

Decomposition of Phenol in Water Using Water Surface Plasma in Wetted-wall Reactor

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Abstract— A scaling up of water surface plasma for decomposition of small amount of organic materials was tried using wetted-wall reactor. Water was flowed through the top edge of the cylinder (made of Aluminum or Plexiglas) forming water film inside the cylinder wall and was circulated by a peristaltic pump. Gas phase pulsed plasma was generated from the high voltage electrode located at the center of the cylinder. Two types of plasma mode, streamer and corona discharge plasmas, were observed between the center electrode and water surface on the cylinder surface in the wetted-wall reactor. Phenol was effectively decomposed in the case of streamer discharge generated in argon gas using aluminum cylinder. Water flow rate did not affect to the decomposition rate. Between four kinds of reactors, such as aluminum cylinder and Plexiglas cylinder with different ground electrode position, the aluminum cylinder with argon or oxygen was the most effective to decompose phenol.

Keywords— Water surface plasma, Wetted-wall reactor, Pulsed discharge, Water purification, Phenol decomposition

I. INTRODUCTION

In recent years, much research has been reported on the removal of trace contaminants in aqueous solutions. Most of these methods focused on hydroxyl radical production directly in the aqueous solution. This is because the hydroxyl radical is a very powerful, nonselective oxidant that has the potential to kill bacteria and to oxidize organic compounds. Recently, electrical treatment by applying high voltage in the aqueous solution, such as corona streamer discharge [1 – 4], spark discharge [5], has been used to degrade trace contaminants.

Water disinfection and the degradation of organic water pollutants using traditional UV-activated hydrogen peroxide and/or ozone has been reported. However, in recent years, a pulsed high voltage process for the treatment of hazardous chemical wastes in water has been developed [4, 6, 7]. Due to collisions of high-energy electrons with molecules, the intense electrical discharge dissociates water molecules to yield active hydroxyl radicals. These radicals combine with almost any organic chemical compound in a very efficient manner. These processes have a synergistic effect in the degradation of organic compounds and also in sterilization. Therefore, this method is considered to be a promising alternative for the treatment of pollutants.

Some researchers reported for decomposition of organic contaminants in water with plasma chemical reaction using pulsed discharge in water by submerged electrodes, or dc/ac discharge in gas phase on the water surface. Direct discharge in water produces some kinds of active species (mainly hydroxyl radical) that react with organic materials into carbon dioxide and water through

the intermediate compounds as mentioned above. On the other hand, corona discharge in air on the water surface also produces active species (different from the case of direct discharge in water) including ozone, hydroxyl radical, NO_x, and so on [8]. They dissolve into the water through the surface layer to react with organic materials in water, but lifetime of the hydroxyl radical is too short to reach to the water surface. The main cause of the reaction to decompose contaminants could be the action of long life active species.

High voltage pulsed streamer discharge in air formed on the water surface to decompose organic materials contained in water was tried [9 – 11]. Organic materials were decomposed by streamer paths that strike the water surface directly and by some kinds of active species produced by the pulsed discharge plasma in gas phase [11 – 14]. In the present study, using wetted-wall reactor, the water surface plasma was scaling up in some kinds of discharge state and environmental gas phase with varying operating conditions.

II. EXPERIMENTAL SETUP AND PROCEDURE

A. Flow System

Schematic of the experimental apparatus is shown in Fig. 1. Pulsed streamer discharge occurs between the center electrode (square wire or disk with different location) and ground electrode (Aluminum cylinder or Plexiglas cylinder with stainless steel foil), where the positive pulsed high voltage is applied to the high voltage electrode. Four kinds of reactors were used as shown in Fig. 2.

The sample liquid was circulated by peristaltic pump with a flow rate of 0.3 – 1.0 L/min, in which the water fell down along with the inner surface of the cylinder forming wetted-wall. Gas (air, oxygen, argon, or their mixture) flowed through the upper part of the reactor with flow rate of 0.3 – 1.0 L/min.

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Total volume of the sample liquid was 200 mL including 50-ppm phenol dissolved in water. Reduction of the phenol concentration was analyzed using high performance liquid chromatography (Shimadzu, LC-9A) with every 10 minutes. Air, argon, oxygen and their mixtures were used as surrounding gas to observe discharge characteristics.

