearance of streamers are shown in Fig. 5. The rise time of the pulsed high voltage used in this study is about 70 ns, and the pulsed width is about 10  $\mu$ s. The average pulse repetition rate is about 10 pps. Since the solution conductivity is relatively high, a streamer discharge consists of a few filaments of less than 5 mm.



Fig. 5. Applied voltage and current waveforms for the discharge and the appearance of streamers in a TA solution.



Fig. 6. Optical emission spectrum of the pulsed streamers in a NaTA solution (V = 24 kV, 10 pps).

From the typical emission spectrum of the pulsed streamers in a NaTA solution, the emission of the hydrogen atomic line  $(H_{\alpha}, H_{\beta}, H_{\gamma})$ , the oxygen atomic line (O) and OH radicals were detected, as shown in Fig. 6.

The fluorescence images of HTA, obtained by irradiating the illumination of LED light source ( $\lambda = 310$  nm), were captured by an ICCD camera as a function of treatment time, as shown in Fig. 7. The exposure time of each image captured by the ICCD camera is 10 ms. OH radicals formed along the streamer propagation were trapped by TA and NaTA molecules to produce HTA. The fluorescence of HTA increased with the increasing treatment time. It was confirmed that the fluorescence of HTA in a neutral NaTA solution (pH = 6.2) was higher than that in an alkaline TA solution (pH = 9.6).

The fluorescence spectra of HTA ( $\lambda = 425$  nm) as a function of treatment time are shown in Fig. 8. The fluorescence intensity of the HTA, indicating the total amount of OH radicals trapped by NaTA, increased with the treatment time. To evaluate the amount of OH radicals in the solution, we calculated the OH density as a function of treatment time, as shown in Fig. 9. The concentration of the OH radicals increased almost linearly at all pH levels: 9.7, 9.6, and 6.2. In particular, it was found that the concentration of the OH radicals in the neutral NaTA solution was larger than that in the alkaline TA solution. This result may be caused by the large difference in the concentration of the OH radicals at different pH levels, as the recombination reaction with hydroxide ions



Fig. 7. Time evolution of the fluorescence of HTA captured by ICCD camera in (a) TA and (b) NaTA solutions (V = 24 kV, 10 pps, exposure time 10 ms).



Fig. 8. Fluorescence spectra in a NaTA solution treated by discharge (V = 24 kV, 10 pps).

normally occurs in alkaline solutions.

$$OH \cdot + OH^{-} \longrightarrow H_2O + O^{\cdot -}$$
 (3)

The influence of pH level on the discharge is reported by a previous study [16]. In fact, at low pH, OH radicals produced by a discharge mainly reacted with TA and NaTA in the solution. As the pH increased, the concentration of  $OH^-$  ions increased, and some of the hydroxyl radicals could combine with  $OH^-$  ions to form water. In addition, it is known that the oxidative potential of the OH radical is dependent upon pH (e.g., 2.70 and 2.34 V at pH 3.0 and 9.0, respectively) [17].

The concentrations of OH radicals and  $H_2O_2$  as function of treatment time are shown in Fig. 10. The amount of  $H_2O_2$  was determined calorimetrically using the reaction of  $H_2O_2$  with titanyl ions at pH 5.9. For comparison, we plotted the OH radicals concentration at pH 6.2 as determined by the chemical probe method shown in Fig. 9. The solution of NaTA and KCl had the same conductivity (250  $\mu$ S/cm). The concentration of OH radicals and  $H_2O_2$  increased almost linearly with plasma treatment time and were  $3.0 \times 10^{-2}$  and  $3.5 \times 10^{-1}$  mM at 20 min, respectively. The production rate of



Fig. 9. Concentrations of OH radicals obtained by the chemical probe method as a function of time.

aqueous OH radicals obtained by the chemical probe method was estimated to be of the order of  $10^{-9}$  to  $10^{-8}$  M/s under the stated experimental conditions. Consequently, the amount of OH radicals estimated from the H2O2 content was about 23 times higher than the estimated OH radicals deduced by the chemical probe method. The difference between the two methods can be considered to be a result of the following two reasons. The first reason is because of the yield of HTA. We assumed a 35% reaction yield from TA and NaTA interacting with OH radicals to produce HTA using references from radiation chemical studies and sonochemistry. However, this may not be the case in a pulsed discharge system, since the formation reaction of OH is fairly complex. In our opinion, the effective reaction of TA and NaTA with OH radicals around the collapsing streamer channel does not occur, because the migration length of the OH radicals in the bulk solution is very short. Thus, it is necessary to consider that a pulsed discharge system will produce a lower yield of HTA. The second reason is the presence of other species such as  $HO_2^-$ ,  $OH^-$ ,  $H^+$ , and  $O^{-}$  that take part in H<sub>2</sub>O<sub>2</sub> generation, as shown in Fig. 11 [17]. Thus, we have to take into account numerous reaction pathways that include the various active particles and reactive species produced by underwater discharge.

In general, the main mechanism of OH radical production is the dissociation of water molecules by their interaction with electrons, excited oxygen atoms, and nitrogen molecules under a second positive band, due to the following reactions:

$$H_2O + e \longrightarrow OH + H + e$$
 (4)

$$O(^{1}D) + H_{2}O \longrightarrow OH + OH$$
 (5)

$$N_2(A^3 \sum +) + H_2O \longrightarrow OH + N_2 + H$$
 (6)

The produced OH radicals can convert  $H_2O_2$  and  $H_2O$  from the recombination of OH radicals and also OH decays occur



Fig. 10. Concentrations of OH and H2O2 as a function of treatment time.



Fig. 11. Simplified scheme of hydrogen peroxide formation [17].

as follows:

$$OH + OH \longrightarrow H_2O_2$$
 (7)

$$OH + OH \longrightarrow H_2O + O$$
 (8)

$$OH + O \longrightarrow O_2 + H$$
 (9)

$$OH + probe \longrightarrow products$$
 (10)

$$OH + H_2O_2 \longrightarrow H_2O + HO_2$$
 (11)

The major  $H_2O_2$  generation pathway has been considered to be reaction (7). However, the OH generating pathway is quite complicated; therefore, we need to take into account the simulation analysis related to these various radicals.

#### **IV. CONCLUSION**

In this study, the OH radicals produced by underwater discharge were quantified using a chemical probe method. Moreover, we compared the amount of OH radicals obtained by the chemical probe method with the amount estimated from  $H_2O_2$  production and evaluated the absolute amount of OH radicals. It was found that the concentration of the OH radicals depended on the pH of the solution, and the concentrations of OH and  $H_2O_2$  almost linearly increased with the plasma treatment time; the concentrations of OH and  $H_2O_2$  were  $3.0 \times 10^{-2}$  and  $3.5 \times 10^{-1}$  mM, respectively, at 20 min under our experimental conditions. Consequently, the amount of OH radicals estimated from the production of  $H_2O_2$  was about 23 times higher than the estimate of OH radicals obtained by the chemical probe method.

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