J. Inst. Electrostat. Jpn.
論　　文

静電気学会誌，38, 1（2014）34-39

Investigation of Organic Compound Decomposition and Microbial Inactivation by a Cylinder Style Pulsed Discharge System in High Conductivity Solution

Takanori TANINO, Yukihiro TAMURA and Takayuki OHSHIMA*, 1

(Received September 10, 2013; Accepted November 19, 2013)

A cylinder style discharge system was applied for organic compound decomposition in high conductivity solution. Effect of the submerging electrode and treatment water conductivity on the degradation of the organic compound by pulsed discharge plasma was investigated by using indigocarmine and oxalic acid. Submerging electrode sheathed with gas flow in the treatment water facilitated decomposition of these organic compounds. It was demonstrated that decomposition ratios of organic compound in the high conductivity solutions, that were equivalent to saline（18 mS/cm）and seawater（51 mS/cm）respectively, were higher than that in the deionized water. And the reachable decomposition ratio was also increased in the adjusted high conductivity solutions. Moreover, application of this system for microbial inactivation was investigated. Similar to the results in the organic compound decomposition, efficient inactivation was also detected in high conductivity solution.

1. Introduction

Discharge plasma that could generate ultraviolet light and active species is one of the applicable advanced technologies to the water treatment. Because of the high dielectric breakdown voltage, generation of the discharge plasma in water is difficult. Several plasma generation systems have been developed to generate discharge plasma in water directly. As the mechanism to generate plasma in water, gas bubble generated at the electrodes submerged in water could be a trigger to decrease dielectric breakdown voltage and generate discharge plasma[1-4], and injection of gas bubble has been investigated as the one of the method to readily generate and utilize discharge plasma in water. We also previously constructed novel submerged style pulse discharge system with gas bubble injection, and reported its characteristics and application to water treatment[5, 6]. This system could readily allow generating continuous discharge plasma in water. Decomposition of organic compound and inactivation of bacteria in water were successfully demonstrated. However, it was difficult to generate and utilize discharge plasma in the treatment water with high conductivity, because the electrodes in this style discharge plasma generation systems were in contact with the treatment water.

Keywords：pulsed discharge plasma in water, conductivity, decomposition, inactivation

* Department of Chemical and Environmental Engineering, Graduated School of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu city, Gunma, 376-8515, Japan
1 tohshima@gunma-u.ac.jp

One of the techniques to treat high conductivity water by discharge plasma is to irradiate from above the treatment water[7]. The other technique is utilizing the cylinder style discharge system with gas flow and high voltage electrode inside of it[8]. In this system, high voltage electrode is placed in gas phase and discharge plasma generated in the gas phase is irradiated to the water surface. It could be submerged and used to generate and utilize discharge plasma in high conductivity water. Except for whether the high voltage electrode is situated above or in water, it is same in both technique that discharge plasma generated in gas phase is irradiated to the gas-water interface.

In this study, the effect of submerging cylinder style discharge system in water on the decomposition of organic compound by the pulsed discharge plasma was investigated. Moreover, the influence of treatment water conductivity on the decomposition of organic compounds and inactivation of microorganism using this system was also investigated.

2. Materials and Methods

2.1 Cylinder style discharge system

The cylinder style discharge system was constructed using 4 mmϕ stainless rod for high voltage electrode and inner diameter 7 mmϕ Plexiglas pipe（350 and 900 mm）for cylinder（Fig. 1）.

As the power supply, a high-voltage pulse generator with a stationary spark gap was used. The discharge capacitor, pulse repetition frequency and applied voltage were 2 nF, 100 Hz and 20 kV, respectively. The high-voltage pulse generator was

