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Comparison of relative concentration of ozone and oh radical produced in discharge space with water droplets

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We have studied a water treatment by spraying into a pulsed discharge space in air. OH radical produced by the discharge decomposes refractory organic compounds because of its high oxidizing power. The well-known process of OH radical production is dissociation of water molecule by electron collision. However, we expect almost all OH radicals are produced via reactions including ozone. To confirm it, relative concentrations of ozone and OH radical, reacting with organic compounds were measured using the indigo method and a florescence method using the disodium salt of terephthalic acid (NaTA), respectively. The measurements were carried out regarding pulsed discharge of repetition rate of 17 and 300 pulse per second. Concentrations of ozone and OH radical increased by higher repetition rate. However, energy yields for those production decreased by higher repetition rate. A possible reason is the increase of decayed ozone. This result shows the possibility that OH radical is produced by the reaction with ozone.

Keywords: *Pulsed power, pulsed discharge, OH radical, ozone, indigo method, terephthalic acid, fluorescence iner transformer driver, plasma water treatment, pulsed streamer discharge, pulsed power control.*

1.0 INTRODUCTION

We have studied a water treatment by spraying into a pulsed discharge space in air, to decompose refractory organic compounds included in industrial waste water [1-4]. Decomposition of organic compounds is caused by OH radical and ozone which are generated by the discharge. Especially, OH radical with a very high oxidizing power, decomposes dioxins and other persistent substances. Therefore, more OH radicals need to be produced by less energy and to be reacted with organic compounds which should be treated, for effective decomposition of refractory compounds. To realize that, we have investigated detailed processes of OH radical production. Generally, OH radical is produced by dissociation of a water molecule by electron energy, as follow.

$$H2O + e \rightarrow \cdot H + \cdot OH + e \quad ...(1)$$

From past experiments for detection of OH radical by Luminol reaction, the discharge in oxygen produced much more OH radicals than the discharge in argon. That means that few OH radicals generated by the equation (1) react to organic compounds in water directly, and there are other OH production processes with oxygen and ozone. From some literature [4, 5], the following reactions are considered.

$$O_3 + \cdot OH \rightarrow HO_4\cdot \rightarrow HO_2\cdot + O_2 \quad ...(2)$$

$$HO_2\cdot \leftrightarrow H^+ + \cdot O_2^- \ \ pKa = 4.8) \quad ...(3)$$

$$\cdot O_2^- + O_3 \rightarrow \cdot O_3^- + O_2 \quad ...(4)$$

$$\cdot O_3^- + H_2O \rightarrow \cdot OH + O_2 + OH^- \quad ...(5)$$

At above process, OH radical is generated via

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reactions with ozone. However, those reactions have not been confirmed by experiments yet. To confirm that, we have investigate the effect of ozone concentration to OH radical production. As one of that investigations, ozone and OH radical dissolved in water, were measured using the indigo method and a fluorescence method, and yields of ozone and OH radical produced by high and low pulse repetition rate were compared.

2.0 WATER TREATMENT SYSTEM

A used water treatment system is shown in Figure 1. The system is a method spraying waste water droplets into a pulsed discharge space, and is composed of a reactor module and a water tank module. In the reactor module, wire-to-cylinder coaxial electrodes are installed in the reactor cylinder, with an inner diameter of 40 mm. The wire electrode is made of stainless steel wire (diameter = 0.28 mm), and the cylindrical electrode is made of stainless steel wire mesh (diameter = 38 mm, length = 300 mm, and mesh size = 1.2 mm × 1.2 mm).

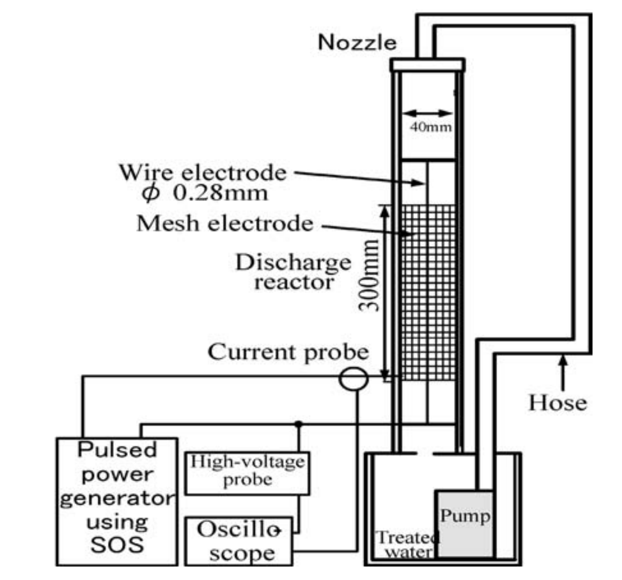

FIG.1. REACTOR FOR THE WATER TREATMENT USING PULSED DISCHARGE GENERATED IN AIR BY SPRAYING WATER DROPLETS.

