Catalyst Effect on Degradation of Organism by Nanoseconds Pulsed Discharge in Gas-Liquid Mixture*)

Guanyang TANG, Ryosuke OHNO, Atsushi KOMURO, Kazunori TAKAHASHI and Akira ANDO

Department of Electrical Engineering, Tohoku University, Sendai 980-8579, Japan

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The gas-liquid mixed phase plasma generated by a streamer discharge in bubbles was used for degradation of acetic acid as treatment of organism pollution in water. The synergistic effect of plasma and catalyst, TiO_2 or Fe ions via electro-Fenton process, was utilized to enhance the production and utilization of hydroxyl radicals. When TiO_2 powder was added to acetic acid solution, the hydrogen peroxide (H_2O_2) concentration formed by the combination of OH radicals significantly increased more than 25%. Whereas, when a grounded electrode was replaced to Fe, iron ions appears in the solution and H_2O_2 was fully resolved into OH radicals in the electro-Fenton process, resulting in the degradation of acetic acid. The energy efficiency of degradation of acetic acid increased from 0.78 g/kWh to 1.18 g/kWh and 1.31 g/kWh with the addition of TiO_2 and replacement of iron electrode, respectively.

Keywords: gas-liquid plasma, degradation of acetic acid, TiO_2, electro-Fenton process, pulsed high voltage, catalyst

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1. Introduction

With the development of organic chemical industry, water pollution caused by persistent organic pollutants (POPs) has been one of the serious environmental issues. As one of the advanced oxidation processes (AOPs), non-thermal plasma has excellent performance in terms of organism degradation [1]. Various discharge types and reactor systems have been investigated, such as pulsed corona, dielectric barrier discharge, gliding arc discharge, hybrid gas-liquid reactor, wire-cylinder reactor and so on [2].

In the process of plasma production in liquid many active species such as oxygen radicals ($\cdot$O), hydroxyl radicals ($\cdot$OH), and ozone (O_3), etc. can be generated to react with organic pollutants and help their decomposition processes. Especially, as the oxidation potential of $\cdot$OH of 2.8 V is higher than most of chemical bonding energy in organic pollutants, they are decomposed into CO_2 or the other carbonates with the reaction of OH radicals [3].

We have investigated gas-liquid mixed phase plasma and utilized it to decolorization, sterilization and degradation of POPs in water [4]. Production of OH radicals was large in plasma production with rare gases, Ar or He. As for the treatment of POPs most of researches focused on the optimization of charge conditions and generated active species in discharges [5]. However, the efficiency of decomposition remains low and significant improvement of the efficiency is required.

In this paper we adopted TiO_2 and iron ions as catalysts for improving the degradation of acetic acid in gas-liquid mixed phase plasma treatment system. We measured H_2O_2 concentration, indicating OH radical production, and total organic carbon (TOC) concentration to evaluate the generation of OH radicals and degradation efficiency of acetic acid, respectively, with or without the effect of TiO_2 or iron ions as catalysts.

2. Experimental Setup

The schematic diagram of a pulse high-voltage circuit is shown in Fig. 1 The circuit consists of a capacitor C, a gap switch GS, an inductor L, and semiconductor opening switch (SOS) diodes (VMI. K25UF×10). Typical temporal evolution of the capacitor voltage V_C, output voltage V_O, and SOS current I_{SOS} are shown in Fig. 2.

The capacitor is firstly charged up by using a DC high voltage power supply (11 kV). When the gap switch is shorted, charge of the capacitor is released and current starts to flow through the inductor and the SOS diodes. When the direction of oscillating current reversed, it is interrupted by the diodes with the delay of 100 ns.

The sudden interruption of the inductor current results in the generation of negative high voltage pulse V_O with a short pulse duration of about 40 ns. When charging voltage and pulsed repetition frequency is set to 11 kV and 30 Hz, respectively, the output voltage can reach about 20 kV.