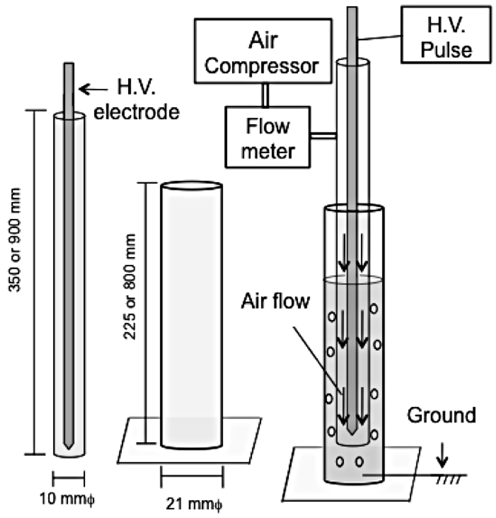

Fig. 1 Cylinder system discharge system

connected to the high voltage electrode and grounded electrode was placed in treatment water. Two different size treatment reactors were constructed with Plexiglas cylinder (225 and 800 mm) and plate (21 mmϕ). The treatment volume of reactor constructed using 225 or 800 mm Plexiglas cylinder was 50 or 220 ml, respectively. The electrodes covered with 350 and 900 mm Plexiglas pipe were combined with 50 and 200 ml volume treatment reactors for plasma treatment, respectively. The cylinder system with 0.5 L/min air flow was situated above or in treatment water, and then 20 kV pulsed voltage was applied to generate pulsed electric discharge.

2.2 Preparation and analysis of treatment water containing organic compound

Indigocarmine and oxalic acid were used for the decomposition experiment, and they were dissolved in deionized water, respectively. Conductivity of the treatment water was adjusted to 18 and 51 mS/cm by adding sodium chloride. These are equivalent to physiological saline and seawater, respectively. Initial concentration of indigocarmine and oxalic acid solutions was 50 mg/L. Indigocarmine concentration in the plasma treated water was measured by spectroscopic analysis using spectrophotometer (UVmini 1240, Shimadzu, Kyoto, Japan). Oxalic acid concentration in the plasma treated water was measured high performance liquid chromatographic analysis using spectrophotometric detector (SPD-6AV, Shimadzu). The column used for separation was ICSep ICE-ORH-801 (Transgenomic INC., Omaha, NE). The HPLC apparatus was operated at 35°C with 0.05 N sulfuric acid at a flow rate of 0.8 ml/min as the mobile phase.

2.3 Preparation and analysis of treatment water containing microorganism

Escherichia coli K-12 strain was used for inactivation experiment. The *E. coli* was cultivated in Luria-Bertain (LB) medium (1% (w/v) peptone, 0.5% yeast extract and 0.5% sodium chloride) at 35℃. The cultivated *E. coli* cells were collected by centrifugation for 5 min at 10,000 × g. Appropriate amounts of collected cells were resuspended in sterilized deionized water. Conductivity of the treatment water was adjusted to 18 and 51 mS/cm by adding sodium chloride. After the plasma treatment, aliquot of treatment water was appropriately diluted with saline, and 100 μl of diluted sample were inoculated onto LB medium plate (LB medium containing 1% agar). Plate were incubated at 35°C for 16 h, and then colony appeared on the plate was counted to determine the survival ratio.

2.4 Calculation of decomposition and inactivation rate constants

Decomposition and inactivation rate constants were calculated by using following formula (Eq. 1):

$$K = -\frac{1}{t}\ln\frac{N}{N_0} \qquad (1)$$

where t is the treatment time, and N_0 and N are the concentration of organic compounds or viable cells per volume before and after discharge plasma treatment, respectively.

3. Results and discussion

3.1 Effect of submerging cylinder style discharge system in water on decomposition of organic compound by pulsed discharge plasma

In the cylinder style discharge system with gas flow, discharge plasma is generated at the edge of high voltage electrode in gas phase and irradiated to the gas-water interface. The high voltage electrode could be situated above or in the treatment water, and discharge plasma itself has no difference when high voltage electrode sheathed with gas flow is situated above or in the treatment water (Fig. 2).

The effect of the submerging high voltage electrode sheathed with gas flow on organic compound decomposition by pulsed discharge plasma was investigated using indigocarmine and oxalic acid when water conductivity was 51 mS/cm.

