Water Purification by Atmospheric DC/Pulsed Plasmas inside Bubbles in Water

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Abstract—Decomposition of acetic acid as a persistent material is successfully demonstrated using DC or pulsed barrier discharge reactor. The DC plasma is generated inside oxygen bubbles formed by the oxygen gas flow or the electrolysis between the metal and water electrodes. In case of oxygen flow, higher speed of gas flow is need for efficient decomposition due to the short life time of oxygen radical, however, almost no flow is need with water electrode system because the plasma directly reacts with the water. In the latter case the emission of OH radical generated in plasma was observed. The pulsed barrier discharge is generated inside bubbles of the foam flow in which the bubble shape and bubble fraction depends on the oxygen flow rate between the barrier electrodes. The flow rate is a crucial factor for the decomposition efficiency.

Keywords—Advanced oxidation technology, O radical, OH radical, DC discharge, barrier discharge

I. INTRODUCTION

Water treatment process has been developed using ozone, which is an effective oxidant for water treatment due to the high oxidation potential and its harmlessness to the environment. Recently, advanced oxidation technology is studied for a next generation of water purification processes using O and OH radicals. The oxidation potentials of these radicals are higher than that of ozone, and they can decompose persistent organics, such as dioxin, which cannot be decomposed by ozone. However, the lifetimes of these radicals are so short to utilize them effectively. Therefore, the direct radical generations by plasmas are widely researched [1], e.g., pulsed corona discharge [2-4] or pulsed arc discharge [5] in water, and discharge inside bubbles [6-8]. Other methods are corona discharges above water using wire electrode [9,10] or multi-needle electrode [11,12], hybrid gas-liquid discharge [13] and barrier discharge in atomized water in oxygen [14]. O radicals and OH radicals are generated by electron impacts with O₂ and H₂O molecules as in (1)-(2), and OH can be also generated by radical impact as in (3).

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\begin{align*}
e + O_2 & \rightarrow O + O + e \quad (1) \\
e + H_2O & \rightarrow H + OH + e \quad (2) \\
O + H_2O & \rightarrow OH + OH \quad (3)
\end{align*}
\]

We have studied radical generations in air [15,16] and water [17,18] using micro-hollow cathode discharge [19]. In this paper, two types of discharge system for water treatment were studied. One is the use of DC driven atmospheric micro plasma, and another is barrier discharge by pulsed power in foam which is the mixed state of gas and liquid. The plasmas were generated inside oxygen bubbles in water, and the decomposition of acetic acid in water was estimated.

II. EXPERIMENTAL SETUP

A. DC Discharge with Micro Channel

Two types of electrode were used for DC discharge system, and one of them, called “metal-metal electrode”, is shown in Fig. 1. GND electrode was metal sheet (thickness: 0.2 mm) with a small hole (diameter: 0.2-0.3 mm), and a H.V. electrode was separated with dielectric sheets (thickness: 0.5 mm). Stable plasma was generated between the electrodes, and O radicals are ejected from the plasma with high-speed oxygen gas flow. Though the lifetime of O radical is very short, the generated radicals can be injected into water directly by this way due to the high-speed radical flow. Oxygen (99.9%) gas flow rate was controlled by a mass flow controller. Positive high voltage was applied by a DC power supply and measured by a high voltage probe with a digital oscilloscope. Sample water was cooled constantly.

Fig. 2 shows the other type of electrode which was called “metal-water electrode”. A dielectric sheet (thickness: 0.5 mm) had a small hole (diameter: 0.1-1.0 mm) in this electrode, and water was used as electrode instead of metal. In this way, more aggressive reaction between the plasma and the water can be achieved, and the durability of electrode improves. This system needs no ballast resistor because the water has electric resistance. Plasma is generated inside bubble as shown in Fig. 2, and micro discharge channel of electrode makes it possible to generate stable plasma differently from the other bubble discharge methods in [6,7]. Oxygen gas is generated by electrolysis at discharge space, so plasma can be generated without gas flow from oxygen cylinder. This aspect is similar to the methods in [7], but our system is unique in its using micro discharge channel for easy plasma generation.

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Fig. 1. Schematic diagram of reactor for DC discharge (metal-metal electrode)

Fig. 2. Schematic diagram of reactor for DC discharge (metal-water electrode)

Fig. 3. Schematic diagram of reactor for barrier discharge system

B. Pulsed Barrier Discharge in foam flow

The diagram of reactor for barrier discharge is shown in Fig. 3. The reactor was composed of an inner glass tube (i.d.=18mm, o.d.=22mm) and an outer glass tube (i.d=26mm, o.d.=30mm). Oxygen bubbles were supplied with a babbler. High voltage electrode was placed inside or outside the inner glass tube and the reactors were called “double barrier type” and “single barrier type”, respectively. Pulsed high voltage was supplied using a DC power supply, a thyratron switch and an energy storage capacitor of 2 nF.