A gas-liquid mixed phase plasma reactor is shown in Fig. 3, which consists of two regions, a gas phase (bottom) and liquid phase (top) separated by an polypropylene plate with 25 numbers of small holes (dia. 1 mm). The wire high voltage electrode (dia. 0.3 mm) is situated in 2 mm

author's e-mail: tang@ecei.tohoku.ac.jp

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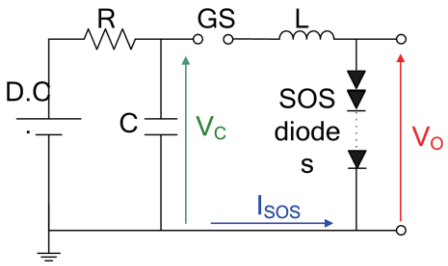

Fig. 1 Schematic diagram of the experimental circuit.

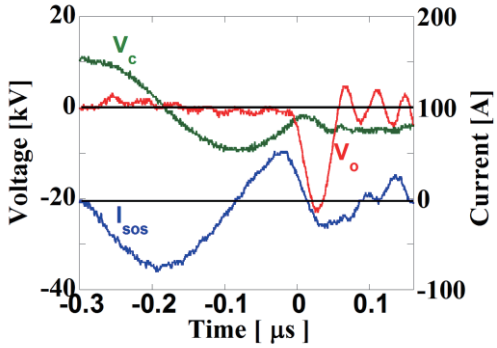

Fig. 2 Waveforms of the LC oscillating current, capacitor voltage and pulse discharge voltage.

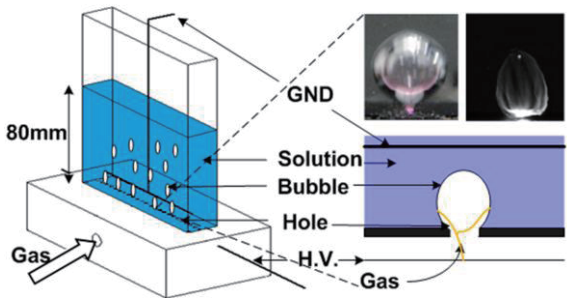

Fig. 3 Schematic diagram of a gas-liquid hybrid plasma reactor.

below the holes in the gas chamber and the GND electrode is immersed in 20 mm above the partition in the solution. Working gas was injected into liquid via separator holes, and a number of bubbles were formed within the liquid phase. With applying the pulse voltage, a streamer-like discharge can be formed in the bubble as shown in Fig. 4.

50 mL acetic acid solution of 10 mg_{TOC}/L was used as organic sewage and argon gas was fed to the gas chamber with the flow rate of 8 L/min. The H_2O_2 concentration and iron ion concentration were measured with colorimetry method (Kyoritsu WAK-H_2O_2 and LR-Fe^T-D) and the TOC concentration was measured with TOC analyzer (Shimadazu TOC-L).

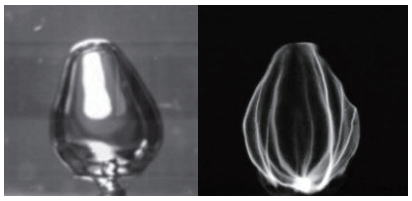

Fig. 4 (a) Photographs of a Ar bubble and (b) a discharge in the Ar bubble.

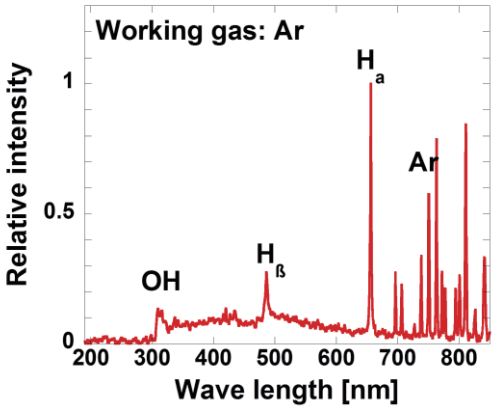

Fig. 5 An Optical emission spectrum of the discharge in an Ar bubble.

3. Experimental Results and Discussion

3.1 OH radical generation and acetic acid decomposition

Figure 5 shows an observed spectrum from the streamer-like discharge distributed on the gas-liquid interface. The emission intensity of OH was obviously found at 309 nm, which plays a great role in acetic acid degradation. Although the lifetime of OH radicals is short, they rapidly combine to each other into H_2O_2 as described in the reaction (1) [6]. Therefore the production of H_2O_2 was used to evaluate the generation of OH radicals. A part of OH radicals would react with acetic acid and decompose it as described in the reaction (2) [7]. We evaluated the degradation effect of acetic acid by the TOC measurement.

$$\cdot OH + \cdot OH \rightarrow H_2O_2, \quad (1)$$

$$CH_3COOH + \cdot OH \rightarrow CO_3C(O) \cdot + H_2O \rightarrow CO_2 + \cdot CH_3 + H_2O. \quad (2)$$

Previous study has reported that the degradation rate of acetic acid by this plasma treatment has reached 0.78 g_{TOC}/kWh without any catalyst [4]. More effective method was expected with a higher degradation rate.

