Improvement of Surfactant Decomposition by Superposition of Pulsed Discharge on the Water and Ozone Injection

S. Kanazawa, S. Geng, T. Okawa, S. Akamine, and R. Ichiki
Department of Electrical and Electronic Engineering, Oita University, Japan

Abstract—In this study, we proposed a novel method to produce OH radicals for the treatment of water including persistent compounds by superposition of pulsed discharge on the water and ozone injection. As a test liquid, an aqueous solution including a surfactant was used to evaluate the water treatment efficiency. Taking into account the nature of the surfactant, the surface discharge mode was adopted. A hollow metal needle was used as the stressed electrode, and the tip of the electrode was set 1mm above the water surface. While a ring electrode was submerged in water as the grounded electrode. A pulsed streamer discharge was generated on the water surface. Moreover, the ozone injection through the needle electrode was performed to investigate the synergistic effect. The results indicated that linear alkylbenzene sulfonate (LAS) was decomposed effectively by using the proposed method. The deformation of the water surface underneath the needle electrode was observed by the gas injection, resulting in the penetration of the streamer into the water. Also the electrohydrodynamic (EHD) flow, induced in water solution, enhances the mixing of the solution.

Keywords—Pulsed discharge on the water surface, ozone, OH radical, LAS, EHD-induced liquid flow, synergistic effect

I. INTRODUCTION

A detergent used for laundry contains surfactant and its exhaust water is released into rivers. The toxicity and environmental persistence of the recalcitrant surfactants are emerging concerns. The surfactant decomposition should be necessary to maintain the water quality. Linear alkylbenzene sulfonate (LAS) is a well-known anionic surfactant and one of the main ingredients in synthetic detergent. In sewage processing, an injection of ozone is widely used. However, the ozone alone does not effectively decompose the recalcitrant surfactant such as LAS. Therefore, the processes called advanced oxidation processes (AOPs) have been studied to enhance the treatment efficiency for the removal of pollutants in water [1]. Especially, hydroxyl (OH) radicals produced by AOPs play an important role for the degradation of persistent substances. In recent years, plasma technology has been received much attention in the field of water treatment [2, 3]. The degradation of several organic compounds dissolved in water has been carried out not only including dyes [4-6], phenol [7-9], acetic acid [10], but also including surfactant such as LAS [11-13] and sodium lauryl sulfate (SLS) [14].

In this study, we proposed a novel AOP method to produce OH radicals by superposition of pulsed discharge on the water surface and ozone injection through the discharging needle electrode. Taking into account the nature of the surfactant, which exists mainly on the interface between water and air, the surface discharge mode was adopted. The degradation of LAS by this method was investigated in comparison with the cases of discharge only or ozone injection.

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

Presented at the 2012 International Symposium on Electrohydrodynamics (ISEHD 2012), in September 2012

II. EXPERIMENTAL

Fig. 1 shows a schematic diagram of the experimental setup. A commercially available separable flask (85 mm in inner diameter, 110 mm in height) was used as a reactor. A hollow metal needle (1.5 mm outer diameter, 1.0 mm inner diameter) was used as the stressed electrode and the tip of the electrode was set 1 mm above the water surface. While a ring electrode (50 mm in inner diameter, 8 mm in thickness) was submerged in the solution as the grounded electrode. As a test liquid, an aqueous solution of sodium linear alkylbenzene sulfonate (Wako Pure Chemical Industries, Ltd., 195-07682) was used. The chemical structure of LAS is shown in Fig. 2. The initial concentration of LAS was 5 mg/L. The volume of the solution in the reactor was 90 mL. The initial solution conductivity and pH were 1.91 μS/cm and 6.13, respectively. LAS concentration was measured by high performance liquid chromatography (HPLC) with fluorescence detection (Shimadzu, Prominence UFLC system with RF-20Axs). LAS was analyzed on a Shim-pack XR-ODS column using 45 : 55 acetonitrile : water containing 0.1 mol/L sodium perchlorate as a mobile phase at 1 mL/min and column temperature of 40^{o}C. The sample volume was 8 μL and detection was achieved with fluorescence detector operating at an excitation wavelength of 221 nm and an emission wavelength of 284 nm.

