Measurement of OH Radicals in Aqueous Solution Produced by Atmospheric-pressure LF Plasma Jet

Seiji Kanazawa, Takashi Furuki, Takeshi Nakaji, Shuichi Akamine, Ryuta Ichiki

Department of Electrical and Electronic Engineering, Oita University, Japan

Abstract—The chemical effects of the plasma are largely related to the formation of reactive oxygen species (ROS). OH radical is one of the ROS and has a strong oxidation potential. In this study, low frequency (LF) plasma jet was generated at atmospheric-pressure and irradiated onto the surface of aqueous solution. A portion of the OH radicals dissolved into aqueous solution was measured by chemical dosimetry. *In-situ* observation of OH radicals in a cuvette was performed and estimated the amount of produced OH radicals as well as the consumption of OH radicals for chemical reactions concerning to the degradation of persistent chemical compound. It is shown that measurement of OH radicals in liquid can be achieved by the terephthalate dosimetry with low cost and simple apparatus by using light emitting diodes (LEDs).

Keywords—LF plasma jet, OH radical, terephthalate dosimetry, LED, fluorescence

I. INTRODUCTION

Various kinds of atmospheric-pressure plasma sources have been developed during the last decades. Among the several plasma sources, atmospheric-pressure plasma jets have received significant attentions due to their unique capabilities (low temperature, low cost, portable and easy operation) and novel applications (analytical chemistry, thin film processing, synthesis of nanomaterial, surface modification, sterilization, cleaning and etching) [1-8]. A dynamics of a plasma jet has been investigated by many researchers [4, 5]. It was found that the plasma jet was composed of trains of plasma bullets travelling at the velocity of 10^4 -10^5 m/s. These plasma bullets have a hollow structure such as a circular ring or a donut. In this discharge mode, the reactive oxygen species (ROS) is produced along the trajectory of the bullets. When the plasma jet is employed to the surface treatment including water such as biological and environmental decontamination of media, those radicals are transported toward the surface containing liquid and induce a chemical change through the gas-liquid interface. Especially, the hydroxyl radical (OH) plays an important role in plasma chemistry and plasma medicine due to a higher oxidation potential and stronger disinfection power compared to other oxidative species.

The identification of OH radicals and its concentration measurement have been performed in the plasma bullets by optical emission spectroscopy (OES) [4-6] and laser induced fluorescence (LIF) [3], respectively. However, the permeation of these ROS into the liquid volume through the plasma-liquid interface has not been clearly understood. This information is very important in plasma disinfection and/or plasma medicine, which are necessary to treat organic materials and living cells/tissues containing water. In this paper, when the plasma jet is applied to the liquid surface, the OH radicals dissolved into aqueous solution is studied by chemical dosimetry.

II. EXPERIMENTAL

A. Plasma jet

Fig. 1 shows schematic diagram of the experimental setup. The plasma jet source is similar device to the atmospheric-pressure plasma jet developed by Teschke *et al.* [1]. A tapered glass tube with a 1 mm inner diameter at the end was used. Two ring electrodes were wound around the tube. When helium gas with a flow rate of 2 L/min is injected from one end of glass tube and the low frequency high voltage (output from an inverter type Neon transformer, 20 kHz) is applied to the two ring electrode, a barrier discharge is generated between the electrodes and a plasma plume is ejected into
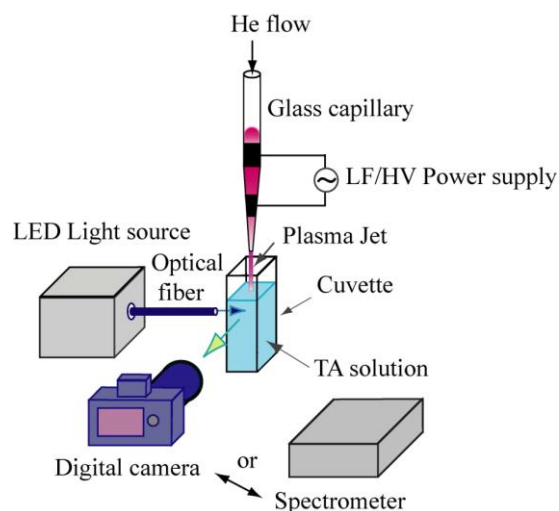

Fig. 1. Schematic of experimental setup.

