pH Dependence on Decomposition of Persistent Organic Compounds in Water Using a DC Corona Discharger

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Abstract—DC corona discharges over water were studied to decompose persistent organic compounds. Since active species with short lifetimes are generated from corona discharges, they can be effectively used for purifying water. Acetic acid, a model persistent organic compound, was decomposed by the corona discharge in oxygen 4 mm above the water surface. As the voltage increased, the decomposition rate increased, which was also enhanced with increasing initial pH. Our results indicate that liquid phase reactions are important for water treatment using a DC corona discharge.

Keywords—DC corona discharge, nondirect treatment using plasma, OH radicals, pH

I. INTRODUCTION

Recently, the use of a discharged plasma for water treatment has been attracting attention [1]–[3] because the plasma can create OH radicals, an active species with a short lifetime, in the water or on its surface. OH is a strong oxidizer with an extremely short lifetime; therefore, its applicability for water treatment is challenging. However, since OH is generated close to the water surface in this treatment method, it is possible to use it for water treatment.

We have previously studied the decomposition of acetic acid, a model persistent organic compound, by a pulsed discharge on water using thin blade electrodes [4]. In this method, a discharge is generated between the blade electrodes and water surface. Therefore, this method directly treats water using a discharge plasma. Although direct plasma processes can decompose persistent organic compounds, OH reacts with scavengers, such as \( \text{H}_2\text{O}_2 \), rather than target compounds in the solution [5], [6].

In general advanced oxidation processes, OH is produced in wastewater by ozone/UV/H\( _2\text{O}_2 \) combination [7]–[9]. OH is generated by liquid-phase reactions in these systems. In the present study, we investigate the characteristics of acetic acid decomposition by a DC corona discharge over water. The corona discharge is 4 mm away from the water surface. Therefore, this method does not directly treat water using a discharge plasma. The occurrence of species \( \text{O}_x \) (\( x = 1 \) to \( 3 \)), \( \text{NO}_x \) and \( \text{H}_2\text{O}_y \) (\( x = 1 \) to \( 2 \); \( y = 1 \) to \( 2 \)) was reported from experiments performed on coronas burning in humid air [10]. Outside corona region, electrons are captured by gas molecules to produce negative ions. \( \text{O}^- \), \( \text{O}_2^- \), \( \text{O}_3^- \), \( \text{H}^- \) and \( \text{OH}^- \) can be generated by the electron attachment in humid air [11], [12]. Such negative ions drift toward the anode by electrostatic force, causing ion wind. The ion wind is expected to carry long-lived active species to water surface. A DC corona was chosen to investigate the liquid-phase reaction of such active species. This study explores the mechanisms involved in the chemical reactions of active species for water treatment using the discharge plasma.

II. EXPERIMENTAL APPARATUS AND METHOD

Fig. 1 shows a schematic of the experimental apparatus. The apparatus was composed of a high-voltage DC power source, a ballast resistor, and a discharge reactor. In the discharge reactor, the electrode on the high-voltage side was set up at the bottom of the reactor and the electrode on the ground was set up in the upper part of the reactor. The high-voltage electrode was a stainless steel plate, and the ground electrodes were stainless steel thin tubes. The inner and outer diameters of the tube electrode were 0.19 and 0.41 mm, respectively. There were eight tube electrodes in total, as shown in Fig. 2. When 10 ml water was placed in the reactor, the distance from the bottom of the reactor to the water surface was 5 mm, and the distance from the water surface to the tip of the thin tube electrode was 4 mm.

The water for treatment consisted of a solution of acetic acid in distilled water (conductivity: \( 1 \mu\text{S/cm} \)). The concentration of the acetic acid solution was approximately 20 mg/l. The discharge treatment experiment was performed by adding 10 ml acetic acid solution to the reactor. The initial pH of the...
solution was adjusted to 3, 4.5, 6, 7.5, and 9 by adding sodium hydroxide or sulfuric acid. During processing, oxygen was supplied to the reactor at a flow rate of 150 ml/min (Fig. 1). Characteristics of acetic-acid decomposition were not changed when the gas was supplied from tube electrode.

When the high-voltage DC was applied to the reactor, a glow corona discharge was produced at the tip of thin tube electrode. The corona discharge was spherical with a diameter of around 0.5 mm.