A pulsed high voltage circuit based on a Blumlein line was used to generate streamers on the water surface. The energy stored in the Blumlein line is transferred to the discharging area by means of a spark gap switch. As the length of each coaxial cable is 10 m, the pulsed high voltage with its width of 100 ns is available. Voltage and current waveforms were recorded on a digital oscilloscope (Tektronix, TDS 5104) using a high-voltage probe (Iwatsu, HV-P06) and a current monitor (Pearson,

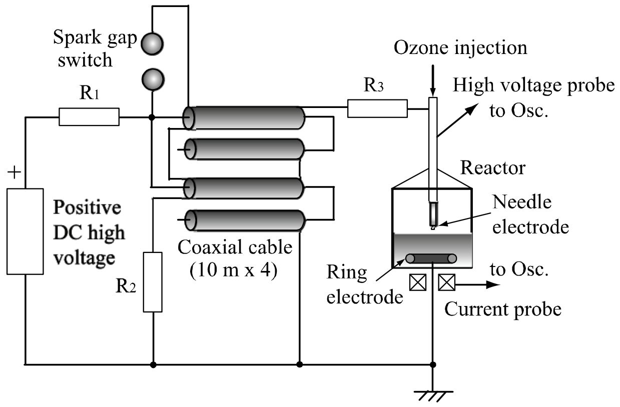


Fig. 1. Schematic diagram of experimental setup.
($R_1 = 10$ MΩ, $R_2 = 200$ Ω, $R_3 = 300$ Ω)

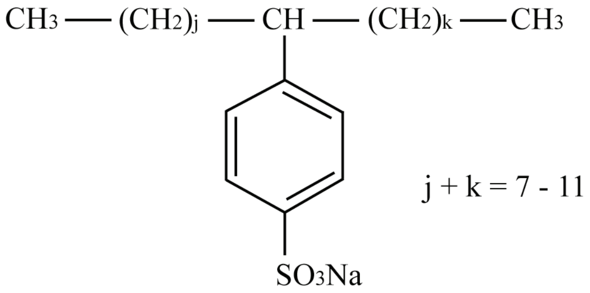


Fig. 2. Chemical structure of linear alkylbenzene sulfonate (LAS), where *x* plus *y* equals 7 to 11 depending on the length of the alkyl chain.

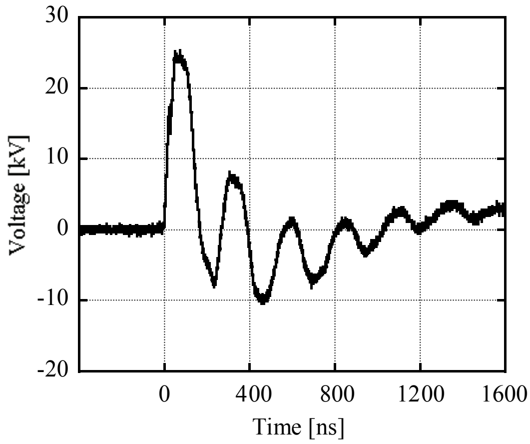
4100), respectively. The digital camera (Nikon, D90) was used to capture the streamer images.

During the discharge, ozone injection was performed through the needle electrode. Ozone was generated from dry air by means of a homemade ozonizer and the flow rate of gas injection was 1 L/min. Ozone concentration for the injection was ca. 200 ppm.

