

Detection of Free Radicals Produced by a Pulsed Streamer Corona Discharge in Solution Using Electron Spin Resonance

Mitsuru Tahara
Textile and Polymer Section
Technology Research Institute of
Osaka Prefecture, Japan
phone: (81)725-51-2580
e-mail: tahara@tri-osaka.jp

Masaaki Okubo
Dept. Mechanical Engineering
Osaka Prefecture University, Japan
phone: (81) 72-254-9230
e-mail: mokubo@me.osakafu-u.ac.jp

Abstract—Experiments are carried out on the detection of free radicals in the plasma induced by a pulsed electrohydrodynamic discharge using electron spin resonance (ESR) measurement. In addition, decolorization of reactive dye (C. I. Reactive RED 106) solution is investigated as a related topic. The plasma reactor is a barrier-type and consists of a stainless needle electrode inside the solution and quartz glass solution container (200 mL) around which the aluminum film grounded electrode is wrapped. A positive pulse high voltage of +35 ~ 65 kV is applied between the electrodes of the plasma reactor. Streamers in solution are induced and the onset voltage of the streamer increases with increase in the electrical conductivity of the solution. In the ESR measurements, a radical trapping agent of DMPO (5, 5-Dimethyl-1-pyrroline N-oxide) is used. When the plasma is solely applied, hydroxyl radical is scarcely detected with the ESR and the decoloration of the reactive dye does not occur because the lifetime of hydroxyl radical is too short to be detected although the generation of hydrogen peroxide H_2O_2 is confirmed. However, after adding iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) including Fe^{2+} before the plasma application, the ESR spectra for hydroxyl radical is clearly detected and the dye solution is decolorized dramatically. It is found that hydrogen peroxide is initially generated by the plasma and is decomposed by Fe^{2+} (Fenton reaction) or under higher pH (~10) condition to form hydroxyl radical in relatively slow chemical reactions. Furthermore, both hydroxyl and hydrogen radical can be detected when the plasma is applied for the solution including DMPO which is added before the plasma application.

I. INTRODUCTION

Recently, it is clarified that a pulsed power technology which can easily generate extremely high voltage in very short time (an order of nanosecond), is very effective to the treatment of hazardous gas [1]–[3], and plasma treatment for NO_x , SO_x , PM (particulate matter) [1], VOC (volatile organic compounds) [2], odor substances and dioxin [3] has been investigated. On the other hand, as it is also possible to generate plasma stably in the water or electrohydrodynamic discharge plasma using pulsed power, researches on application concerning solution purification [4], sterilization [5], [6], and decolorization

[7]–[9] using the technology have been extended [4]–[14]. However compared with researches of gas-phase plasma, they have relatively shorter history. Therefore, we cannot say that basic phenomena such as decomposition reaction mechanism in solution, type of generated gas by discharge in solution, difference between electrolysis reaction and plasma reaction, and phase-change inside the plasma are completely clarified. Especially we have relatively a few cases of research on radical identification in electrohydrodynamic discharge induced plasma although chemical probes [10], [11] and optical analysis [12] are applied to do it.

In the present paper, we reported experimental results on decolorization of reactive dye solution which is relatively strong dye and cannot be decompose only by the plasma, and detection of free radicals produced by a pulsed electrohydrodynamic discharge using electron spin resonance (ESR) measurement.

II. EXPERIMENTAL APPARATUS AND METHOD

A schematic diagram for the experimental setup is shown in **Fig. 1**. A Pyrex glass beaker (inner diameter = 6.24 cm, thickness of the glass = 1.8 mm, liquid volume = 200 mL) is filled with pure water or dye solutions. A part of stainless steel needle electrode (diameter = 1 mm, the whole region except the tip is covered by PTFE plastics) is immersed at 3 cm below the water surface and used as a positive electrode. Aluminum foil is wrapped around the outside and bottom surfaces of the beaker as grounded electrode. A pulse high voltage is applied between the electrode using sphere gap type direct-current pulse high-voltage electric power source (gap = 4 ~ 6 mm, Masuda Research Inc., Japan) with applied voltage output of 10 to 65 kV, pulse width of 500 ns and pulse frequency of 120 pps (pulse per second, 120Hz). In the circuit, protect resistance = $3\text{M}\Omega$, load resistance = $50\text{ k}\Omega$, condenser capacitance = 1 nF , and inductance = 4.7 mH . A photograph of the circuit is shown in **Fig. 2**. The voltage and current waveforms are measured with a digital storage oscilloscope (Yokogawa Electric Co. DL1740) through a high voltage divider (Nissin Pulse