B. Pulse Source

High voltage pulse generator with a stationary spark gap was used. From voltage controlled dc power supply, the pulse forming capacitor was charged through 20 M Ω resistor and then the stationary spark gap switch was sparked to make pulse voltage. The pulse forming capacitor, pulse repetition frequency, and applied voltage were 0.8 nF, 100 Hz, and 25 - 35 kV, respectively. The pulse voltage and current were measured using oscilloscope (Tektronix TDS3032) with a high-voltage probe (Tektronix P6015A) and a wide band current transducer (Pearson Electronics M411), respectively. Average current was measured by installing ammeter with parallel capacitor put into the ground line of the reactor.

Consumed electrical energy in the reactor was calculated by following equation:

$$W = U_{peak} I_{average} t / V$$

where W is consumed energy in this system [J/mL], U is pulse voltage [V], I is average current [A], t is treatment time [s], V is volume of sample liquid [mL], respectively.

C. Reactors

As shown in Fig. 2, four kinds of reactors were used. Basically water was flowed from the top of the cylinder edge that formed thin water film on the cylinder inner surface.

Reactor #a is made of aluminum cylinder and center electrode with 1 x 1 mm tungsten square wire. Inner surface of the cylinder was treated by corona discharge before starting the experiment to increase contact angle between aluminum and water.

Reactor #b has Plexiglas cylinder with point electrode located at the top of the cylinder, and grounded metal foil is glued at the bottom of the cylinder.

Reactor #c is almost the same as a reactor #b, but the discharge electrode is 20 mm diameter disk plate instead of the point electrode.

Reactor #d is modified reactor of the reactor #c, where the disk electrode is set at the middle of the cylinder and grounded electrodes are glued at the top and the bottom of the Plexiglas cylinder.

III. RESULTS AND DISCUSSION

Our object in this study was to generate non-thermal plasma near the surface of treated water to decompose phenol dissolved in water. Kim et al. reported that wetted-wall reactor for SO₂ oxidation or gas cleaning of flue gas is effective [15, 16]. To decompose aqueous phenol, we adopted wetted-wall reactor system. Reactor #a shown in Fig. 2 has the basic structure of our study, in which square wire are allocated at the center of cylindrical ground electrode. When oxygen gas or air

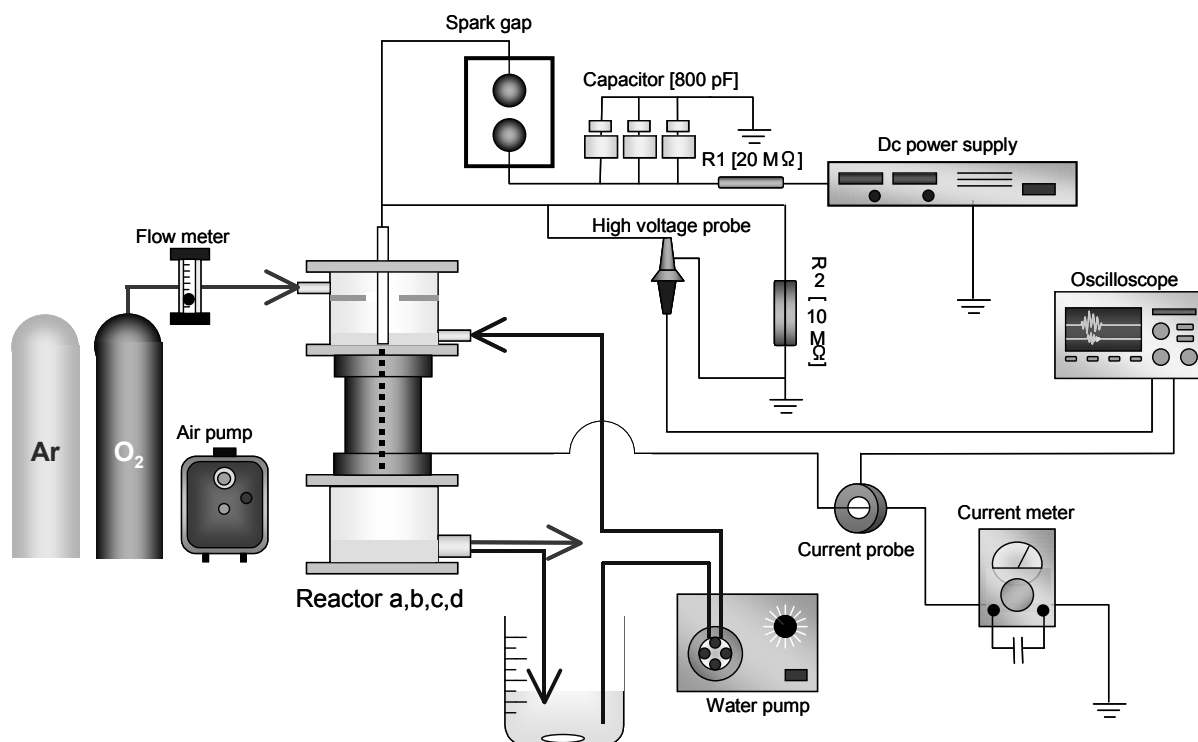


Fig. 1 Schematic diagram of organic materials decomposition system using wetted-wall reactor.

