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学 位 論 文 題 目　Experimental and Numerical Analysis of Water Treatment Characteristics by Dielectric Barrier Discharge with Mist and Vapor Flows（ミスト流および蒸気流を用いた誘電体バリア放電による水処理に関する特性解析）
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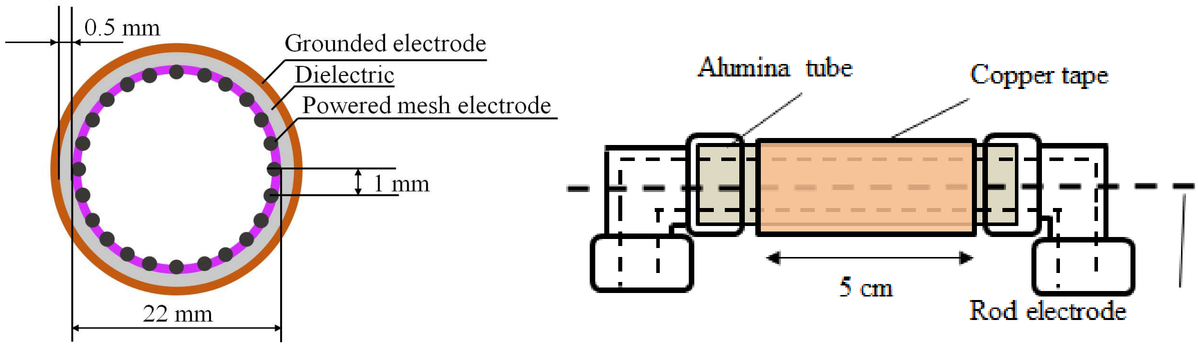
論文内容要約

In this dissertation, development of the novel water treatment methods using dielectric barrier discharge (DBD) in contacting with liquid are described. Two types of DBD tube, surface micro discharge (SMD) tube and coaxial DBD tube are originally developed. The cross section of SMD tube and configuration of coaxial DBD tube are shown in Figures 1 (a) and (b). Firstly, the numerical simulation model for surface micro discharge (SMD) tube including water droplets are proposed. Generation of reactive species in SMD tube are simulated and the results are compared with that of experiment. Secondary, a water treatment method using coaxial DBD tube with mist flow are developed. The processing solution is atomized and introduced into the DBD tube. Thirdly, a water treatment method using coaxial DBD tube with vapor flow are developed. The processing solution is vaporized and introduced into the DBD tube. The atomized or vaporized processing solution is passed through the discharge region only once with short residence time in this treatment. The detailed chemical reactions of non-thermal plasma with water are clarified using purified water as a processing solution. In addition, the characteristics of persistent organics decomposition are clarified using acetic acid solution as a processing solution. The main chapters in this dissertation are divided into 5 chapters, which are briefly summarized as follows.

In chapter 1, the background and purpose of this dissertation are introduced. Water is the most popular and basic liquid for human consumption, and it is necessary for our lifestyles and for industrial processes. 748 million people still relied on untreated drinking water and 2.5 billion people worldwide lacked access to improved sanitation facilities in 2012. Biological and chemical processes are generally used for water treatment. The main objective of water treatment is to remove organic pollutants, odor, and color. However, a large number of oxidizing agents contribute to secondary water pollution. Therefore, attention is being paid to advanced oxidation processes (AOPs) based on plasma technology, which are water treatment methods that use highly reactive species, especially the hydroxyl (OH) radical. Because of the short life times of these reactive species, to utilize them more effectively, plasma has to be generated near the solution. Various discharge methods that employ contact with water, such as direct discharge in water, above water, in bubbles, and spraying water into a discharge, have been studied. It was reported that a water treatment method that sprays a solution into a discharge shows high energy efficiency for dye decolorization. Therefore, a water treatment method that involves introducing a solution as a mist or vapor into a DBD



(a) (b)

Figure 1 Schematic illustration of SMD tube cross section (a) and coaxial DBD tube configuration (b).[1, 2]