On the experiment using indigocarmine in the 50 ml treatment reactor, high voltage electrode sheathed with gas flow was situated at the height of 10 mm above the water

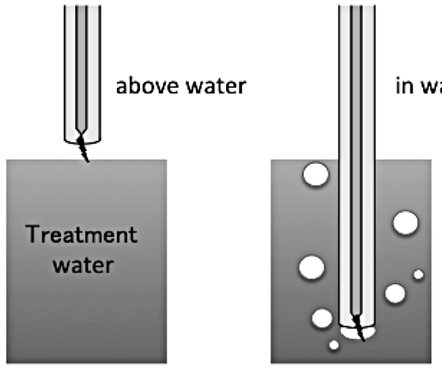

Fig. 2 Schematic illustration of submerging cylinder style discharge system in water

surface or at the depth of 100 mm under the water surface. Decomposition of indigocarmine, especially initial decomposition, was clearly facilitated by submerging high voltage electrode. The decomposition ratio achieved after 2 min discharge plasma treatment in water was 2.6-fold higher than that above water（Fig. 3）.

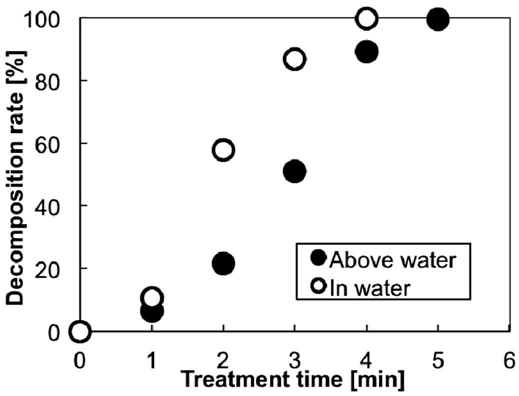

Fig. 3 Effect of submerging cylinder style discharge system on indigocarmine decomposition by discharge plasma

The effect of depth to submerge on the decomposition of organic compound was also investigated on the experiment using oxalic acid in the 220 ml treatment reactor（Fig. 4）. Compared to situating high voltage electrode at the height of 10 mm above the water surface, situating high voltage electrode at the depth of 100 mm under the water surface did not show clear facilitation in the decomposition of oxalic acid. However, increasing the depth of submerging high voltage electrode to 300 and 500 mm facilitated decomposition, and final decomposition ratio was also increased. Especially situating high voltage electrode at 500 mm under the water surface clearly facilitated the oxalic acid decomposition. The decomposition ratios achieved by discharge plasma treatment at the depth of 500 mm under the water surface after 120 min

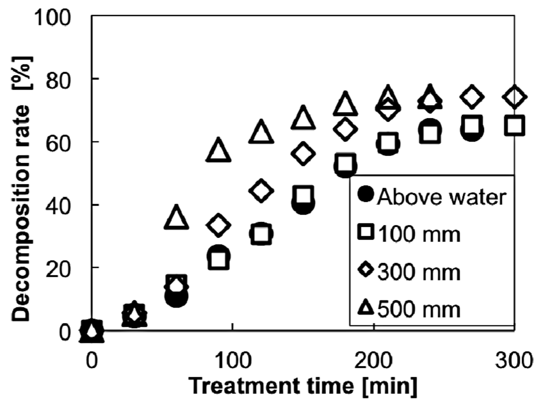

Fig. 4 Effect of submerging cylinder style discharge system on oxalic acid decomposition by discharge plasma

and above water after 240 min were almost same. Form these results, it was demonstrated that submerging high voltage electrode is also effective on the facilitation of oxalic acid decomposition by pulsed discharged plasma.

Submerging high voltage electrode sheathed with gas flow in the treatment water, *i.e.* generating pulsed discharge plasma in water on a macroscopic meaning, facilitated decomposition of the indigocarmine and oxalic acid. One of the reasons for these facilitations of organic compound decomposition might be efficient diffusion and utilization of relatively long-life active species such as ozone in the treatment water. The facilitation of the decomposition of indigocarmine with submerging high voltage electrode（Fig. 3）seemed to be with ozone solved in the treatment water. However, it is reported that oxalic acid could not be decomposed by ozone[9], and we also confirmed no decomposition of oxalic acid by injection of 10 ppm ozone into the treatment water at the flow rate 0.5 L/min（data not shown）. Therefore, ozone did not play an important role for oxalic acid decomposition. Direct interaction of discharge plasma and water surface, in which short-life active species such as hydroxyl radical are produced and contribute to decomposition of oxalic acid, should be necessary, and major reason of facilitation in oxalic acid decomposition must be an improvement of mixing condition by the injected bubble in the treatment water（Fig. 4）.