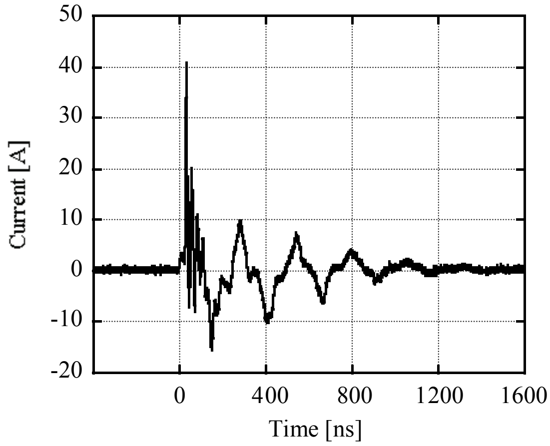
III. RESULTS AND DISCUSSION

Typical voltage and current waveforms of the pulsed discharge with ozone injection are shown in Fig. 3. The maximum output voltage and peak discharge current are 24 kV and about 40 A, respectively. The pulse repetition rate was 12 pps. The energy per pulse was 15.7 mJ. The average power dissipated in the discharge was about 0.19 W.

Fig. 4 shows the typical time integrated images of the discharges without and with gas (dry air) injection, respectively. The streamer discharge is initiated at a tip of the needle electrode and propagates along the water surface with a filamentary structure. In the case of superposition of the discharge and gas injection as shown in Fig. 4 (b), the dip is created underneath the needle electrode due to the gas injection and streamers intrude into the dip through the interface between air and water. Fig. 5 shows the flow pattern in the liquid volume captured by a planar Mie scattering technique. A light



(a) Applied voltage

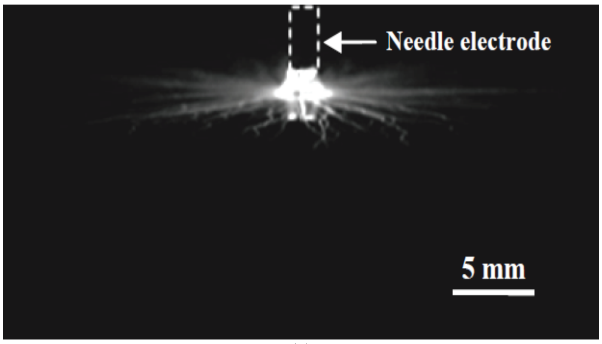


(b) Current

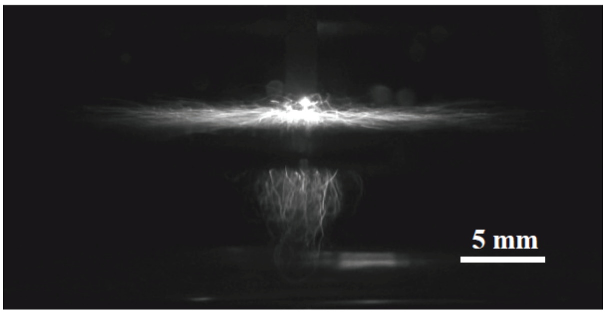
Fig. 3. Applied voltage and current waveforms for pulsed discharge on the water surface.

scattered by small particles (cross-linked polymethylmethacrylate, mean diameter = 50 μm, specific gravity = 1.2) from He-Ne laser light sheet illumination was observed and recorded by the digital camera. The liquid-phase electrohydrodynamic (EHD) flow formed vortexes, which cause the liquid mixing as shown in Fig. 5 (a). The ionic wind progressed from the stressed electrode along the air-liquid interface, resulting in the motion of the liquid. In addition to this effect, more complicated flow structure was generated when the gas was injected through the needle electrode (Fig. 5(b)). These liquid-phase EHD flows might be affected to the water treatment efficiency.