was introduced into the reactor #a and 30 kV of pulsed voltage was applied to the center wire, corona discharge can be generated around the wire electrode. On the other hand, argon gas as environmental gas generated streamer-like discharge from wire electrode toward the cylindrical ground electrode. However, the elongation of discharge path was not observed in this case because the short-circuit would be occurred through the water film. To extend the streamer discharge near the water surface, we have modified the combination of wire electrode and ground electrode, as called reactor #b, #c, and #d. In the

reactor #b, tip of wire was located at the top of Plexiglas cylinder, and ground electrode, which was stainless steel foil belt inside the Plexiglas cylinder, was placed at the bottom of the cylinder. The discharge path generated from the tip of the high-voltage wire electrode struck the surface of water, and then expanded toward the ground electrode. The streamer mode in this reactor, however, was unstable and occasional spark discharge was occurred. To maintain stable streamer discharge mode, aluminum disk electrode, which diameter was 20 or 26 mm, was used in stead of wire electrode in the reactor #c

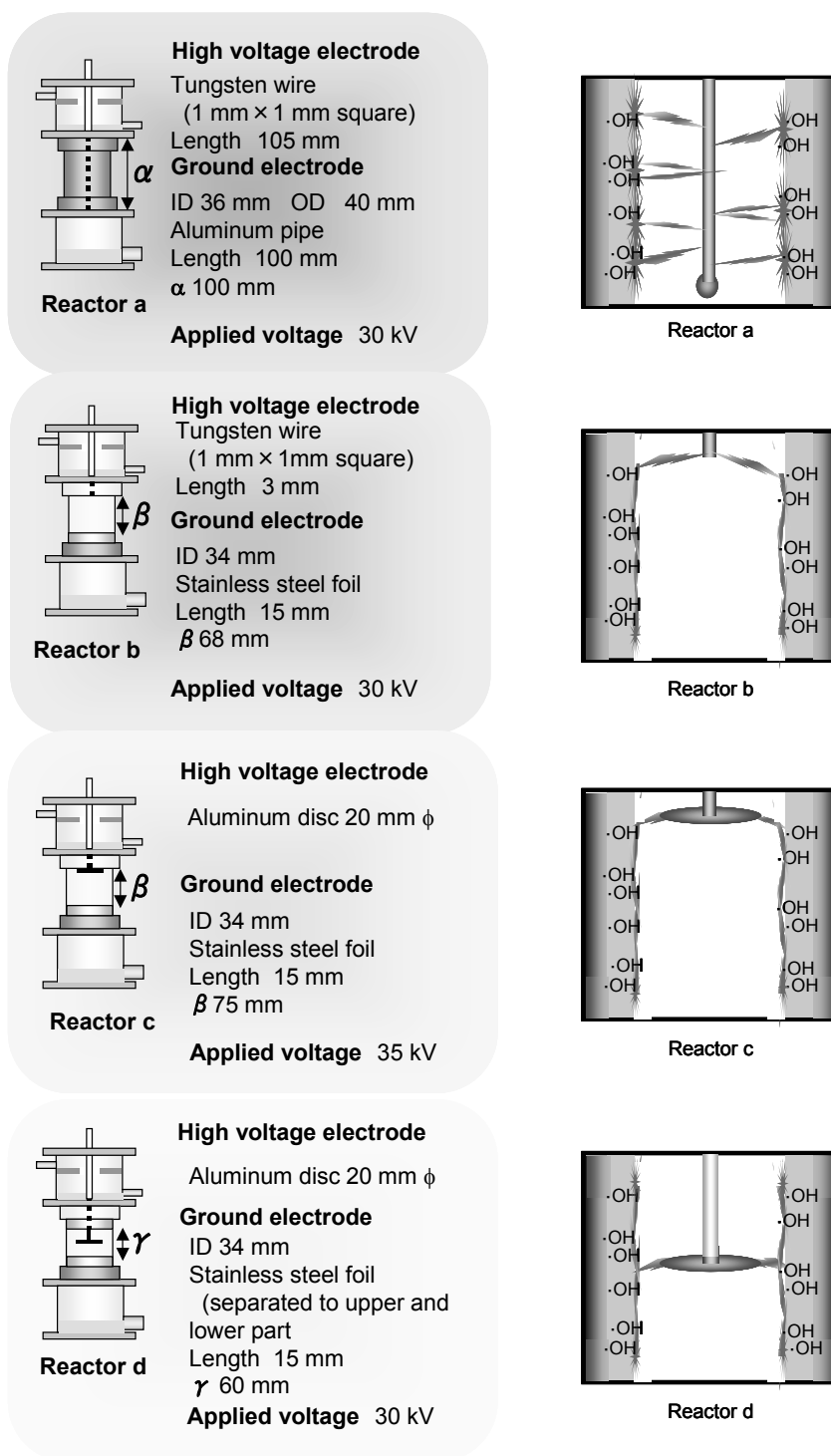


Fig. 2 Illustration of four kinds of reactors.

and #d to keep narrow electrode gap. In the reactor #d, disk electrode was placed at the middle of the Plexiglas cylinder and ground electrodes (stainless steel foil belt) were set at the top and bottom of cylinder. The discharge path generated at the edge of the disk electrode in reactor #d struck the surface of the water film and then prolonged toward the top or bottom ground electrode.

Using a reactor #a, water flow rate was varied to change the thickness of the water film. Decomposition rate of phenol was almost similar with changing the water flow rate between 0.3 and 1.0 L/min. When the gas content was varied, discharge mode changed as: (1) in the case of argon, streamer-like discharge occurred from the center wire electrode to the water surface, and decomposition rate of phenol was high (85 % decomposition at 60 min treatment). However, the streamer mode easily shifted to sparking mode, because the streamer discharge paths could touch to the surface of the aluminum cylinder through the thin water film. (2) in the case of air or oxygen, the discharge mode was corona, and the decomposition rate in the case of oxygen was a little less than the above case (1).