Corresponding author: Seiji Kanazawa
e-mail address: skana@oita-u.ac.jp

surrounding air. The visible length of the plasma jet flame was approximately 15-30 mm in open air, depending on the operational conditions. The distance between the nozzle and the surface of the liquid was changed in the range of 15 -25 mm.

The applied voltage and the current were measured by a high voltage probe (Iwatsu, HV-P30) and a current probe (Pearson Electronics, 2877), respectively. An ICCD camera (Andor, i-Star) was used to capture the dynamics of the plasma plumes. A spectrometer (Ocean Optics, USB2000) was used to measure the emission spectra of the plasma.

B. Chemical dosimetry

In order to measure the OH radicals dissolved in the liquid, we used chemical dosimetry [9] based on terephthalic acid (TA). Terephthalic acid is a well known OH scavenger which does not react with other radicals, such as O_2^-, HO_2 and H_2O_2. As shown in Fig. 2, the OH radical can convert terephthalic acid to 2-hydroxyterephthalic acid (HTA) though the reaction [9]

$$C_6H_4(COOH)_2 + \cdot OH \rightarrow C_6H_4(COOH)_2 OH. \quad (1)$$
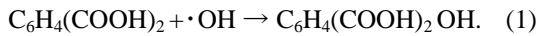
HTA can be detected by fluorescence measurement. When the solution containing TA and HTA molecules is irradiated by UV light (λ=310nm), HTA molecules emit light at λ=425nm, while TA molecules do not. The fluorescence intensity of HTA is independent of pH in the range of 6-11. Since TA (Aldrich) does not dissolve in acidic/neutral liquid, aqueous solution of TA was prepared by dissolving TA in the distilled water containing NaOH (Wako Pure Chemical Industries). The initial concentrations of TA and NaOH were 2 mM and 5 mM, respectively. The initial values of pH and conductivity of the solution were 10 and 323 μS/cm, respectively. The solution volume in a cuvette was ca. 3 mL. The LED (Sandhouse Design, λ=310 nm, FWHM 10 nm) was used as a light source to excite HTA. At various time intervals during the plasma jet irradiation, a collimated beam from the LED output is passed through the liquid in a cuvette, approximately 5 mm below the surface of the liquid. The fluorescence (λ=425 nm, center wavelength) image was captured by a digital camera (Nikon, D90) and the spectrum around λ=425 nm was recorded through an optical fiber by the spectrometer
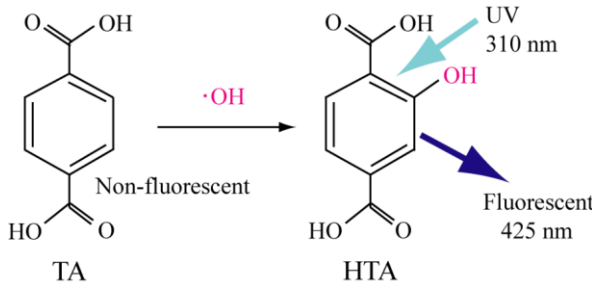

Fig. 2.Formation of HTA through the reaction of TA and OH radical.

(Fig.1). In order to quantify the OH radical concentration in the liquid, a calibration curve for known OH radicals concentrations was prepared using the standard HTA (Atlantic Research) solution.

III. RESULTS

A. Characteristics of the plasma jet

Fig.3 shows the typical applied voltage and discharge current waveforms for the plasma jet. The applied voltage is 6 kVp-p at 20 kHz. The discharge operates in a dielectric barrier discharge (DBD) mode. The discharge current includes a fast component (current pulses for the generation of plasma jet) and a slow component (displacement current). During the positive half-cycle of the voltage, the plasma jet is launched from the exit of the tapered glass tube. The plasma bullet velocity is about 30 km/s, which is one order of magnitude lower than that of the repetitive pulse high voltage operation [5]. The discharge power can be obtained by the voltage-charge (Lissajous) figures and average power calculated is 5 W under our operating condition.

