Determination of Dissolved Total Phosphorus in Water by a Pin-Liquid Dielectric Barrier Discharge Treatment

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Abstract: We describe a pin-to-liquid dielectric barrier discharge (DBD) structure that used a water-containing vessel body as a dielectric barrier to determine dissolved total phosphorus in lakes and rivers. It was confirmed that the phosphorus compound was decomposed into orthophosphate by generating a pin-to-liquid DBD inside the atmospheric pressure plasma reactor, and the total phosphorus amount and decomposition efficiency were measured by quantifying the decomposed orthophosphate.

Keywords: Atmospheric pressure air plasma, phosphorus compound decomposition, pin-to-liquid dielectric barrier discharge, pin-to-liquid discharge.

1. Introduction

Recently, non-thermal plasma (NTP) has proved to be an important tool for efficient water treatment [1]. In particular, NTP generated in the gas–liquid phase can produce in situ highly reactive species such as N_2, NO•, O2, H_2O^+, OH^-, OH•, H_2O_2 which contribute to the decomposition of organic materials [2]. Among the various NTP sources, the pin-to-plate discharge is one of the simplest methods to effectively generate NTP containing reactive species radicals at atmospheric pressure. The pin-to-plate electrode configuration facilitates air discharge without the use of additional gas due to the pointed tip of the pin-shaped electrode, which induces local electric field enhancement. As this NTP device has a simple structure and is easy to control, which is advantageous for device miniaturization. More recently, a pin-to-liquid dielectric barrier discharge (DBD) structure using a water-containing vessel body as a dielectric barrier for total phosphorus monitoring in water has been reported [3].

In this study, to use the pin-to-liquid DBD device as a pretreatment module of water quality sensor for measuring dissolved total phosphorus in water, the treatment characteristics using a pin-to-liquid DBD are investigated in three different ambient air conditions: open atmosphere (Case A), closed atmosphere (Case B), and closed atmosphere with airflow (Case C).

2. Experimental setup

Fig. 1(a) shows the schematics of pin-to-liquid DBD structure and AP plasma system used in this study. A sinusoidal voltage with a peak value of 7.5 kV and a frequency of 27 kHz was applied to the pin-to-liquid DBD structure using an inverter-type power source. To observe temporal electrical properties during plasma generation, voltage and current waveforms from the powered electrode were monitored using a high-voltage probe (P6015A, Tektronix Inc.) and a current transformer (4100, Pearson Electronics Inc.) The equipment for APP decomposition has been described in detail by G.T. Bae et. al [3]. The detailed conditions of the proposed pin-to-liquid DBD structure are shown in Table 1.

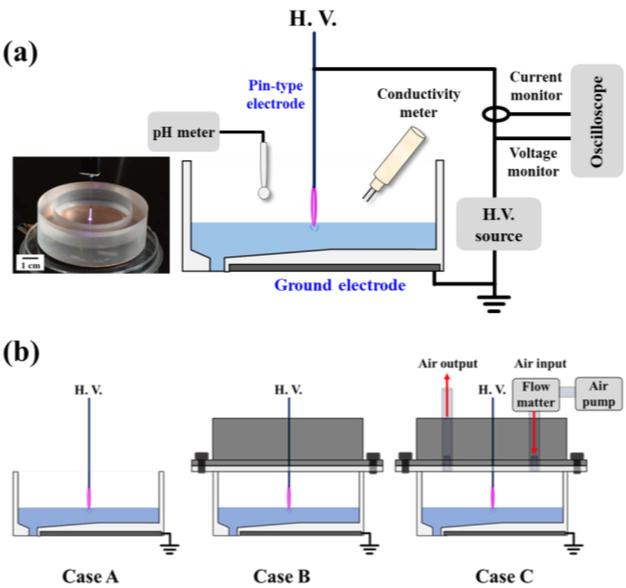

Fig. 1. (a) Schematics of the atmospheric pressure plasma system by using a pin-to-liquid dielectric barrier discharge (DBD) system, and (b) three different air-supply conditions: open atmosphere (Case A), closed atmosphere (Case B), and closed atmosphere with airflow (Case C).

Table 1. Detailed conditions for proposed pin-to-liquid DBD structure

Sample	β-glycerol phosphate disodium salt pentahydrate (BGP) sample
AC voltage amplitude	7.5 kV_p
Driving Frequency	27 kHz
Electrode gap	8 mm

The pin-to-liquid DBD uses a vessel body containing water/solution as a dielectric barrier between a metal pin electrode and a metal plate electrode. In the electrode configuration of the proposed DBD structure, the powered electrode was pin-shaped to facilitate air discharge without additional inert gas by inducing local electric field enhancement and the ground electrode was used as a copper plate covering the bottom surface of the outside of the vessel, as shown in Fig. 1(a). The distance between the pin electrode and the water surface was optimized to 8 mm.