Streamer discharge mode was not observed with flowing the oxygen or air in the reactor #a because of a wide electrode gap between wire and cylinder. Using the reactor #b, a steady streamer discharge was expected between point and metal foil electrodes. However, no remarkable result was obtained on the decomposition of phenol.

Using a disk plate with sharp edge as a discharge electrode, it was possible to keep streamer mode even in the case of air, oxygen, and argon gases. In the streamer mode, the decomposition rate of phenol was higher in argon (40 % after 60 min) than the case of oxygen (25 %). It was because the discharge paths strike the water surface and produced active species by direct dissociation of water molecules.

Figure 3 shows the effect of environmental gases (oxygen, argon, and air) in the discharge zone when reactor #d was used, in which gas flow rate was 1 L/min. As shown in Fig. 3, introducing argon gas was effective than the other gases. The discharge plasma generated in these environmental gases was quite different from each other obviously. The discharges in argon gas were intense and blue colored, though weak discharge paths were observed in the case of air and oxygen. Ozone, which reacts with phenol, could be generated in the cases of air and oxygen. However, the decomposition rate in the case of argon was higher than the cases of air and oxygen. It was suggested that direct dissociation of water molecules that results in the generation of OH radicals was effective in our experimental apparatus.

It is important to check the effect of electrical conductivity of the liquid on the decomposition of phenol because wastewater containing phenol has various conductivities. Fig. 4 shows the decomposition rate when the conductivity was varied with adding NaCl in the liquid using reactor #d. Although most effective point could be found around 9.2 mS/cm, effective decomposition of dissolved phenol could be achieved

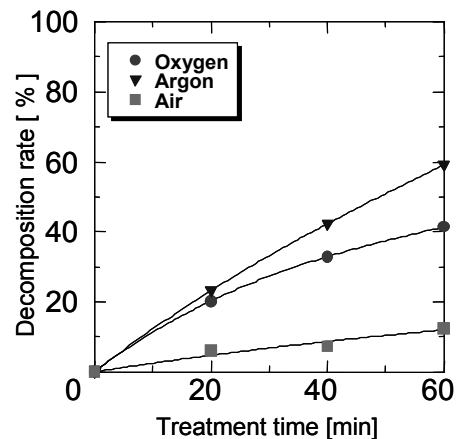


Fig. 3 Effect of gas component on decomposition of phenol using reactor #d, where gas flow rate: 1 L/min, water circulation rate: 0.8 L/min.