Measurement of the acetate ion concentration in the solution during treatment was performed by Nissin Business Promote using an ion chromatograph. A spectrophotometer (UVmin-1240, Shimadzu) and chemical coloration reagent (WAK-H2O2, Kyoritsu CHEMICAL-CHECK Lab., Corp.) were used to measure the hydrogen peroxide concentration in the solution.

The voltage of the ballast resistor was measured with a voltage probe (EP-100K, Pulse Electronic Engineering). The applied voltage value between the electrodes had assumed differences between the value of the power supply meter (HAR-20R60, MATSUSADA Precision) and the ballast resistor voltage. The discharge current was determined by the voltage of the ballast resistor (20 MΩ). The light spectrum emitted from the discharge was analyzed using a spectrometer (S-2431, SOMA OPTICS).

III. RESULTS

Fig. 3 shows the discharge current as a function of the applied voltage. When the voltage was higher than 6.1 kV, the corona discharge occurred at the tip of all the electrodes. At other pH values, the voltage current characteristics were nearly identical.

Fig. 4 shows a typical light emission spectrum of the DC corona discharge. The observed peaks indicate the existence of active species in the gas phase. Peaks of 309 and 777.7 nm were observed, which respectively corresponds to OH and O radical emissions.

Fig. 5 shows the time variation of the amount of acetic acid at an applied voltage of 7.46 kV in the solution at a pH of 4.4. The amount of acetic acid is the product of the acetate ion concentration and the amount of the solution. The amount of acetic acid decreased linearly over the discharge period. This decrease was exhibited for all experimental conditions. The decomposition rate \( v \) was determined by an approximate straight line (Fig. 5). The decomposition rate \( v \) (\( \mu g/min \)) was determined by Eq. (1), where \( \Delta A \) is the decrease in the amount of acetic acid and \( \Delta t \) is the operation time.

\[
v = \frac{\Delta A}{\Delta t}
\]  

\( (1) \)
Fig. 6 shows decomposition rate $v$ versus the applied voltage in the solution at a pH of 4.4. The decomposition rate $v$ was increased by increasing the applied voltage. In addition, the discharge power increased because the discharge current increased as a result of the increase in the applied voltage. At the lowest voltage of 6.3 kV, the discharge power was 1.17 W. At the highest voltage of 7.7 kV, the electric discharge power was 2.43 W.

Fig. 7 shows the decomposition rate $v$ as a function of solution pH at an average applied voltage of 7.47 kV. pH had little impact on the voltage and current. However, the decomposition rate $v$ increased with increasing pH. When the pH was larger than 7.5, the decomposition rate $v$ did not change.

Fig. 8 shows the time variation of the concentration of dissolved hydrogen peroxide at various pH. The concentration of hydrogen peroxide increased with operation time at a low pH. However, when the initial pH was above 6.0, the concentration of hydrogen peroxide decreased with time. The concentration of ozone was saturated with time and independent of pH (Fig. 9).

Fig. 10 shows the time variation in pH. At pH of 3.0, 4.5, and 6.0, there was no change over the discharge period. Both pH values of 7.5 and 9.0 decreased after 1 min.

IV. DISCUSSION

The acetic acid decomposition reactions in the solution are as follows [13],

$$\text{CH}_3\text{COOH} + \cdot \text{OH} \longrightarrow \text{CH}_3\text{C(O)O} \cdot + \text{H}_2\text{O}$$  \hspace{1cm} (2)

$$\longrightarrow \text{CO}_2 + \cdot \text{CH}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (3)

As shown in Fig. 4, excited OH radicals were observed in the gas phase. OH radicals are formed by the DC corona discharge
via the following reaction.

\[ \text{H}_2\text{O} + e \rightarrow \text{OH} + \text{H} + e \]  
(4)

However, the distance between the corona discharge and the water solution was 4 mm. Thus, it is difficult for the short lived OH radicals to undergo processing in water. As a result, the probability that OH radicals generated in the gas phase react with acetic acid in the liquid phase is low.