C. Measurement of TOC

Water treatment effect was examined with solution of acetic acid (CH$_3$COOH) as a persistent organic. Total organic carbon (TOC) concentration was measured by TOC analyzer (Sievers 810) for detecting the decomposition of acetic acid. Initial TOC concentration was 10 ppm, and the volume of sample water was 10 mL.

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\eta = \frac{w\Delta C}{mW\Delta t}
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where \( \eta \) [mol/J] is the energy efficiency for the decomposition of acetic acid, \( w \) [g] is the weight of the water sample, \( \Delta C \) is the reduction of TOC concentration, \( m \) [g/mol] is the weight of carbon in 1 mol (\( m=24 \) in case of CH$_3$COOH), \( W \) is the discharge power and \( \Delta t \) [s] is the processing time. The decomposition energy efficiencies with these methods were compared.

III. RESULTS AND DISCUSSION

A. DC Discharge System

Fig. 4 shows the discharge voltage with metal-metal electrode, and the voltage doesn't include the drop by ballast resistor. The voltage got high and unstable when the gas flow rate was higher than 800 sccm.
TOC concentration reduced by the discharge, and the decomposition rate became high with increasing gas flow rate. Fig. 5 shows the energy efficiency of decomposition of acetic acid molecule calculated by (4). The decomposition energy efficiency became high with increasing gas flow rate, and it was higher when the hole-diameter was smaller. The gas flow speed becomes high with decreasing hole-diameter at same gas flow rate. From these results, it seemed that high-speed radical flow is the most crucial factor in metal-metal electrode system because of the very short lifetime of O radical.

When metal-water electrode was used, plasma was generated inside a bubble, and it could be stably generated even if oxygen gas wasn't supplied from external oxygen cylinder because oxygen was generated at discharge space by electrolysis. The voltage with metal-water electrode at $d=0.1 \, \text{mm}$ and $Q=0 \, \text{sccm}$ is shown in Fig. 6. In this case, the voltage of the plasma couldn't be measured directly, so the observed voltage includes the voltage drop by the water. The observed voltage is changed by the conductivity of water because of the voltage drop by water, so it becomes low with increasing temperature of water. The values in Fig. 6 were measured when the water temperatures ($T_w$) were 40°C. The measured voltage when the solution of acetic acid, whose conductivity was 25$\mu\text{S/cm}$ at $T_w=27 \, ^\circ\text{C}$, was much higher than that using tap water.

The optical emission spectrum from the discharge is shown in Fig. 7. The emission of OH radical (309 nm) was observed. OH radicals were generated directly by the plasma.

The decomposition energy efficiency is shown in Fig. 8. The trend was much different from the result of metal-metal electrode. In this case, the high-speed gas flow is not critical factor unlike metal-metal electrode. It seems that the main factor of decomposition is not O radicals flow but rather OH radicals which are generated directly by the plasma. In this case, fast oxygen flow is not important in the treatment reaction. Although the efficiency was not so different from that by metal-metal electrode type, the metal-water electrode type has advantages over metal-metal electrode. One of them is that it does not need much oxygen gas, and another is the higher durability of electrode.
B. Pulsed Barrier Discharge System

Typical waveforms of discharge voltage and current in the double barrier type are shown in Fig. 9. The applied voltage was changed from 16 kV to 22 kV. The total input energy in discharge was 3.8-7.8 mJ/pulse with double barrier type reactor, and 13.4-22.7 mJ/pulse with single barrier type reactor. The energy consumption in single barrier type was larger than that in double barrier type due to the larger discharge current which was up to -40 A at peak. That is because series capacitance of single barrier type is larger than that of double barrier type and the high voltage electrode is in contact with water.

Fig. 10 shows the efficiency of acetic acid decomposition. The applied voltage was 22 kV and the oxygen gas flow rate was 800 sccm. In this case, double barrier type had higher effect for decomposition of acetic acid than single barrier type. The effect of decomposition depends on the state of foam flow, and the decomposition was not observed at low gas flow rate. When gas flow rate increases, the size of bubbles which flow between electrodes becomes large, and the area of discharge and the mixed state of gas-liquid change. In this system, the state of foam flow is an important factor. Large amount of gas volume is desired for effective discharge and OH radical generation.

IV. CONCLUSION

For advanced water treatment, some methods were examined, such as DC discharge and barrier discharge in water.

Two types of DC discharge electrode were used. One of them was metal-metal electrode, and it seems that high-speed radical flow is a crucial factor for effective utilization of O radicals. The other was metal-water electrode, and the decomposition effect didn't depend on gas flow rate because the main factor is OH generation by the plasma.

In barrier discharge system, the decomposition efficiency using double barrier reactor was higher than that using single barrier reactor. The volume balance between liquid and gas is a crucial factor for the decomposition rate of acetic acid. The efficiency was higher than that using DC discharge system.

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REFERENCES