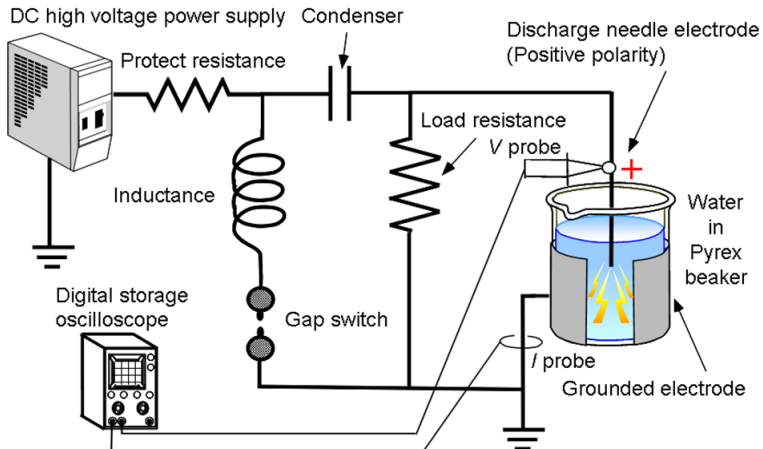


Fig. 1 Schematic diagram of experimental setup for liquid-phase plasma

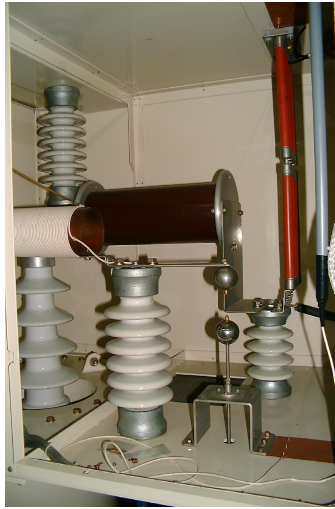
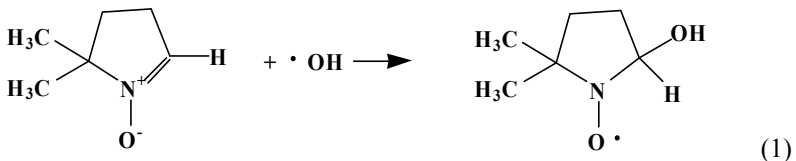


Fig. 2 Photograph of the circuit for high-voltage power supply

Electronics Co., Ltd., 5000:1 high voltage probe, EP-100K) and a current probe (Pearson Electronics, Inc. 2878). The plasma reactor is a barrier-type electrohydrodynamic discharge plasma one, and stable discharge can be realized with the dielectric barrier between the electrodes.

ESR measurement is conducted with a free radical monitor apparatus using electron spin resonance under a magnetic field (JEOL Ltd., Japan, JES-FR30). The measurement is carried out mainly under the following condition: microwave output power of 4 mW, resonance frequency of 9.425 GHz, magnetic field strength of 336.5 mT, and sweep width of the magnetic field of 5.000 mT, and sweep time of 2.0 min. All data are averaged three times. After the plasma application, solution of 0.13 mL is sampled from the beaker and put into a measurement container. The sample is placed inside the cavity resonator of the ESR apparatus for the measurement. The period between the end of the plasma application and the beginning of the ESR measurement is less than 3 min. Manganese (Mn) marker is used to calibrate the measured data. DMPO (5.5-Dimethyl-1-pyrroline N-oxide, $C_6H_{11}NO$) is used as a radical (spin) trapping agent or radical stabilizer because the lifetime of radicals is generally very short ($\sim \mu s$). The concentration of added DMPO is 2 g to 200 mL liquid throughout the experiments. When DMPO reacts with hydroxyl radical, a spin adduct of DMPO-OH with longer lifetime ($\sim hr$) is generated according to the chemical reaction (1):



The treated liquids are as follows: pure water and solutions of reactive dye (C. I. Reac-

tive RED 106, $C_{25}H_{18}O_8N_3S_4Na$) with the concentration of 0.1 g/L, 0.05 g/L, and 0.01 g/L. The electrical conductivity is measured with a measuring apparatus (Hach Co., Japan, CO150). The optical absorption of the dye solution is measured with optical emission spectroscopy analyzer (Shimadzu Corporation, Japan, UV-1600PC).