3.2 Synergistic effect of plasma and TiO_2

The TiO_2 as a kind of photocatalyst has been wildly used for self-cleaning coatings [8], sterilization [9] and a number of applications. We utilized TiO_2 powder of 0.03 g into the solution and expected to produce more OH radicals

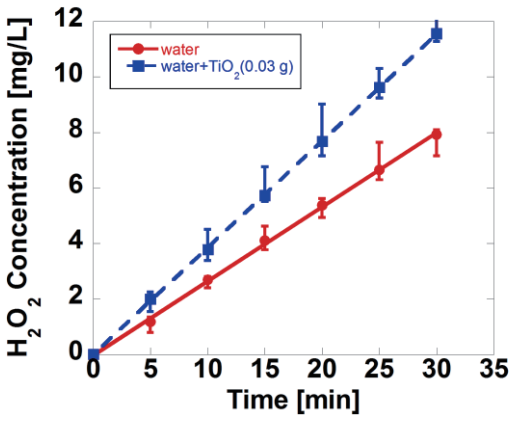

Fig. 6 Time variation of H_2O_2 concentration with or without TiO_2.

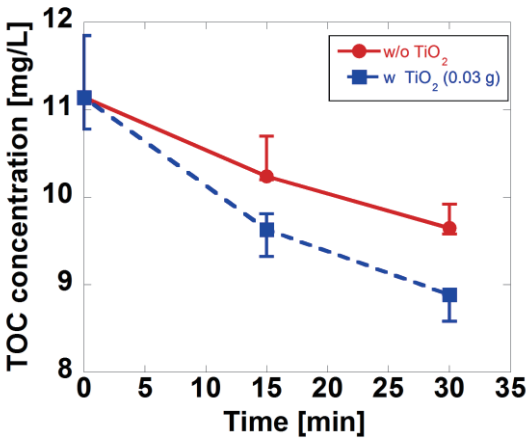

Fig. 7 TOC concentration of acetic acid solution in plasma system and plasma/TiO_2 system.

to participate in the decomposition reaction of acetic acid, since TiO_2 could be activated by UV photons to generate photoelectrons and the vacancies. The vacancies which have a strong oxidation power could generate OH radicals in water environment as in the following reactions. (3)-(5) [10].

$$TiO_2 + hv \rightarrow e^- + h^+, \quad (3)$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+, \quad (4)$$

$$OH^- + h^+ \rightarrow \cdot OH. \quad (5)$$

It was found that the generation concentration of H_2O_2 obviously increased in the presence of TiO_2 as shown in Fig. 6. The increment rate (≈3.9 μM/min) was more than twice larger than that (≈1.5 μM/min) of UV/TiO_2 [11] with smaller amount of powder. It is considered the synergistic effect of plasma and TiO_2, as observed in the research of plasma sterilization [12]. Plasma also can activate the TiO_2 and the electric field can help the separation process of photo-generated carriers to enhance the catalytic effect [13].

The degradation effect of acetic acid was observed in the TOC concentration. It decreased due to the catalysis with plasma as shown in Fig. 7. Degradation rate was enhanced to 75.6 μg/L·min and the energy efficiency of degradation increased to 1.18 g/kWh which attained to an upper level in organism decomposition with plasma [14]. Figure 8 shows the concentration of H_2O_2 in water and acetic acid solution with and without TiO_2. The concentration of H_2O_2 decreased in the acetic acid solution due to the consumption of OH radicals working for the decomposition. The effect of TiO_2 additive that was the increase of the concentration of H_2O_2 was still observed in the acetic acid solution.