Fig. 6 shows the typical chromatograms of the LAS solution. Fig. 6 (a) shows the chromatogram before treatment, while Fig. 6 (b) shows the chromatogram of the solution after 15 min treatment performed by superimposition of pulsed discharge on the solution and ozone injection. Test aqueous solution consists of LAS homologues (C10, C11, C12 and C13) as shown in Fig. 6(a). Each peak area for the LAS homologue decreased with increasing the treatment time, indicating the decomposition of the LAS homologue. Quantification

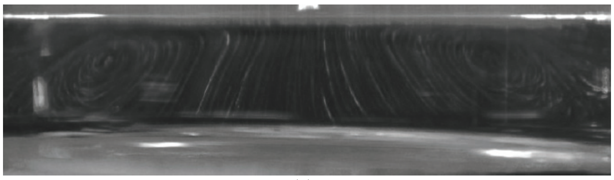


(a)

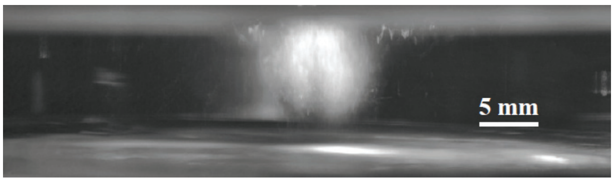


(b)

Fig. 4. Typical discharge images of (a) without gas injection and (b) with gas injection (applied voltage: 24 kV, exposure time of the digital camera: 10 s).

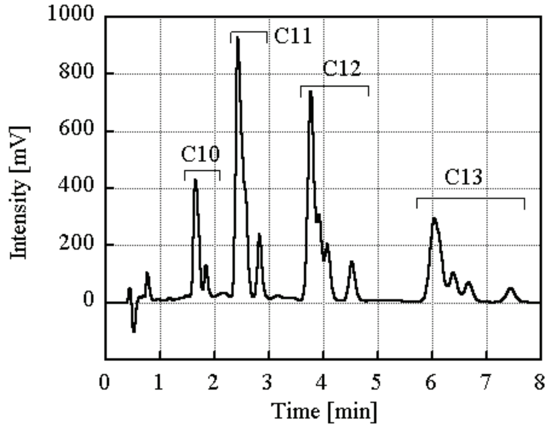


(a)

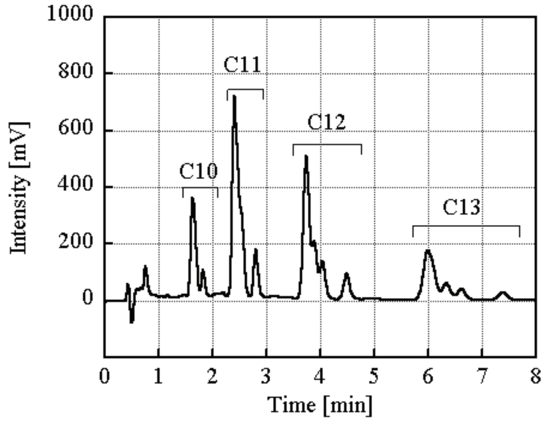


(b)

Fig. 5. Typical liquid flow pattern observed by the Mie scattering technique of (a) without gas injection and (b) with gas injection (applied voltage: 24 kV, exposure time of the digital camera: 8 s).



(a)



(b)

Fig. 6. HPLC chromatograms of LAS, (a) before treatment and (b) after 15 min discharge with ozone treatment.

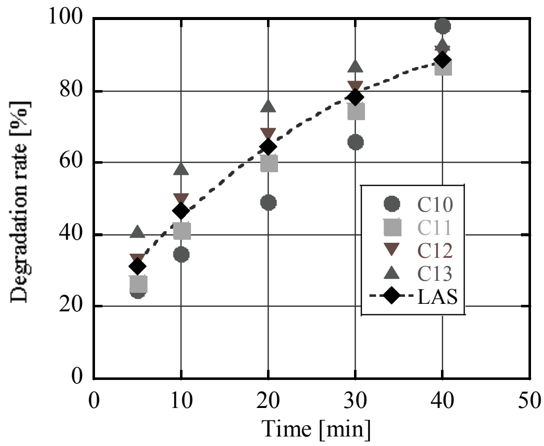


Fig. 7. Degradation rate of LAS as a function of treatment time by means of superposition of pulsed discharge and ozone injection.

was performed by comparing the ratios of peak areas for the LAS homologues in test solution to those of standard solutions. In Fig. 6 (b), the degradation rate of LAS homologues of C10, C11, C12, C13, and total-LAS are 25%, 24.8%, 31.5%, 37.2%, and 29.5%, respectively. Fig. 7 shows the degradation rate of LAS as a function of treatment time. All LAS homologues were decomposed as the time elapsed. Approximately 90% of LAS can be degraded in 40 min by means of proposed superposition technique. In this case, the energy efficiency is 28 g/kWh.