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Generation of plasma induced by electrohydrodynamic discharge

First, a minimum voltage to generate plasma in distilled water (electrical conductivity = $2.6 \mu S/cm$) is determined. For instance, when the applied voltage is 50 kV (pulse width of 520 ns and pulse frequency of 120 pps), a series of streamer of the electrohydrodynamic discharge is observed as shown in **Fig. 3**. Significant amount of small bubbles are generated in the discharge. The components of these bubbles are investigated using a gas de-

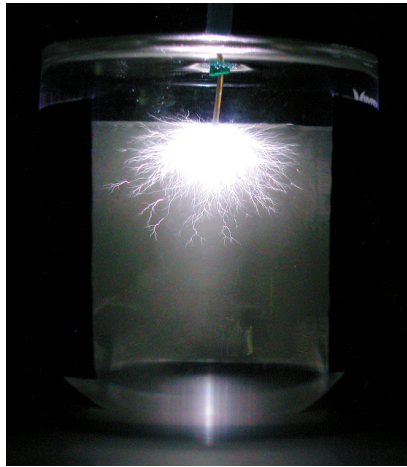
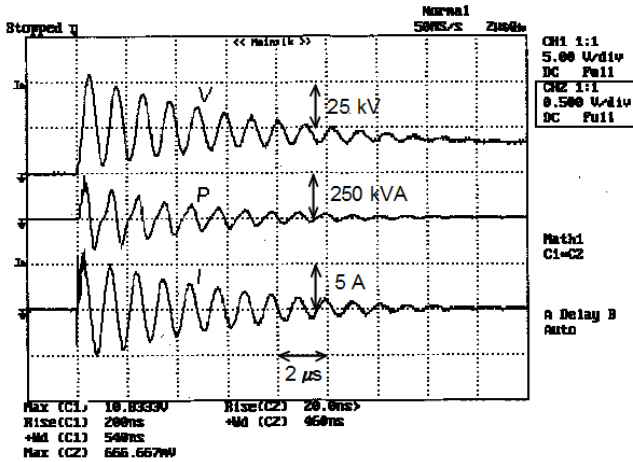
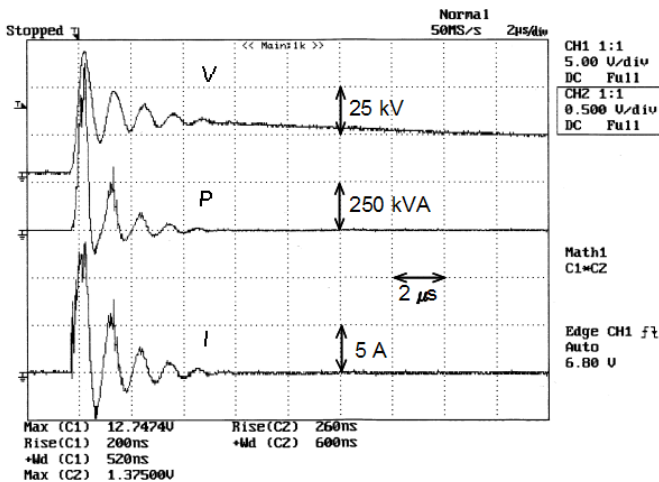


Fig. 3 Photograph of plasma induced by the electrohydrodynamic barrier discharge

tection tube (Gastec Corp.). As a result, ozone (~ 60 ppm) and hydrogen ($\sim 0.1\%$) are confirmed.

Figure 4 shows measured waveforms of the voltage V , current I , and instantaneous power P for distilled water. The self-attenuating pulse discharge is induced with the spark-gap. The power to the reactor is calculated by multiplying energy per single pulse with the pulse frequency and estimated as 37.8 W. The rate of the water temperature increase is approximately $2 \text{ }^\circ C /min$. Next, electrohydrodynamic discharge inside reactive dye solution is examined. In the dye solution with higher electrical conductivity, streamer discharges are not stable, but periodic when the applied voltage is 50 kV. The filamentous discharge or streamers almost stop with increase in the electrical conductivity. On the conditions of the dye solutions with the concentration of 0.05 g/L (electrical conductivity = $51 \mu S/cm$) and the applied voltage of 64 kV (pulse width of 540 ns and pulse frequency at 120 pps), a series of streamer discharges is observed. The waveforms of pulse high-voltage for the dye solution are shown in **Fig. 5**. The discharge power is estimated as 55.3 W