The production of active species in the gas phase likely has little effect on the stable discharge power as a function of solution pH. Consequently, initial pH influences the chemical reaction in the liquid phase. The acid dissociation constant, \( pK_a \), of hydrogen peroxide is 11.6. However, at a pH of 7, the acetic acid is decomposed by the advanced oxidation process following Eqs. (5) and (6).

\[
\text{H}_2\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{HO}_2^- + \text{H}_3\text{O}^+ \quad (pK_a = 11.6) \quad (5)
\]

\[
\text{HO}_2^- + \text{O}_3 \rightarrow \cdot \text{OH} + \cdot \text{O}_2^- + \text{O}_2 \quad (6)
\]

Hydrogen peroxide and gaseous ozone were formed following Eqs. (7), (8), and (9).

\[
\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M} \quad (7)
\]

\[
\text{O}_2 + e \rightarrow 2\text{O} + e \quad (8)
\]

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (9)
\]

Dissolved hydrogen peroxide and gaseous ozone were detected (Figs. 8 and 9). However, dissolved ozone was not observed. In addition, the concentration of hydrogen peroxide decreased with time when the initial pH was high (Fig. 8). Since the discharge power was the same at different OH radical concentrations, the OH radical concentration at different pH should also be the same. Moreover, an equal amount of hydrogen peroxide should be produced, as indicated by Eq. (7). Since the concentration of hydrogen peroxide decreased, it is possible that the chemical reaction given by Eqs. (5) and (6) occurred.

As shown in Fig. 10, pH is almost the same in the operation time at pH of 7.5 and 9.0. It is interpreted from these results, indicating that the decomposition rate is the same at pH of 7.5 and 9.0.

The gas-phase production of HO\(_2\) radicals is given by Eq. (10) [13, 14].

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad (10)
\]

Possibly, there is another reaction for producing OH besides the dissociation of hydrogen peroxide. OH is produced from ozone in the liquid phase by advanced oxidation processing, where one of the initial reactions is given by the following equation [15].

\[
\text{O}_3 + \cdot \text{O}_2^- \rightarrow \cdot \text{O}_3^- + \text{O}_2 \quad (11)
\]

Thereafter, OH is generated by the following equations.

\[
\cdot \text{O}_3^- + \text{H}^+ \rightarrow \cdot \text{HO}_3 \quad (12)
\]

\[
\cdot \text{HO}_3 \rightarrow \cdot \text{OH} + \text{O}_2 \quad (13)
\]

\( \cdot \text{O}_2^- \) is in equilibrium with \( \cdot \text{HO}_2 \), as shown in Eq. (14) [16], and the abundance of both depends on pH. Since \( pK_a \) is 4.8, pH is greater than 4.8 and the abundance of \( \cdot \text{O}_2^- \) increases.

\[
\cdot \text{O}_2^- + \text{H}^+ \leftrightarrow \cdot \text{HO}_2 \quad (pK_a = 4.8) \quad (14)
\]

Therefore, our data suggest that acetic acid decomposes faster because \( \cdot \text{O}_3^- \) increases with an increase in solution pH. Presumably, \( \cdot \text{O}_2^- \) and \( \cdot \text{HO}_2 \) are generated in the gas phase by the DC corona discharge and then transferred to the solution by ion wind.

Moreover OH produced by a plasma device was observed at distances greater than 1 m from the discharge [17]. A possible mechanism is the chemistry of ozone shown in Eqs. (15), (12) and (13).

\[
\text{O}_3 + e^- \rightarrow \text{O}_3^- \quad (15)
\]

However, these reactions cannot explain about the pH dependency shown in Fig. 7. Future work will focus on the detection of gas-phase \( \text{O}_3^- \), \( \cdot \text{HO}_2 \) and \( \cdot \text{O}_3^- \) over the solution.

V. CONCLUSION

In this study, we decomposed acetic acid, a model persistent organic compound, by a DC corona discharge. The optimal discharge treatment conditions were investigated by varying the applied voltage and the initial pH of the solution. The following conclusions were drawn. The decomposition rate increases with the applied voltage. However, high efficiency treatment by changing the applied voltage is difficult because the decomposition rate does not increase with increasing discharge power, rather it increases by an increase in pH at the same voltage and discharge power. The results show that reactions in the liquid phase are important for water treatment using a DC corona discharge. To reveal reaction mechanism of the acetic acid during nondirect plasma process, further work is needed.

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REFERENCES