Fig. 8 shows compares the degradation rate of LAS after 15 min treatment among the three different methods under the present condition. The superposition technique based on the simultaneous use of the discharge and ozone is much more effective than singularity use of discharge or ozone to remove LAS. From the results obtained in our experiment, it is found that the degradation rate of LAS by ozone alone is not significant under the present experimental condition. In the filament of the streamers OH radicals are effectively produced, because large amounts of water vapor are available both over the solution surface due to the discharge-induced

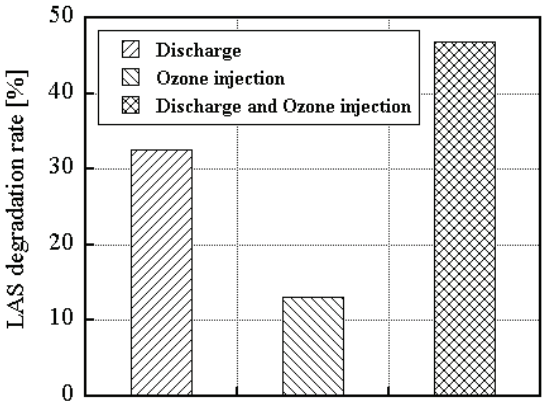


Fig. 8. Comparison of three types of LAS solution treatments in terms of LAS degradation rate.

vaporization of water and on the solution surface. We have observed OH radicals on the water surface by laser-induced fluorescence [15, 16]. The principal reaction for the OH radical formation is as follows:

$$e + H_2O \rightarrow H + OH + e \tag{1}$$

Besides this process, other reactions of OH radical formation are thought to be important and are summarized in [16, 17].

Although the ozone production is suppressed by the existence of large amounts of water vapor in the surface discharge system, under our experimental condition ozone is intentionally introduced in the discharge region by means of gas injection. If ozone is present in the discharge area, ozone is easily decomposed (the dissociation energy of O_3 is 1.04 eV):

$$e + O_3 \rightarrow O(^1D) + O_2 + e \tag{2}$$

And OH radicals are produced through the following reaction:

$$O(^1D) + H_2O \rightarrow 2OH(X) \tag{3}$$

Note that this process is also one of the main production mechanisms of OH radical in the discharge induced plasmas. In the presence of hydroperoxyl radicals (HO_2) in the plasma, OH radical is formed directly by the reaction with ozone [10]:

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{4}$$

In addition to the above OH production processes, the subsequent reaction occurs at pH values above 5 [18]:

$$O_3(aq) + H_2O_2 \rightarrow OH + HO_2 + O_2 \tag{5}$$

Since OH radical is responsibility for LAS degradation [19], increasing the concentration of OH radicals would contribute to the degradation of LAS. In fact, we measured the amount of OH radicals trapped by radical scavenger. As a result, the concentration of OH in aqueous solution under the superposition of the discharge and ozone injection was higher compared to those of discharge only or discharge with air injection.

The synergistic effect of superposition of pulsed discharge plasma and ozone injection was also confirmed in the treatment of dye solution. We have observed that the decolorization of indigo solution was accelerated [20].