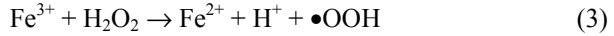
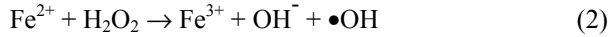
Fig. 4 Waveforms of the voltage V , current I , and instantaneous power P for distilled waterFig. 5 Waveforms of the voltage V , current I , and instantaneous power P for the dye solution (C. I. Reactive RED of 0.5g/L)

B. Optical absorption by plasma application to dye solution under existence of Fe^{2+}

After electrohydrodynamic discharge induced plasma is generated for a certain period (maximum 25 min) in the dye solution with the concentration of 0.05g/L, the change in the optical absorption at the wavelength of 400 ~ 500 nm is measured. As a result, it is known that decolorization scarcely occurred by the application of plasma only. Because of more stable structure, the decolorization of reactive dye could be more difficult compared with the other dye such as direct dye and acid dye treated in the references [8], [9] which is

relatively easily decomposed by the plasmas only. It is considered that most radicals, especially $\bullet\text{OH}$ is converted to H_2O and H_2O_2 before it decolorize the dye. Although the decolorization [7]–[9] is achieved by cleavage of double bond among color components by radicals such as hydroxyl radical ($\bullet\text{OH}$), perhydroxyl radical ($\bullet\text{OOH}$), and superoxide anion ($\bullet\text{O}_2^-$), relatively large amount of them is required.

In order to generate much hydroxyl radical, the following Fenton reactions (2) and (3) is tested by adding iron (II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).



After adding 0.01 g/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the dye solution with the concentration of 0.05 g/L, plasma applications are conducted for 0 – 25 min. The result on the changes in optical absorption is shown in **Fig. 6**. It is known from this graph that the decolorization advances and optical absorption near 500 nm decreases with increase in the plasma application time. However, when the application time excels 25 min, streamer discharge becomes unstable and periodic, resulting in extinction. The phenomenon may be caused by the gradual increase in electrical conductivity under the influence of ion and other agents newly generated by the electrohydrodynamic discharge.

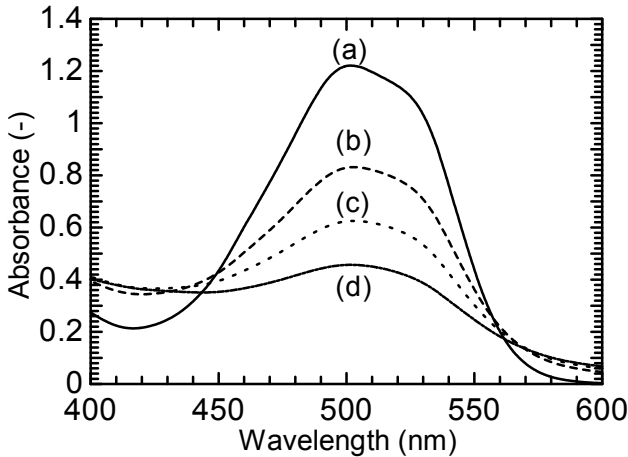


Fig. 6 Change in optical absorbance of the mixed solution of Reactive RED 106 (0.05 g/L) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.01 g/L) treated by the plasma for various periods: (a) no treatment (b) 10 min treatment, (c) 20 min treatment, and (d) 25 min treatment

Figure 7 shows time-dependent changes in optical absorption of the same solution as that of **Fig. 6** after the application for 10 min. It is known from this graph that the decolorization advances and the optical absorption decreases with increase in the time. The result shows that the existence of Fe^{2+} significantly affect the decolorization, and can supply enough radicals to decolorize the reactive dye according to the Fenton reaction

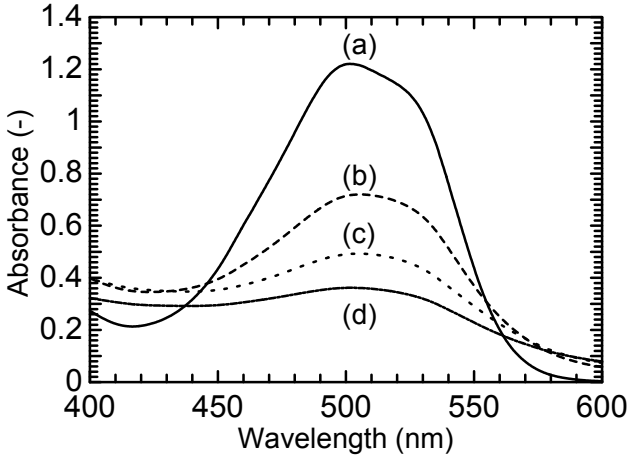


Fig. 7 Change in optical absorbance of the mixed solution of Reactive RED 106 (0.05 g/L) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.01 g/L) treated by the plasma for 10 min. (a) untreated (b) immediate data after the plasma application, (c) 1 hr after the plasma application, and (d) 1 day after the plasma application

[13]–[15].