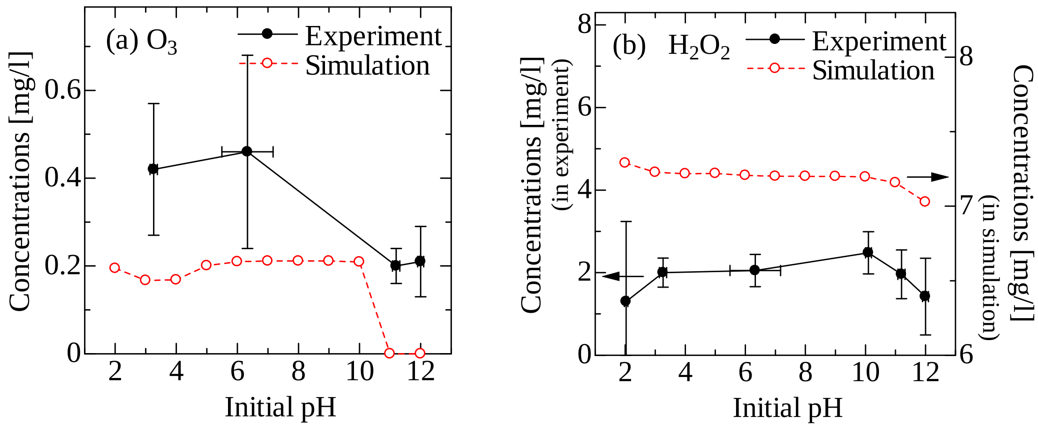


Figure 2 Plots of the concentration of dissolved ozone (a) and hydrogen peroxide (b) versus initial solution pH after 100 s of treatment.[1]

was developed in this study.

In chapter 2, a three step numerical simulation, including three phases (plasma, gas and liquid), is described for a wide range of initial solution pH values based on the experiment of the SMD tube with mist flow. The chemical reactions and diffusion between the plasma and gas phases are simulated by zero-dimensional simulation in the first step. The number densities simulated in the first step are used for the boundary condition of the 1-D cylindrical numerical simulation for the diffusion of chemical species in the SMD tube including water droplets. This simulation shows that OH radical dissolution is most enhanced at a few mm away from the tube wall. In the final step, the chemical composition in the droplets after the treatment was calculated by a 0-D simulation over a long time period. The simulated results of H_2O_2 and O_3 concentration are compared with experimental results as shown Figures 2 (a) and (b). The obtained results are summarized as follows:

1. The way of reactive species diffusion from plasma to droplet in SMD tube is simulated. The OH radical is effectively dissolved and generated in droplet which is few mm away from the tube wall.

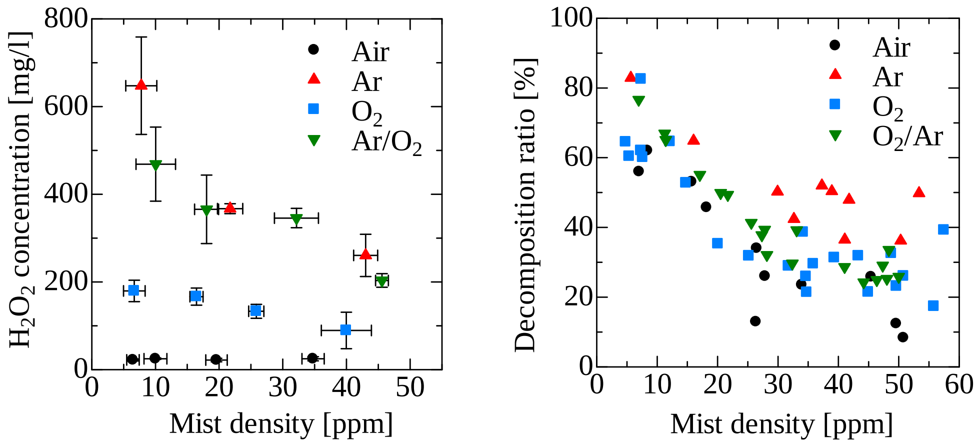


Figure 3 Hydrogen peroxide concentration and acetic acid decomposition ratio for various carrier gases.[2]

2. The dissolved ozone and hydrogen peroxide concentrations in simulation tentatively agree with that in experiment.
3. The pH dependence of reactive species dissolution is shown by experiment and numerical simulation.

In chapter 3, a water treatment method spraying a solution into a coaxial DBD tube was developed. Atomized processing solution (water or acetic acid solution) was introduced into the DBD tube as a mist flow and passing through the discharge area only once with carrier gases (air, Ar, O_2 or Ar/O_2 mixture gas). Because the discharge can be in contact with droplets directly, it is thought that the free radicals, which generally deactivated before reaching to liquid, can dissolve into droplets. Furthermore, the large specific surface area of fine droplets enhance the dissolution efficiency. Figures 3 (a) and (b) shows the characteristics of the hydrogen peroxide generation and acetic acid decomposition. Despite of the short life time, hydrogen peroxide is dissolved with high concentration and the acetic acid can be decomposed at most 80%. The obtained results are summarized as follows:

1. OH radical emission is observed with Ar, O_2 and Ar/O_2 mixture gas. Although OH radical emission was not observed for the air plasma, OH radical in the ground state is considered to have been generated because acetic acid is successfully decomposed with air.
2. The highest H_2O_2 concentration and H_2O_2 energy yield are obtained with Ar as a carrier gas. H_2O_2 cannot be dissolved into the droplet with air as a carrier gas because OH radical, which is one of the main source of H_2O_2, is consumed for NO_x oxidation.
3. Despite the short residence time, almost 80% of the acetic acid was decomposed using Ar, O2 or Ar/O_2 mixture gas with low mist densities.