Finally, we will consider the degradation pathway of LAS. In biological degradation of LAS [21], the formation of sulfo phenyl carboxylates (SPCs) has been reported as a result of an oxidation of the methyl groups followed by stepwise shortening of the alkyl chain via cleavage of C_2 fragments. In next step, SPCs aromatic ring cleavage occurs, leading to CO_2, H_2O, SO_4^{2-} and biomass as final byproducts. On the other hand, in photo(UV)-oxidative process the aromatic ring is primary attacked due to the molecular structure of LAS (Fig. 2) [22]. In the case of discharge-induced plasma treatment including the reactions due to OH radicals, it is expected that the aromatic ring cleavage takes place as well as the shortening of the alkyl chain, which is similar reaction pathway with the case of decomposition for chemical compounds including the aromatic ring such as phenol [13, 14, 18]. Especially, it is considered that OH radical reactions are the main route of LAS degradation [19]:

$$\begin{aligned} LAS + OH &\rightarrow \text{intermediates} \rightarrow \\ &\text{final products } (CO_2, SO_4^{2-}, H_2O) \end{aligned} \tag{6}$$

This simple reaction pathway indicates that LAS degradation is dominantly due to the OH radicals produced by present AOP because the ring opening of LAS is caused by the OH radical attack. However, the information of intermediates is also an important to understand the degradation kinetics. The measurement of liquid phase total organic carbon (TOC) content is now underway. TOC is useful in assessing the extent of total oxidation of LAS to carbon dioxide that had occurred. TOC is also an indicative factor to estimate the residual amount of intermediates.

IV. CONCLUSIONS

From the present study, the degradation of LAS is enhanced by superposition of pulsed discharge on the water and ozone injection. OH radicals play an important role of LAS degradation such as aromatic ring cleavage. The gas injection through the needle electrode made a deformation of water surface, resulting in the increase of the contact area between the streamers and liquid. Under the combination of the discharge-induced plasma and ozone injection, approximately 90% of LAS with the density 5 mg/L can be degraded within 40 min at the energy efficiency of 28 g/kWh.

ACKNOWLEDGMENT

This study was partly supported by the Japan Society for the Promotion of Science, Grant-in-Aid for Scientific Research (No. 23360127).

REFERENCES

[1] K. Ikehata and M. G. El-Din, "Degradation of recalcitrant surfactants in wasterwater by ozonation and advances oxidation processes: A review," *Ozone-Science & Engineering*, vol. 26, pp. 327-343, 2004.

[2] H. Akiyama, "Streamer discharges in liquids and their applications," *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 7, pp. 646-653, 2000.

[3] B. R. Locke, M. Sato, P. Sunka, M. R. Hoffmann, and J. S. Chang, "Electrohydraulic discharge and nonthermal plasma for water treatment," *Industrial & Engineering Chemistry Research*, vol. 45, pp. 882-905, 2006.

[4] A. T. Sugiarto, S. Ito, T. Ohshima, M. Sato, and J. D. Skalny, "Oxidative decoloration of dyes by pulsed discharge plasma in water," *Journal of Electrostatics*, vol. 58, pp. 135-145, May 2003.

[5] Y. Kinoshita, H. Ikeda, R. Iguchi, K. Takashima, S. Katsura, and A. Mizuno, "Decolorization of indigocarmine by discharge on and above the liquid surface" (in Japanese), *Journal of the Institute of Electrostatics Japan*, vol. 30, pp.32-37, 2006.

[6] H. J. Wang, H. Li, and M. Quan, "Decoloration of azo dye by a multi-needle-to-plate high-voltage pulsed corona discharge system in water," *Journal of Electrostatics,* vol. 64, pp. 416-421, 2006.

[7] A. A. Joshi, B. R. Locke, P. Arce, and W. C. Finney, "Formation of hydroxyl radicals, hydrogen-peroxide and aqueous electrons by pulsed streamer corona discharge in aqueous-solution," *Journal of Hazardous Materials,* vol. 41, pp. 3-30, 1995.

[8] M. Sato, T. Tokutake, T. Ohshima, and A. T. Sugiarto, "Aqueous phenol decomposition by pulsed discharges on the water surface," *IEEE Transactions on Industry Applications,* vol. 44, pp. 1397-1402, 2008.