3.2 Influence of treatment water conductivity on decomposition of organic compound by pulsed discharge plasma

In the cylinder style discharge system with gas flow, high voltage electrode is not in contact with treatment water. So regardless of whether the conductivity of treatment water is high or low, the pulsed discharge plasma itself could be readily generated in water on a macroscopic meaning. However, strength and input energy of the pulsed discharge plasma might be changed by the conductivity of treatment water. And those factors affect the amount of the radical produced at gas-water interface. The influence of treatment water conductivity on organic compound decomposition by pulsed discharge plasma was investigated using indigocarmine（Fig. 5）and oxalic acid（Fig. 6）. These experiments were carried out in 50 ml treatment reactor, and high voltage electrode sheathed with gas flow was situated at the depth of 100 mm under the water surface. The indigocarmine decomposition ratios in the high conductivity solutions（18 and 51 mS/cm）were higher than that in deionized water（0.26 mS/cm）. However, significant difference of decomposition ratio was not observed between the conductivities of 18 and 51 ms/cm. Indigocarmin was almost completely decomposed after 4 and 12 min in the high and low conductivity treatment water, respectively. Decomposition rate constants of discharge plasma treatment in 0.26, 18, 51mS/cm conductivity treatment water are 4.39×10^{-3}, 1.13×10^{-2} and 1.73×10^{-2} /sec, respectively. It was clearly shown that increasing conductivity of treatment water facilitated decomposition of indigocarmin by pulsed electric discharge.

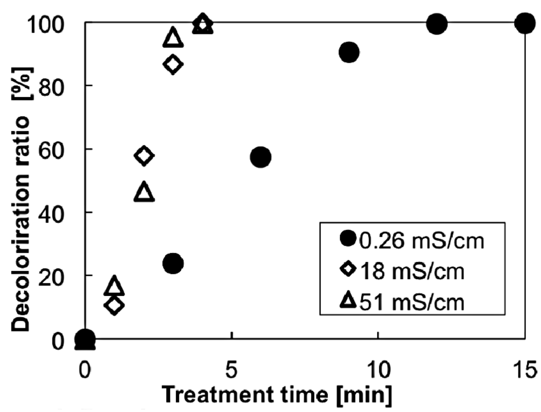

Fig. 5 Influence of conductivity on indigocarmine decomposition by discharge plasma

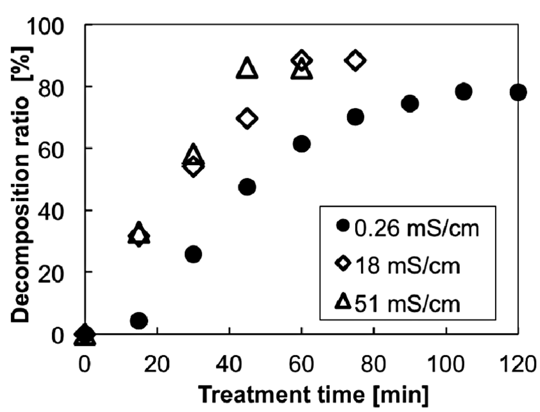

Fig. 6 Influence of conductivity on oxalic aicd decomposition by discharge plasma

Similar tendencies to the decomposition of indigocarmine were also observed on the decomposition of oxalic acid though more treatment time was necessary for the decomposition of oxalic acid than that of indigocarmine. The oxalic acid decomposition ratios in the high conductivity solutions（18 and 51 ms/cm）were almost same, and those are higher than that in deionized water. In the high conductivity treatment water, the required time to decompose 50% of oxalic acid was almost half of that in low conductivity treatment water. Decomposition rate constants of discharge plasma treatment in 0.26, 18, 51mS/cm conductivity treatment water are 2.68×10^{-4}, 4.42×10^{-4} and 7.31×10^{-4} /sec, respectively. And the reachable decomposition ratio was increased in the high conductivity solutions.