Next, after dye solution with lower concentration of 0.01 g/L is treated by the plasma, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ of 0.1 g/L is added. The result on the optical absorption is shown in **Fig. 8**. In this experiment, the plasma application is followed by $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ addition. This procedure is different from those in **Figs. 6** and **7** where the application is done for the solution previously mixed with dye and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution. The result shows that the optical absorption at the wavelength of 500 nm disappears and the solution is almost completely

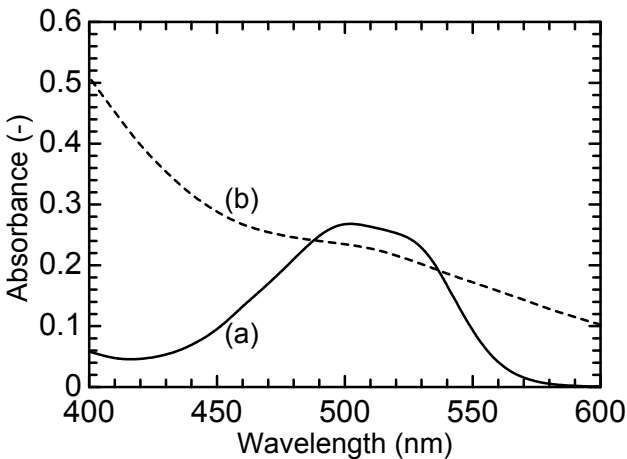


Fig. 8 Change in optical absorbance in the solution of Reactive RED 106 (0.01 g/L) treated by the plasma for 10 min followed by $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.1 g/L) addition, (a) for untreated solution, (b) for plasma treatment (10 min) followed by 0.1 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ addition

decolorized. Note that absorption at the wavelength less than 400 nm is caused by Fe^{2+} .

C. ESR spectra for the plasma application to water and solutions

Figure 9 shows other ESR spectrum for untreated distilled water. DMPO is added immediately after the plasma application. In this result, no radical is detected because the plasma is not applied and it is confirmed that DMPO is not oxidized by the environment. Peaks near 331 and 340 mT is caused not by radicals, but by the Mn marker for the cali-

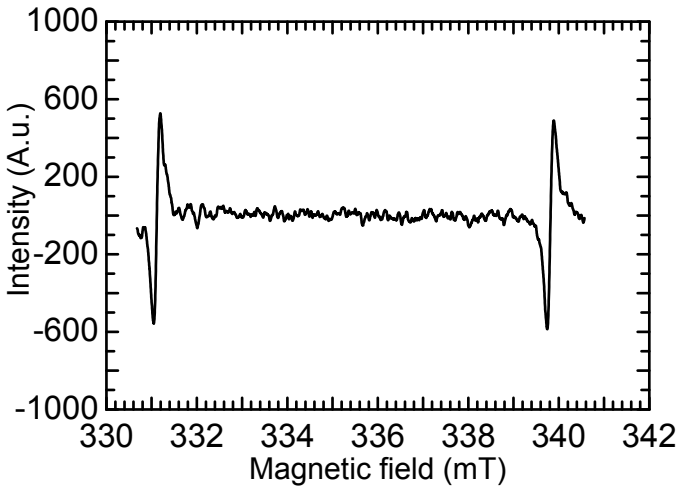
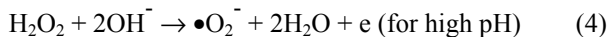


Fig. 9 ESR spectrum for untreated distilled water (DMPO is added before the ESR measurement)

bration of the spectrum.