Fig.4 shows the typical emission spectrum of the plasma plume taken at an axial distance of ca. 10 mm from the exit of the glass tube. In the plasma ejected into ambient air, the emission spectrum is dominated by N_2
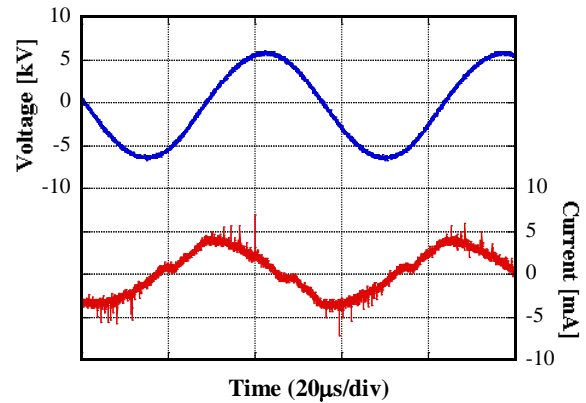

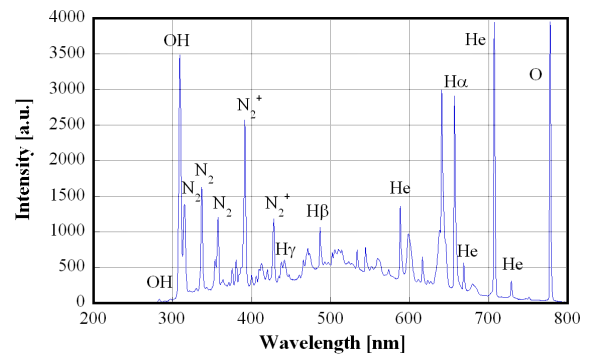Fig. 3.Applied voltage and current waveforms for plasma jet.

Fig. 4.Optical emission spectrum of LF He plasma jet.

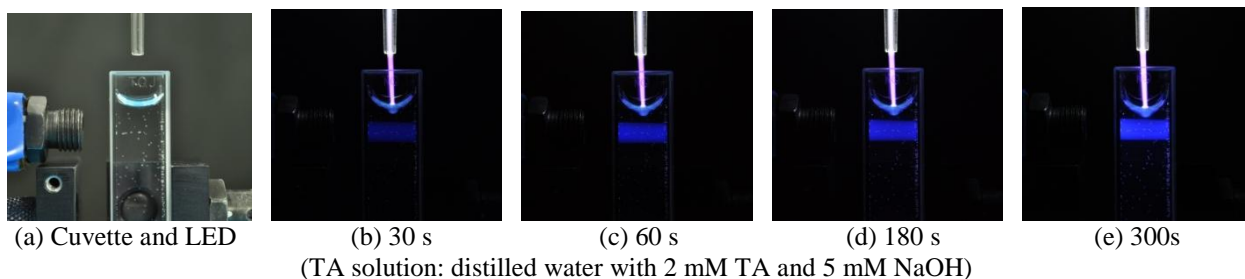|				
(a) Cuvette and LED	(b) 30 s	(c) 60 s	(d) 180 s	(e) 300s

(TA solution: distilled water with 2 mM TA and 5 mM NaOH)

Fig. 5. Photographs of fluorescence from TA solution during plasma jet exposure.

first negative band ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) and also by N_2 second positive band ($C^3\Pi_u \rightarrow B^2\Pi_g$). The yield of N_2^+ is attributed to Penning ionization by helium metastable atoms (He*, 19.8 eV, 21.0 eV). While, N_2 excitation is due to direct electron impact excitation [5]. Although it is said that the corona discharge-induced streamers is similar to the plasma jet, N_2 second positive band is dominantly observed and no N_2^+ emission is observed for the streamers in air. Therefore, it is considered that N_2 ionization by He* may play an important role in the propagation of the plasma bullets and solitary surface ionization waves may be responsible for the creation of the bullets with the ling-like structure [4]. Atomic oxygen, O and H_α, H_β lines are also present in the spectrum.

On the other hand, the excited state of OH radicals was identified in the spectrum as seen in Fig.4. From the results of OES [4] and LIF [3], the intensities of both excited and grounded states of OH radicals gradually decreased with the increase of the distance from the glass nozzle. Therefore, this fact indicates that the OH radicals transported into the liquid may reduce as the distance between the nozzle and liquid surface increases. The result shown in next section (see, Fig. 8) indicates this tendency indirectly. Moreover, the presence of the highly energy states of He* as well asenergetic electron in the plasma bullets can be contributed to the production of OH and H species at the plasma-liquid interface where they impinge on the water surface.

B. Characteristics of the OH radicals in liquid

Fig. 5 shows time-dependent fluorescence images under the illumination of the LED light sourcewhen the plasma jet is in contact with liquid surface during 10-min treatment. Thisfluorescence image is also observed by our naked eye. The water surface is deformed by helium gas flow with a velocity 10 m/s and water vapor is continuously generated and diffused into the free space above the surface. Consequently, OH radicals are formed from both water vapors in the ambient air and water at the surface of the liquid solution.The intensity of the fluorescence increased with time elapsed and its part is almost uniform even though no stirring of the liquid was performed, indicating homogeneous HTA diffusion from the plasma/gas-liquid interface.