3.3 Influence of treatment water conductivity on inactivation of microorganism by pulsed discharge plasma

Inactivation of microorganism by pulsed discharge plasma in high conductivity treatment water was investigated using *E. coli* as the model microorganism. It was examined that *E. coli* is not inactivated in high conductivity water（51 mS/cm）before the experiment using pulsed discharge plasma（data not shown）. Figure 7 shows the results of *E. coli* inactivation by pulsed discharge plasma in different conductivity treatment waters.

In high and low conductivity treatment waters, almost complete inactivation of treatment water（no colony formation on LB plate）was confirmed after 2 and 8 min discharge plasma treatment, respectively. Inactivation rate constants of discharge plasma treatment in 0.26, 18, 51mS/cm conductivity

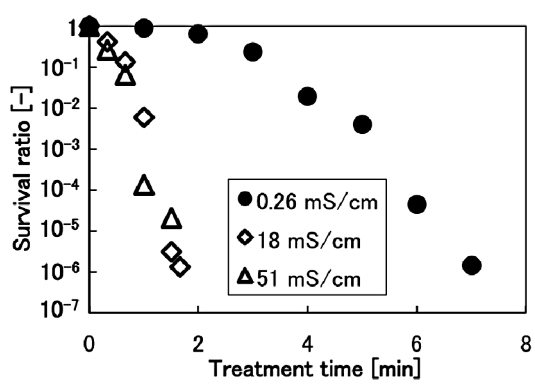

Fig. 7 Influence of conductivity on *E. coli* inactivation by discharge plasma

treatment water are 3.20×10^{-2}, 1.41×10^{-1} and 1.49×10^{-1} / sec, respectively. Similar to the results of organic compound decomposition, inactivation of *E. coli* was also facilitated in high conductivity treatment water. Comparing with the decompositions of indigocarmine and oxalic acid, inactivation of *E. coli* is most sensitive for the pulsed discharge plasma treatment.

3.4 Energy of pulsed discharge plasma

Bright discharge plasma with loud sound was observed in the high conductivity treatment water. Discharge voltage and current waveforms in high and low conductivity treatment water were observed with oscilloscope（Fig. 8）. Change of waveform between high and low conductivity treatment water was observed in both discharge voltage and current.

Energy of pulsed discharge plasma in high and low conductivity treatment water was calculated with the observation of discharge voltage and current（Fig. 9）. The electric energy stored in the capacitor in our pulse generator was 0.4 J, therefore, 75-80 % of stored energy was consumed as the discharge plasma generation in high conductivity treatment water. The energy per pulsed discharge plasma in high conductivity treatment water was at least 6-fold higher than that in low conductivity treatment water. This high-energy input into the treatment water as the discharge plasma could generate a lot of active species and facilitate decomposition of oxalic acid.

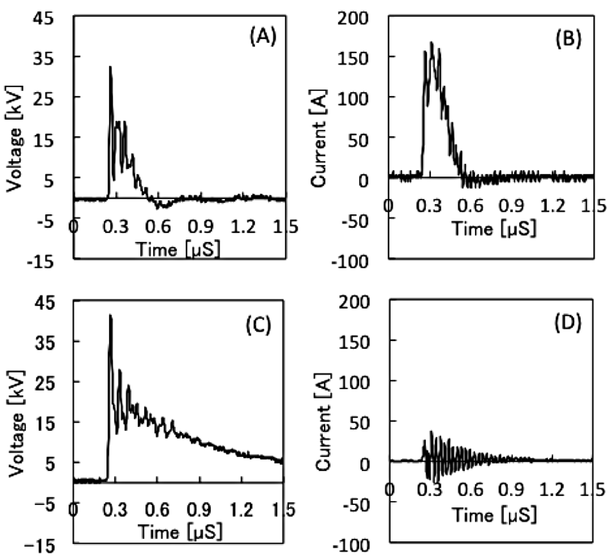

Fig. 8 Discharge voltage waveforms in high（A）and low（C）conductivity treatment water, and current waveforms in high（B）and low（D）conductivity treatment water.

The decomposition of oxalic acid plotted against the input energy was shown in Fig. 10. Decomposition efficiency per input energy in low conductivity treatment water is approximately 3-fold superior to that in high conductivity treatment water. This means that active species generated by pulsed discharge plasma were not sufficiently utilized to decompose oxalic acid in high conductivity treatment water. The rate-limiting factor might be diffusion of oxalic acid to gas-water interface.