Figure 10 shows ESR spectra for the plasma application to solution and distilled water. The curve (a) shows an ESR spectrum for 10 min plasma application to distilled water, and the curve (b) 10 min plasma application to distilled water solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with the concentration of 0.01 g/L. In these results, DMPO is added immediately after the plasma application. For the curve (a), weak peaks at the magnetic field marked with asterisks * shows hydroxyl radical ($\bullet\text{OH}$) are observed. In the curve (b), the strong peaks show the existence of larger amounts of $\bullet\text{OH}$. This result indicates that hydrogen peroxide is generated by the plasma application and is later gradually decomposed to $\bullet\text{OH}$ according to the Fenton equation (1).

Figure 11 shows an ESR spectrum for 10 min plasma application to NaOH solution (pH = 10). DMPO is added immediately after the plasma application. In the figure, peaks for $\bullet\text{OH}$ can be observed clearly. It is known that under alkaline condition the dissociation of hydrogen peroxide advances, and superoxide anion ($\bullet\text{O}_2^-$) and perhydroxyl radical ($\bullet\text{OOH}$) are induced according to the chemical reactions (4) – (6).



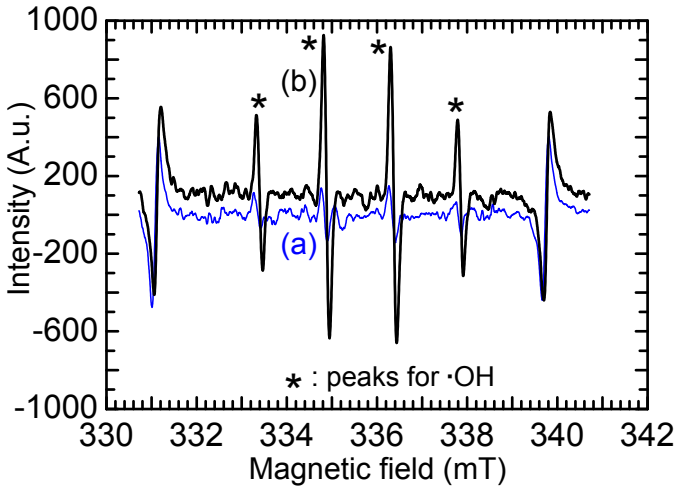


Fig. 10 ESR spectra for (a) 10 min plasma application to distilled water and (b) 10 min plasma application to distilled water solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with the concentration of 0.01g/L (DMPO is added after the plasma application)



It is known as the following Haber-Weiss reaction [16] is known in which $\bullet\text{O}_2^-$ easily reacts with H_2O_2 and easily converted to $\bullet\text{OH}$.

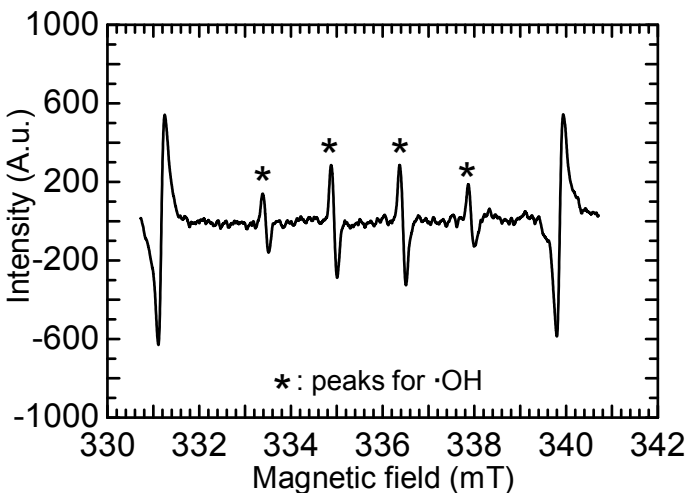
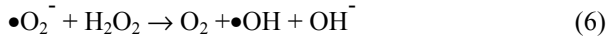


Fig. 11 ESR spectrum for 10 min plasma treatment of NaOH solution of pH = 10 (DMPO is added after the plasma treatment)

Furthermore, it is known that DMPO traps $\bullet\text{OH}$ more easily than $\bullet\text{O}_2^-$ and $\bullet\text{OOH}$ [17]. Therefore, it is considered that only $\bullet\text{OH}$ is detected in the present experiment.

Figure 12 shows an ESR spectrum for 10 min plasma application to distilled water solution of DMPO. This treatment can help to detect short-lived radicals because the radical trapping agent of DMPO can trap them immediately after its generation. As the result, the remarkable peaks of $\bullet\text{OH}$ can be seen in the figure. Other peaks for hydrogen radical $\bullet\text{H}$ are detected. Hydrogen radical disappears quickly in the case of adding DMPO after the plasma application due to its extremely short life. Therefore, it is considered that they cannot be caught as strong peaks in **Figs. 9** and **10**.