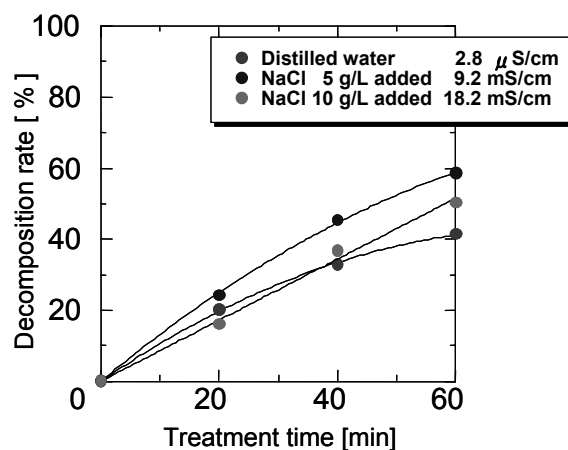


Fig. 4 Effect of electrical conductivity of water to decomposition rate, where operating conditions are same as Fig. 3.

without being dependent on the solution conductivity. Considering the electrical conductivity of tap water is about 0.15 mS/cm and wastewater is 0.5 - 2 mS/cm, the present wetted-wall reactor is seemed to be applicable to treat tap or waste waters.

In the reactor #d, diameter of the disk electrode was changed from 20 to 26 mm in order to make electrode distance shorter. Distribution of the discharge paths (26 mm) were almost the same of the case of 20 mm, and decomposition of phenol was similar in both cases.

Finally Fig. 5 shows comparison of decomposition rate of phenol with varying reactors #a to #d in the case of argon (A) and oxygen (B), respectively. Discharge modes were corona (oxygen gas in reactor #a) and streamer (other cases). When reactor #c or #d was used, discharge path in argon gas was strong and elongated on the water surface than that in oxygen gas. The decomposition of phenol could be depended on the region of discharge plasma near the water surface, and longer streamer discharge generated in argon resulted in the higher decomposition rate of phenol than in oxygen

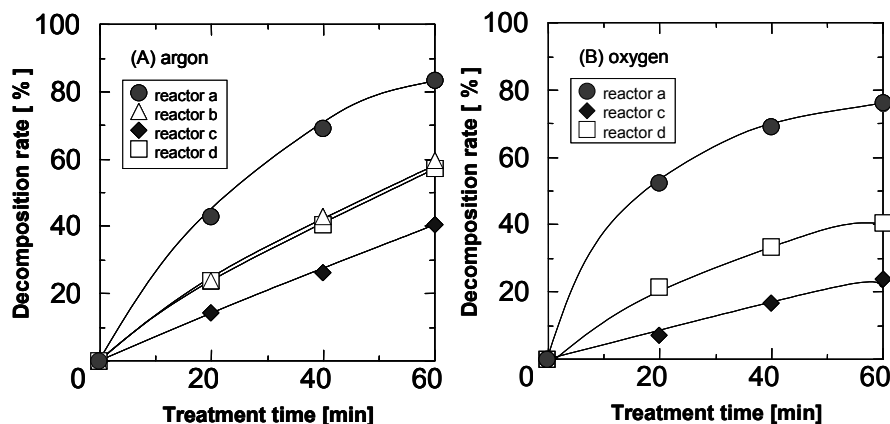


Fig. 5 Comparison of four kinds of reactors in argon (A) and oxygen (B), where operating conditions are same as Fig. 3.

(Fig. 5 (A) and (B)). On the other hand, in the case of reactor #a, the decomposition rates in argon and oxygen were almost the same (Fig. 5 (A) and (B)) though the strength of plasma was quite different between corona in oxygen and streamer in argon. Corona discharge in oxygen gas would generate ozone efficiently, and the ozone seemed to contribute the decomposition of phenol in water. On the other hand, it has been known that the decomposition rate of phenol is depended on the pH of treated solution [13]. A study of the pH effect should be necessary in further study in our wetted-wall reactor system.

In this study, we demonstrated the decomposition of phenol in water by using four types of wetted-wall plasma reactor. Reactor #a was most effective for phenol decomposition in the cases of argon and oxygen as the environmental gases, and our system seems to be applicable to various wastewater treatment

IV. CONCLUSION

Water surface plasma in wetted-wall reactor was generated by pulsed high voltage discharge with varying some kinds of reactor design and gas phase. The discharge paths were distributed to the water surface and phenol was decomposed by active species that were formed at the water surface due to the discharge plasma extension.

- Water flow rate did not affect to the decomposition rate.

- In the streamer discharge mode, the decomposition rate was high in the case of argon gas.

- Between four kinds of reactors, using "reactor #a" with argon or oxygen was the most effective to decompose phenol.

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