In order to evaluate the amount of OH radicals trapped into TA solution, fluorescence spectra for various treatment times are shown in Fig.6. The fluorescence intensity corresponds to a time integrated OH radical concentration in the liquid. As the time elapsed, the fluorescence intensity increased, indicating the increase of the total amount of OH radicals trapped by TA. Using the fluorescence intensity integrated over the wavelength (shown in Fig.6) and the calibration curve for known concentrations of OH radicals, we calculated the OH radical density in the solution as a function of treatment time as shown in Fig.7. The concentration of OH radicals in the cuvette almost linearly increases with increasing the time. Besides trapping of OH by TA, however, other reactions that consume OH radicals also
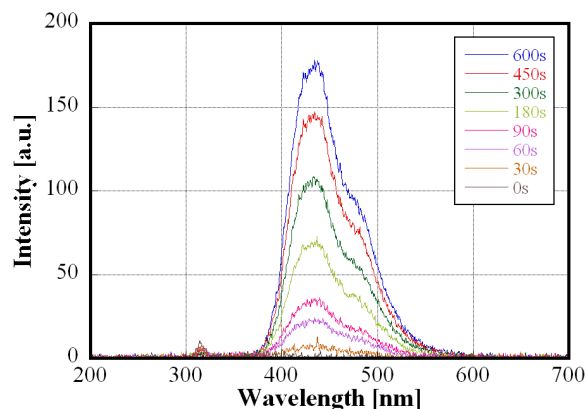

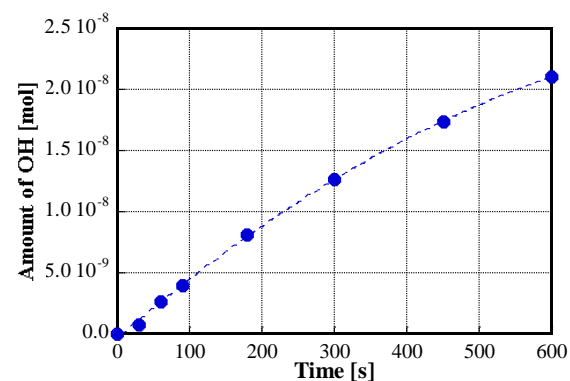Fig. 6. Fluorescence spectra of aqueous TA solutions irradiated by plasma jet.

Fig. 7. Formation of OH radicals in aqueous TA solution as a function of treatment time. Parameters as in figure 6.
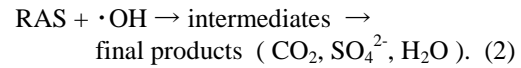
occurred. In the present case, the HTA yield was assumed to be 35%, according to [10]. Furthermore, the plasma jet produces ozone and the presence of dissolve ozone in liquid may lead to additional OH production under the illumination of UV LEDs. In fact, we observed that the TA solution performed by ozonation suggested the ozone-originated OH production through the terephthalate dosimetry. In the present study, however, the concentration of the ozone produced by the plasma jet is less than 1 ppm, the ozone interference is negligible.

Fig.8 shows the effect of the position of the plasma jet nozzle against the liquid surface on the total amount of OH radicals after 10-min irradiation. In this case, we used small water tank (liquid volume = 19.5 mL) instead of the cuvette. The tip of the plasma jet is just in contact with the liquid surface at the distance of 25 mm from the exit of the glass tube. When the exit of the plasma jet device approaches the liquid surface, plasma jet with gas flow makes the dip onto the water surface, resulting in an enlargement of the contact area between the plasma and liquid. Moreover, an impact of the plasma bullets affects the generation of OH radicals at the interface between the gas and liquid. From the result of Fig.8, a large amount of OH radicals is available by moving the exit of the plasma jet device closer to the liquid surface. It is found that OH radicals trapped by TA is independent on the volume of the TA solution (compare a value of 10-min operation in Fig.7 with a value at the distance of 25 mm in Fig.8) and its production rate is about 1.0×10^{-8} to 4.7×10^{-8} M/s depending on the position of the plasma jet nozzle against the liquid surface. Under our another experiment, the rate of production of OH radicals is of the order of 10^{-9} M/s for the surface pulsed streamer discharge on the liquid [11]. Recently, Sahni et al. [12] have reported that the production rate of OH radicals was 1.67×10^{-8} M/s for the direct discharge in water at an applied voltage of 45 kV and input power delivered to the water of 64 W. Joshi et al. [13] have determined the rate of formation of OH radicals using the free radical scavenging property of carbonate ions. They reported the value of 9.25×10^{-10} M/s for the pulsed streamer

corona discharge in an aqueous solution. At the present stage, we attribute these differences to various factors, such as discharge types, reactor size, operating conditions, and different measuring methods.