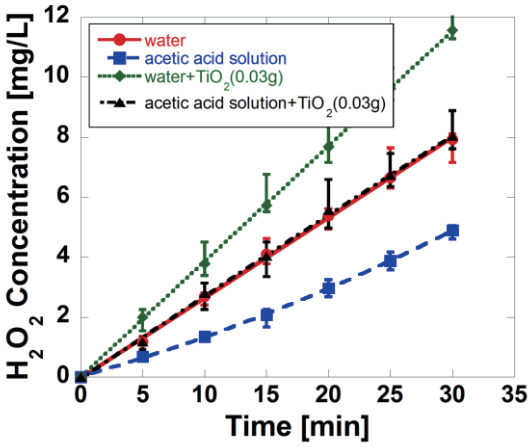

Fig. 8 Concentration of H_2O_2 in water and acetic acid solution with and without TiO_2.

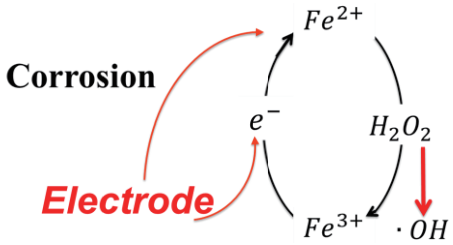

Fig. 9 The electro-Fenton process in acid solution.

3.3 Electro-Fenton process in plasma system

Although OH radicals has high oxidation potential and react with organism, most of OH radicals combine into H_2O_2, where the oxidation potential of H_2O_2 is too low to compose the acetic acid [15]. In order to improve the utilization rate of OH radicals, the electro-Fenton process in equations (6)-(7) should be utilized as an efficient advanced oxidation processes (AOP) [16]. We investigated the effect in the plasma system to increase the degradation of acetic acid in the solution. Therefore, a SUS316 GND electrode was replaced to an iron electrode, and then the iron ions could come into the solution due to the corrosion of acetic acid. Fe^{3+} ions could be replaced with Fe^{2+} by the contact with the electrode to compensate the low reaction

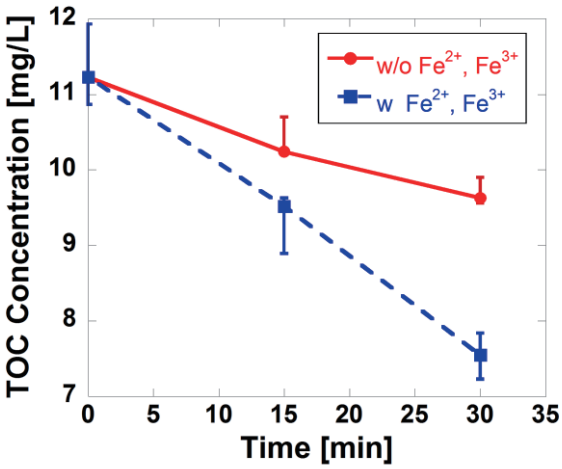

Fig. 10 TOC concentration of acetic acid solution in the plasma system with and without the iron ions.

rate of equation (7) [17]. The whole process was shown in Fig. 9.

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+}, \quad (6)$$

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + HO_2^- + Fe^{2+}. \quad (7)$$

After 30 min treatment with the iron electrode, there was no residual H_2O_2 and the concentration of iron ions reached 4 mg/L. The degradation effect of acetic acid was significantly enhanced as shown in Fig.10. Degradation rate was enhanced to 115 μg/L·min and the energy efficiency of degradation increased to 1.31 g/kWh.

4. Conclusion

The gas-liquid mixed phase plasma utilizing pulsed high voltage was used for degradation of acetic acid. The catalysts were introduced into the plasma treatment system to improve the degradation effect. Firstly the photocatalyst TiO_2 was adopted with the help of UV light from discharge to enhance OH radical production due to the synergistic effect of plasma and TiO_2, leading to an obvious improvement in acetic acid degradation and energy efficiency. Whereas, an iron electrode was used to replace a SUS316 grounded electrode in the solution to utilize the electro-Fenton process. Because of the corrosion of acetic acid solution, an iron ions could be formed in the plasma treatment system. In the process H_2O_2 formed by the combination of OH radicals was fully used for the degradation of acetic acid. As a result the degradation rate and energy efficiency of degradation became nearly double. Therefore the addition of catalyst increased the production or utilization rate of OH radicals, resulting in higher degradation rate of organism.

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