[9] M. Dors, E. Metel, and J. Mizeraczyk, "Phenol degradation in water by pulsed streamer corona discharge and Fenton reaction," *International Journal of Plasma Environmental Science and Technology*, vol. 1, pp.76-81, 2007.

[10] Y. Matsui, N. Takeuchi, K. Sasaki, R. Hayashi, and K. Yasuoka, "Experimental and theoretical study of acetic-acid decomposition by a pulsed dielectric-barrier plasma in a gas-liquid two-phase flow," *Plasma Sources Science & Technology*, vol. 20, 034015, 2011.

[11] T. Tanino, F. Kakamura, T. Ohshima, and M. Sato, "Surfactant decomposition by discharge plasma in microbubble dispersed water" (in Japanese), *Journal of the Institute of Electrostatics Japan*, vol. 34, pp.31-36, 2010.

[12] Y. Minamitani, T. Kobayashi, Y. Ohba, and Y. Higashiyama, "The characteristic of decomposition of LAS in a water droplets spray by pulsed power discharge in air" (in Japanese), *IEEJ Transactions on Fundamentals and Materials*, vol. 130, pp.561-566, 2010.

[13] E. S. Bobkova, V. I. Grinevich, N. A. Ivantsova, and V. V. Rybkin, "A study of sulfonol decomposition in water solutions under the action of dielectric barrier discharge in the presence of different heterogeneous catalysts," *Plasma Chemistry and Plasma Processing*, vol. 32, pp. 97-107, 2012.

[14] E. S. Bobkova, V. I. Grinevich, N. A. Ivantsova, and V. V. Rybkin, "Influence of various solid catalysts on the destruction kinetics of sodium lauryl sulfate in aqueo*us solutions by DBD," Plasma Chemistry and Plasma Processing*, vol. 32, pp. 703-714, 2012.

[15] S. Kanazawa, M. Hirao, S. Akamine, R. Ichiki, T. Ohkubo, M. Kocik, and J. Mizeraczyk, "LIF detection of OH radicals produced by a discharge over water surface" (in Japanese), *Journal of the Institute of Electrostatics Japan*, vol. 34, pp.14-18, 2010.

[16] 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 the surface of a liquid," *Plasma Sources Science & Technology,* vol. 20, 034010, 2011.

[17] P. Bruggeman and D. C. Schram, "On OH production in water containing atmospheric pressure plasmas," *Plasma Sources Science & Technology*, vol. 19, 045025, 2010.

[18] P. Lukes and B. R. Locke, "Plasmachemical oxidation processes in a hybrid gas-liquid electrical discharge reactor," *Journal of Physics D-Applied Physics,* vol. 38, pp. 4074-4081, 2005.

[19] F. J. Beltran, J. F. Garcia-Araya, and P. M. Alvarez, "Sodium dodecylbenzenesulfonate removal from water and wastewater. 1. Kinetics of decomposition by ozonation," *Industrial & Engineering Chemistry Research,* vol. 39, pp. 2214-2220, 2000.

[20] S. Geng, S. Kanazawa, S. Akamine, R. Ichiki, M, Kocik, and J. Mizeraczyk, "Decolorization of indigo carmine solution by superimposition of streamer discharges on the water surface and ozone" (in Japanese), in *Proc. of 2011 Annual Meeting of the Institute of Electrostatics Japan*, pp. 227-228, 2011.

[21] A. Di Corcia, F. Casassa, C. Crescenzi, A. Marcomini, and R. Samperi, "Investigation of the fate of linear alkyl benzenesulfonates and coproducts in a laboratory biodegradation test by using liquid chromatography/mass spectrometry," *Environmental Science & Technology,* vol. 33, pp. 4112-4118, 1999.

[22] J. Fernandez, J. Riu, E. Garcia-Calvo, A. Rodriguez, A. R. Fernandez-Alba, and D. Barcelo, "Determination of photodegradation and ozonation by products of linear alkylbenzene sulfonates by liquid chromatography and ion chromatography under controlled laboratory experiments," *Talanta,* vol. 64, pp. 69-79, 2004.