C. Persistent wastewater treatment

Finally, we focus on the OH radical detection by the terephthalate dosimetry during a model wastewater treatment. Here, linear alkylbenzenesulfonates (LASs), which is a typical surfactant used in detergent and is included in sewage water, is used as a model wastewater because conventional techniques such as ozonation have little effect on the removal of LAS. LAS (Wako Pure Chemical Industries) aqueous solution, including TA, was analyzed by high-performance liquid chromatography (Shimadzu, Prominence) using a Shim-pack XR-ODS column and an RF detector, the mobile phase being a mixture of water and acetonitrile (45:55 v/v), at a flow rate of 1.0 mL/min. Fig.9 shows the relationship between the amount of decrease of LAS compound and the amount of OH radical consumed for the reactions as a function of the concentration of LAS aqueous solution. Regardless of the initial concentration of LAS in the solution, the degradation rate is about 60 %. According to [14], it is considered that OH radical is responsibility for RAS degradation through the reaction:

$$RAS + \cdot OH \rightarrow intermediates \rightarrow$$
$$final\ products\ (\ CO_2,\ SO_4^{2-},\ H_2O\ ).\ (2)$$

Astonishingly, Fig.9 indicates that the removal of RAS is achieved by one stoichiometry of OH (i.e., [OH]/[RAS]= 1) under the reaction of (2).

IV. CONCLUSION

In this study, we focused on the hydroxyl radical in the low frequency plasma jet and its concentration in liquid was estimated by the terephthalate dosimetry. Instead of the use of conventional fluorescence
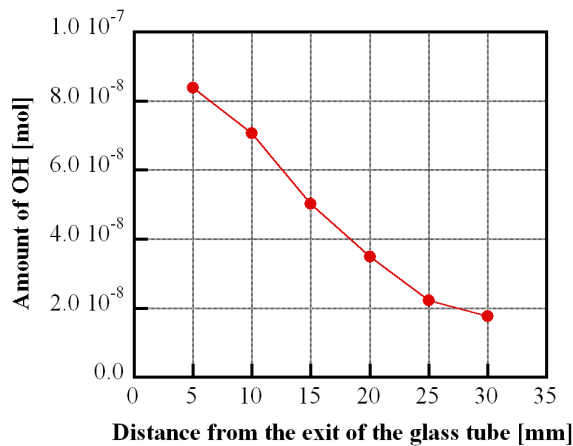

Fig. 8. Effect of treatment distance on OH radical production.
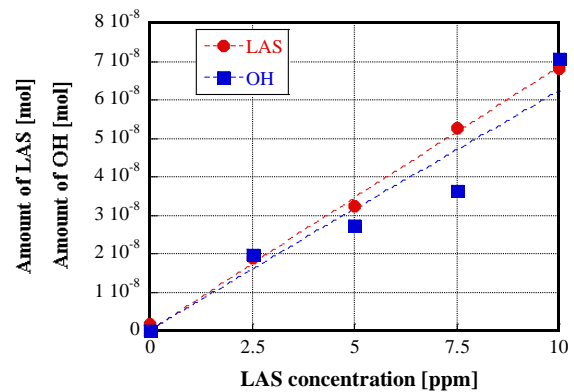(Plasma jet irradiation period: 10-min)

Fig. 9. Relationship between the amount of RAS degradation and the amount of OH radical consumption for various initial LAS concentrations.
(Plasma jet irradiation period: 10-min)

measurement equipment, a novel fluorescence observing system by using a light-emitting diode (LED) as a light source and a simplified spectrometer as a detector was developed. The results obtained are as follows:

1) It is considered that the OH radicals detected in liquid phase are caused either by a transport of OH radicals to the surface of the liquid by means of the plasma jet or a direct generation from the liquid in contact with the plasma bullet.

2) The fluorescence intensity due to the trap of OH by TA increased with time elapsed during the jet irradiation onto the liquid surface. The production rate of OH radicals in the liquid was estimated to be of the order of 10^{-8} M/s under our experimental conditions. No significant O_3 was observed for the obstacle of measurement of OH radical concentration.