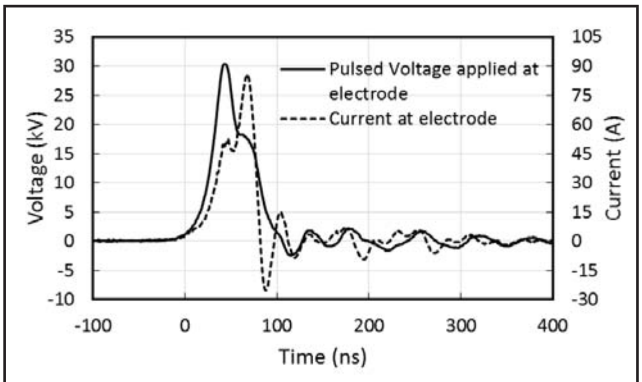

FIG. 2. VOLTAGE AND CURRENT WAVEFORMS AT ELECTRODE DURING WATER TREATMENT.

The water tank is provided with a pump for circulation of treated water. The treated water is transformed to droplets by the nozzle and sprayed into the reactor from the top of the lid. The diameter of the droplets is 0.5-1.5 mm.

3.0 OZONE MEASUREMENT BY INDIGO METHOD

As a method of measurement of ozone concentration, indigo method is adopted. This is a method for measuring ozone from absorbance of indigo trisulfonate solution, which is decreased by ozone. The indigo molecule contains only one C=C double bond which can be expected to react with ozone with a very high reaction-rate constant. Ozone rapidly and stoichiometrically (1:1) decolorizes indigo trisulfonate in acidic solution. The decrease in absorbance is linear with increasing ozone concentration over a wide range. The proportionality constant at 600 nm is 20,000 $L \cdot Mol^{-1} \cdot cm^{-1}$.

TABLE 1

CONCENTRATION AND YIELD OF OZONE IN CASE OF PULSED DISCHARGE OF 17 PPS AND 300 PPS

	Repetition rate	
	17pps	300 pps
Ozone concentration per second (ì M/s)	0.11	1.20
Ozone yield (mol/kWh)	0.62	0.36

To measure ozone concentration in the discharge space, indigo solution which consists of potassium indigo trisulfonate, 1.33 g/L of phosphoric acid, and 1 g/L of sodium dihydrogen phosphate, was sprayed into the discharge space at the flow rate 10 L/minute. Concentration of ozone was calculated from the difference between absorbance of the treated solution and of the untreated one, by using the following equation [6],

$$\text{Ozone concentration} = \Delta A/20000 \text{ (mol/L)}$$

$$= (\Delta A \times 48)/20 \text{ (mg/L)} \qquad ...(6)$$

where ΔA=Difference in absorbance between treated untreated indigo solutions. Total volume of the solution was 1.5 L. A typical pulsed high voltage and discharge current which were applied to the electrode are shown in Figuer 2. The ozone measurement was carried out regarding pulsed discharge of repetition rate of 17 and 300 pulses per second. When the repetition rate was 17.5 pps and 300 pps, the concentration of the indigo trisulfonate was 15.4 and 30.8 mg/L, respectively.

The result is shown in TABLE 1. That shows that ozone yield decreases by increasing repetition rate, although ozone concentration in the plasma reactor increases.