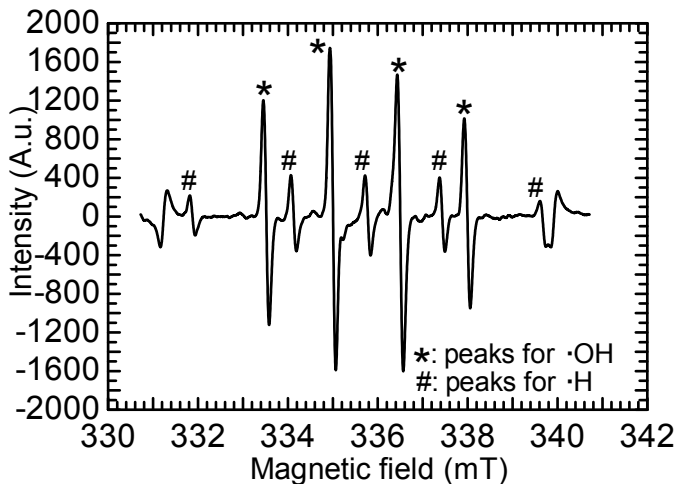


Fig. 12 ESR spectrum for 10 min plasma treatment of distilled water solution of DMPO

D. Comparison of procedures for ESR measurements

The procedures in the ESR measurements are summarized in **Table 1**. It is known from this table that a large amount of radicals are lost immediately after the plasma application because they have extremely short life. However, a part of them can be detected by adding radical trapping agent of DMPO immediately after the plasma application. In the plasma applications for FeSO_4 , NaOH , and DMPO solutions, a large amount of radicals can be detected due to relatively late progress in the reaction of radicals' generation and loss.

TABLE 1: PROCEDURES FOR ESR MEASUREMENTS

	Liquid	→	Treatment	→	Stabilizer	→	ESR measurements
Fig. 9	Water	→	No	→	DMPO	→	No radical
Fig. 10(a)	Water	→	Plasma	→	DMPO	→	Low $\bullet\text{OH}$
10(b)	FeSO_4	→	Plasma	→	DMPO	→	High $\bullet\text{OH}$
Fig. 11	NaOH	→	Plasma	→	DMPO	→	High $\bullet\text{OH}$
Fig. 12	DMPO	→	Plasma	→	→	→	High $\bullet\text{OH}$ and $\bullet\text{H}$

IV. CONCLUSION

Detection of free radicals produced by plasma induced by a pulsed streamer corona discharge in solution using ESR, and clarification of decolorization of reactive dye RED 106 solution with the plasma treatment in solution are carried out. The following results are newly obtained.

(1) Although plasma application generates hydroxyl radical, superoxide anion, and hydrogen radical in solution, these radicals disappear before decolorization of dye solution due to its extremely short life, quickly converted to H_2O and H_2O_2 . However, addition of Fe^{2+} at the stage helps hydrogen peroxide to decompose gradually into hydroxyl radicals by Fenton reaction, advancing decolorization of the dye solution.

(2) In the ESR measurements, the generation of hydroxyl radicals ($\bullet\text{OH}$) and hydrogen radicals ($\bullet\text{H}$) are confirmed. Most radicals are lost quickly after the plasma application because they have extremely short life. However, the part of them can be detected by adding radical trapping agent of DMPO immediately after the plasma application. In the plasma application to FeSO_4 , NaOH , and DMPO solutions, more radicals can be detected due to relatively late progress in the generation and loss of radicals.

From the results, it is considered that an efficient decomposition of hydrogen peroxide which is generated by the plasma treatment is a key for water treatments. Except the method using Fenton reaction and pH control mentioned in this study, ultraviolet ray irradiation and catalyst in water could be also considered as an interesting alternative which can be combined with the plasma in future investigation.

ACKNOWLEDGEMENT

The authors immensely thank Mr. T. Hibino (formally a graduate student of Osaka Prefecture University, currently a researcher of Mitsubishi Electric Corporation.) and Mr. K. Hayashi (Technology Research Institute of Osaka Prefecture) for their technical support in the experiments.