In chapter 4, water treatment method, which involves vaporizing solution and introducing into a coaxial DBD tube with Ar carrier gas was developed. The DBD tube configuration was basically same with that in chapter 3. The hydrogen peroxide generation, electric conductivity and solution pH changes were measured as liquid properties. Acetic acid decomposition was

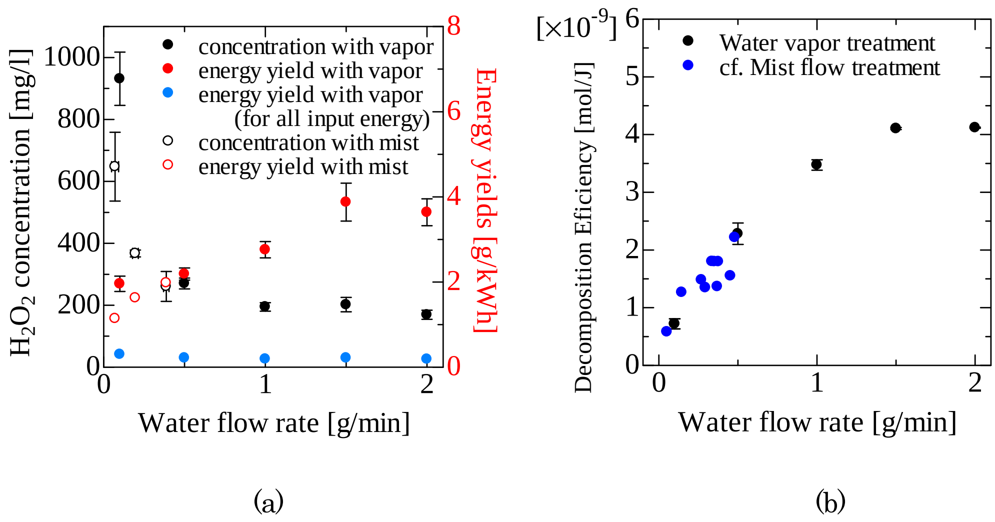


Figure 4 Characteristics of H_2O_2 generation (a) and acetic acid decomposition efficiency (b) with various water flow rate by water vapor treatment and mist flow treatment.

demonstrated to evaluate the characteristics of the persistent organics decomposition. In order to investigate the effect of water vapor flow rate, the supplying water flow rate was controlled by the liquid source vaporization system. Finally, the efficiency of hydrogen peroxide generation and acetic acid decomposition between water vapor treatment and mist flow treatment are compared. Figures 4 (a) and (b) shows the efficiency of hydrogen peroxide and acetic acid decomposition. water vapor treatment show higher efficiency rather than mist flow treatment because the water flow rate can be controlled in a wide range in water vapor flow rate.

1. The highest H_2O_2 concentration and energy yield are approximately 900 mg/l and 4 g/kWh, respectively in this system.
2. H_2 can also be generated by DBD with water vapor because of water dissociation reaction. However, the H_2 energy yields is lower than other various plasma system because H_2 generated in gas phase might be oxidized by H_2O_2 which is also generated in gas phase simultaneously.
3. The highest decomposition ratio of acetic acid reaches up to approximately 70 % with 0.1 g/min of water vapor flow rate. The highest efficiency (4×10^{-9} mol/J) is obtained at 1.5 g/min of water vapor flow rate.

In chapter 5, the conclusions of this dissertation are described with distinct results.

Reference

[1] T. Shibata and H. Nishiyama, Numerical Study of Chemical Reactions in a Surface Microdischarge Tube with Mist Flow Based on Experiment, J. Phys D: Appl. Phys., 2014, 47 (10), 105203.

[2] T. Shibata and H. Nishiyama, Acetic Acid Decomposition in a Coaxial Dielectric Barrier Discharge Tube with Mist Flow, Plasma Chem Plasma Process, 2014, 34 (6), pp. 1331-1343.