4.0 OH RADICAL MEASUREMENT BY FLUORESCENCE METHOD

In order to measure the OH radicals, a fluorescence method was adopted [7]. The probe selected for the fluorescence experiment is the disodium salt of terephthalic acid (NaTA). NaTA reacts with OH radicals to form 2-hydroxyterephthalic acid (HTA), that gives a bright stable fluorescence. When the solution containing NaTA and HTA molecules is irradiated by UV light (λ=310 nm), HTA molecules emit light at λ=425 nm, while NaTA molucules do not. In this measurement, 2L NaTA solution of 2 mM was sprayed into the pulsed discharge space at 10 L/Minute of flow rate. After treatment, the emitted fluorescence spectrum was recorded. For fluorescence emission from HTA, a LED (LLS 310, λ=310 nm, Sabdhouse Design) was used. The fuorescence spectrum was recorded through an optical fiber by a spectrometer (FLAME-S, Ocean Optics). In order to quantify the HTA concentrationin in water, a calibration curve for known HTA concentration was used. Obtained molar concentration of HTA corresponds to molar concentration of OH radical reacted with NaTA. Those measurements were carried out regarding the pulsed discharge of 17 and 300 pps.

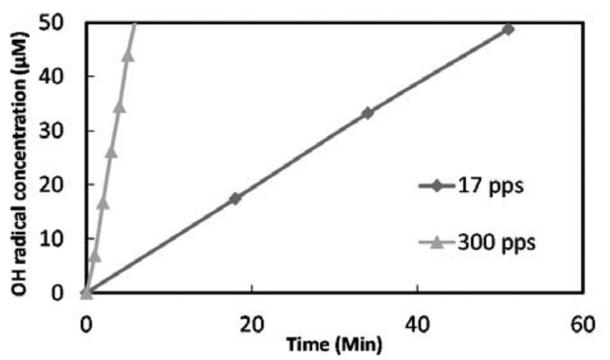

FIG. 3. OH RADICAL CONCENTRATION REACTED WITH NATA, AT VARIOUS TREATMENT TIME.

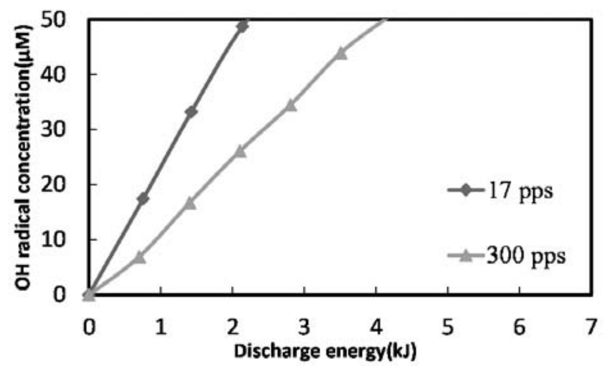

FIG 4. RELATION BETWEEN OH RADICAL CONCENTRATION AND TOTAL DISCHARGE ENERGY IN THE REACTOR.

Figure. 3 shows OH radical concentration reacted with NaTA, at various treatment time. By increasing repetition rate, OH radical concentration at same treatment time increased. Figure. 4 shows the relation between OH radical concentration and total discharge energy in the reactor. OH radical concentration increased with an increase of total energy, however, an increase of high repetition rate led to low yield for OH radical production. Calculating from Figure. 4, the yields are 0.030 and 0.017 M/kWh when the repetition rate is 17 and 300 pps, respectively.

5.0 DISCUSSION

Both energy yields for ozone and OH radical production decreased by increasing repetition rate from 17 to 300 pps. Ozone which does not react with organic compounds until next pulsed discharge, increases by the decrease of period of pulse, and the remained ozone is decayed by the electron or O radical, generated by the next pulsed voltage, as follows.

$$O_3 + e \rightarrow O_2 + O \quad ...(7)$$

$$O_3 + O \rightarrow 2O_2 \quad ...(8)$$

That is a possible reason of the decrease of the ozone production yield by high repetition rate.

On the other hand, OH radical is so short life time that there is no OH radical remained until next pulsed discharge even if repetition rate is 300 pps. Therefore, if OH radical is produced by reaction of the equation (1) only, the yield of OH radical is not affected by the repetition rate. However, if OH radical is produced by the equation (2)-(5) including ozone reactions, the yield decreases by high repetition rate, owing to the decrease of the yield of ozone production. Hence, this result shows possibility that the equation (2)-(5) is caused in the discharge.

6.0 CONCLUSION

Concentrations of ozone and OH radical, produced in a pulsed discharge space with water droplets was measured by the indigo method and the fluorescence method, and the concentrations and the yields of those produced in the case of 17 and 300 pps were compared. The yields of those decreased in the case of higher repetition rate. From the result, the possibility that OH radical is produced by the reaction with ozone, is confirmed.

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