REFERENCES

- [1] T. Kuroki, M. Takahashi, M. Okubo, and T. Yamamoto, "Single-stage plasma-chemical process for particulates, NO_x , and SO_x simultaneous removal, IEEE Transactions on Industry Applications, 38(5), 2002, pp. 1204–1209.
- [2] T. Kuroki, M. Okubo, T. Oishi, and T. Yamamoto, "Bromomethane decomposition using a pulsed dielectric barrier discharge", IEEE Transactions on Industry Applications, accepted, 2012.
- [3] K. Yoshida, T. Yamamoto, T. Kuroki, and M. Okubo, "Pilot-scale experiment for simultaneous dioxin and NO_x removal from garbage incinerator emissions using the pulse corona induced plasma chemical process", Plasma Chemistry and Plasma Processing, 29(5), 2009, pp. 373–386.
- [4] B. R. Locke, M. Sato, P. Sunka, M. R. Hoffmann, and J.-S. Chang, "Electrohydraulic discharge and nonthermal plasma for water treatment", Industrial and Engineering Chemistry Research, 45(3), 2006, pp. 882–905.
- [5] M. Sato, "Sterilization of microorganisms by a high-voltage, pulsed discharge under water", Int. Chem. Eng. 30, 1990, pp. 695–698.
- [6] O. L. Li, N. Takeuchi, Z. He, Y. Guo, K. Yasuoka, J. S. Chang, and N. Saito, "Active species generated by a pulsed arc electrohydraulic discharge plasma channel in contaminated water treatments", Plasma Chemistry and Plasma Processing, 32(2), 2012, pp. 343–358.
- [7] H. Wang, J. Li, and X. Quan, "Decolorization of azo dye by a multi -needle-to-plate high-voltage pulsed corona discharge system in water", J. Electrostatics, 64, 2006, pp. 416–421.

- [8] A. T. Sugiarto, S. Ito, T. Ohshima, M. Sato, and J. D. Skalny, "Oxidative decoloration of dyes by pulsed discharge plasma in water", *J. Electrostatics*, 58 (1-2), 2003, pp. 135–145.
- [9] A. T. Sugiarto, T. Ohshima, and M. Sato, "Characteristics of ring-to-cylinder type electrode system on pulsed discharge in water", *J. Adv. Oxid. Technol.*, 5, 2002, pp. 211–216.
- [10] M. Sahni and B. R. Locke, "The effects of reaction conditions on liquid-phase hydroxyl radical production in gas-liquid pulsed-electrical-discharge reactors", *Plasma Processes and Polymers*, 3 (9), 2006, pp. 668–681.
- [11] M. Sahni and B. R. Locke, "Quantification of hydroxyl radicals produced in aqueous phase pulsed electrical discharge reactors", *Industrial and Engineering Chemistry Research*, 45 (17), 2006, pp. 5819–5825.
- [12] J. Y. Park, P. V. Kostyuk, S. B. Han, J. S. Kim, C. N. Vu, and H. W. Lee, "Study on optical emission analysis of AC air–water discharges under He, Ar and N₂ environments", *J. Phys. D: Appl. Phys.*, 39(17), 2006, pp. 3805–3813
- [13] B. Sun, M. Sato, and J. S. Clements, "Use of a pulsed high-voltage discharge for removal of organic compounds in aqueous solution", *J. Phys. D: Appl. Phys.* 32 (15), 1999, pp. 1908–1915.
- [14] D. R. Grymonpré, A. K. Sharma, W. C. Finney, and B. R. Locke, "The role of Fenton's reaction in aqueous phase pulsed streamer corona reactors", *Chemical Engineering Journal*, 82 (1-3), 2001, pp. 189–207.
- [15] S. H. Bossmann, E. Oliveros, S. Göb, S. Siegwart, E. P. Dahlen, L. Payawan, Jr., M. Straub, M. Wörner, and A. M. Braun, "New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions", *J. Phys. Chem. A*. 102 (28), 1998, pp. 5542–5550.
- [16] I. M. Kolthoff and J. Jordan, "Oxygen induced electroreduction of hydrogen peroxide and reduction of oxygen at the rotated gold wire electrode", *J. Am. Chem. Soc.*, 74 (19), 1952, pp. 4801–4805.
- [17] H. Miyazawa, T. Yoshikawa, M. Tanigawa, N. Yoshida, S. Sugino, M. Kondo, M. Nishikawa, and M. Kohno, "Measurement of serum superoxide-dismutase activity by electron-spin resonance", *J. Clin. Biochem. Nutr.*, 5, 1988, pp. 1–7.