3) When RAS aqueous solution was treated by plasma jet, approximately 60% of RAS was decomposed with one stoichiometry of OH radical reaction.

REFERENCES

[1] M. Teschke, J. Kedzierski, E.G. Finantu-Dinu, D. Korzec, and J. Engemann, "High-Speed Photographs of a Dielectric Barrier Atmospheric Pressure Plasma Jet," *IEEE Trans. Plasma Sci.*, vol.33, no.2, pp.310-311, 2005.

[2] C. Tendero, C. Tixier, P. Tristant, J. Desmaison, and P. Leprince, "Atmospheric pressire plasma: A review," *Spectrochim. Acta Part B*, vol. 61, pp. 2-30, 2006.

[3] T. Yuji, H. Kawano, S. Kanazawa, T. Ohkubo, and H. Akatsuka, "Laser-Induce Fluorescence Image of OH Radicals for Atmospheric-Pressure Nonequilibrium Dry Air Gas DC Pulse Plasma Jet," *IEEE Trans. Plasma Sci.*, vol. 36, no. 4, pp. 976–977, 2008.

[4] N.M.-Bourdet, M. Laroussi, A. Begum, and E. Karakas, "Experimental investigations of plasma bullets," *J. Phys. D: Appl. Phys.*, vol. 42, 055207 (7pp), 2009.

[5] Z. Xiong, X. Lu, Y. Xian, Z. Jiang, and Y. Pan, "On the velocity variation in atmospheric pressure plasma plumes driven by positive and negative pulses," *J. Appl. Phys.*, vol.108, 103303(4pp), 2010.

[6] Y. Xian, X. Lu, Z. Tang, Q. Xiong, W. Gong, D. Liu, Z.Jiang, and Y. Pan, "Optical and electrical diagnostics of an atmospheric pressure room-temperature plasma plume," *J. Appl. Phys.*, vol.107, 063308(5pp), 2010.

[7] S. Ikawa, K. Kitano, and S. Hamaguchi, "Effects of pH on Bacterial Inactivation in Aqueous Solutions due to Low-Temperature Atmospheric Pressure Plasma Application," *Plasma Process Polym.*, vol.7, pp.33-42, 2010.

[8] S. Kanazawa, T. Iwao, S. Akamine, and R. Ichiki: "Improving Single-Chamber Solid Oxide Fuel Cell Performance by Plasma Treatment Using an Atmospheric-Pressure Helium Plasma Jet", *Japanese Journal of Applied Physics*, vol.50, 08KA04 (5pp), 2011.

[9] T. J. Mason, J. P. Lorimer, D. M. Bates, and Y. Zhao, "Dosimetry in sonochemistry: the use of aqueous terephthalate ion as a fluorescence monitor," *Ultrason. Sonochem.*, vol. 1, no. 2, pp. S91–S95, 1994.

[10] X. Fang, G. Mark, and C. von Sonntag, "OH radical formation by ultrasound in aqueous solutions Part I: chemistry underlying the tereohthalae dosimeter," *Ultrason. Sonochem.*, vol.3, pp.57-63, 1996.

[11] S. Kanazawa, H. Kawano, S. Watanabe, T. Furuki, S. Akamine, R. Ichiki, T. Ohkubo, M. Kocik, and J. Mizeraczyk, "Observation of OH radicals produced by pulsed discharges on thesurface of liquid," *Plasma Sources Science and Technology*, vol.20, no.3, 034010 (8pp), 2011.

[12] M. Sahni and B. R. Locke, "Quantification of Hydroxyl Radicals Produced in Aqueous Phase Pulsed Electrical Discharge Reactors," *Ind. Eng. Chem. Res.*, vol.45, pp. 5819-5825, 2006.

[13] A. A. Joshi, B. R. Locke, P. Arce, and W. C. Finney, "Formation of hydroxyl radicalas, hydrogen peroxide and aqueous electrons by pulsed streamer corona discharge in aqueous solution," *J. Hazard. Mater.*, vol.41, pp. 3-30, 1995.

[14] F.J. Beltran, J. F. Garcia-Araya, and P. M. Alvarez, "Sodium Dodecylbenzenesulfonate Removal from Water and Wastewate. 1. Kinetics of Decomposition by Ozonation," *Ind. Eng. Chem. Res.*, vol.39, pp.2214-2220, 2000.