In our study, the cylinder style discharge system was applied for high conductivity water treatment. High conductivity of the treatment water allows efficient utilization of stored electric energy in capacitor for discharge plasma generation though energy efficiency in high conductivity water was lower than that in low conductivity water. To improve the energy consumption efficiency in decomposition of organic compound in water by pulsed discharge plasma, facilitation of organic material diffusion to gas-water interface by mixing and adoption of suitable capacitor for high-voltage pulse generator with a stationary spark gap should be important.

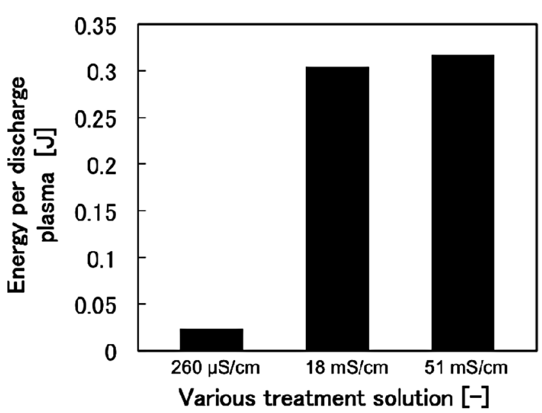

Fig. 9 Calculated energy per discharge plasma in various conductivity treatment waters

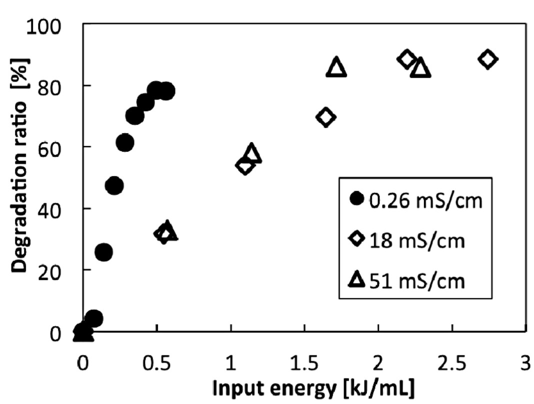

Fig. 10 Oxalic acid decomposition plotted against the energy of discharge plasma

4. Conclusion

The submerging cylinder style discharge system was demonstrated to facilitate the decomposition of organic compound in various conductivity solutions. This facilitation might result from efficient utilization of active species and improvement of mixing condition with air supply. It was also demonstrated that high conductivity treatment water could also facilitate decomposition of organic compounds and inactivation of microorganism. High conductivity treatment water allows efficient utilization of stored electric energy in capacitor in spark gap system of high-voltage pulse generator.

Acknowledgement

This research was supported by a Grand- in-Aid for Scientific Research（C）from Japan Society for the Promotion of Science（22510082）.

References

1） J.F. Kolb, R.P. Joshi. S Xiao and K.H. Schoenbach: J. Phys. D. Appl. Phys., **41**（2008）234007
2） S. Ghershman, O. Mozgina, A. Belkind, K. Becker and E. Kunhardt: Contrib. Plasma Phys., **47**（2007）19
3） K. Schoenbach, L. Kolb, S. Xiao, S. Katsuki, Y. Minamitani and R. Joshi: Plasma Sources Sci. technol., **17**（2008）24010
4） L. Quian: J. Apple. Phys., **97**（2005）113304
5） T. Ohshima, T. Tanino, and Y. Naruke: Seidenkigakkaishi, **35**（2011）212（in Japanese）
6） T. Tanino, M. Yanagisawa, and T. Ohshima: Seidenkigakkaishi, **36**（2012）37（in Japanese）
7） M. Sato, T. Tokutake, T. Ohshima and A. T. Sugiarto: IEEE. T. Ind. Appl., **44**（2008）1397
8） A. Yonezawa, K. Takahashi, N. Satta and K. Takaki: Seidenkigakkaishi, **35**（2011）31（in Japanese）
9） S. Kousai and H. Matsumoto: Mizukannkyougakkaishi, **20**（1997）539