The pin-to-liquid DBD structure does not use any additional discharge gas other than the atmosphere, thus the generated reactive nitrogen species (RNS) originates from atmosphere. Therefore, the plasma decomposition of phosphorus compound solutions into phosphates by the pin-to-liquid DBD were investigated under three different air-supply conditions: open atmosphere, closed atmosphere, and closed atmosphere with airflow as depicted in Cases A, B, and C of in Fig. 1(b).

As a phosphorus compound sample, 9.9 mg of β-glycerol phosphate disodium salt pentahydrate (BGP) was dissolved in 1 L of deionized (DI) water to prepare a BGP solution with a phosphorus concentration of 1.0 mg/L. 10 mL of the prepared BGP solution was dispensed into the water vessel of the pin-to-liquid DBD reactor and irradiated with plasma for 10 minutes. The total amount of phosphate in the BGP solution decomposed by three different plasma irradiations was confirmed by the ascorbic acid reduction method, a colorimetric method [4].

3. Results

In order to develop an effective pretreatment method suitable for water quality monitoring related to aqueous phosphorus detection, phosphates produced from plasma-treated BGP solutions under three different air-supply conditions were determined and compared with each other. To identify the reactive species generated by the pin-to-liquid DBD in ambient air, the emission spectra of a plasma plume were monitored using the fiber optic spectrometer. Fig. 2(a) shows the emission spectra from 250 to 800 nm, indicating that excited N_2, N_2^+, and N^+ existed in the plasma plume. As this AP-plasma system did not use discharge gases such as Ar or He, the several excited nitrogen species were primarily from the atmosphere [3].

Fig. 2(b) shows that the liquid temperature in Case B was about 20 ˚C higher than in Case A due to the enclosed space. In the presence of airflow under enclosed air conditions, the air channel also served as the channel for heat dissipation, resulting in a slight decrease in liquid temperature (Case C).

Fig. 2(c) shows the resultant decomposition efficiency of BGP solution into phosphate by plasma pretreatment in Cases A, B, and C. The degradation efficiency of the BGP solution increased significantly after 10 minutes of plasma treatment. This indicates that plasma treatment can decompose $C_3H_7Na_2O_6P{\cdot}5H_2O$ type BGP into PO_4^{3-} type orthophosphate. Fig. 2(c) shows the decomposition efficiency in the closed atmosphere is lower than that in the open atmosphere. By circulating air using an air pump, efficiency of decomposition increased in a state similar to an open atmosphere.

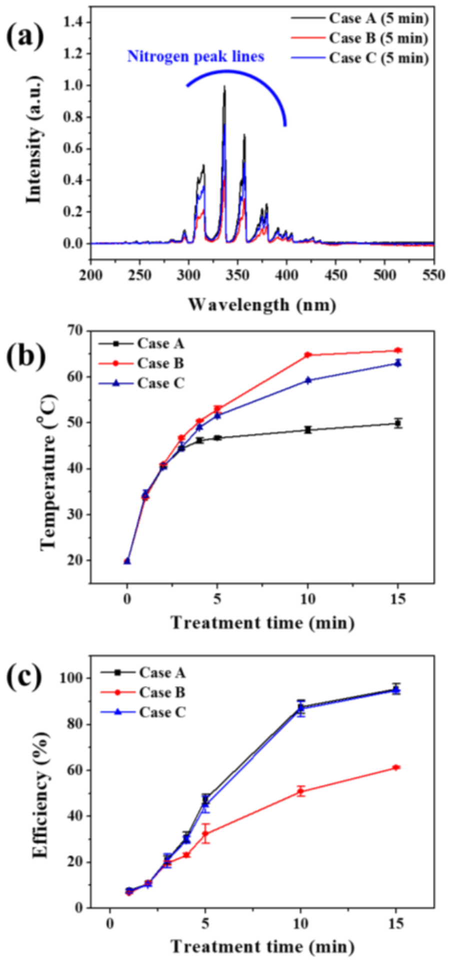

Fig. 2. (a) Optical emission spectrum, (b) Temperature change of BGP solution treated by pin-to-liquid DB, and (c) decomposition efficiency measured during pin-to-liquid DBD structures under three different air-supply conditions: open atmosphere (Case A), closed atmosphere (Case B), and closed atmosphere with airflow (Case C).

As a result, the water treatment efficiencies were different under three different air-supply conditions by comparing the decomposition properties of phosphorus compounds. The percentage of degradation efficiency according to the three cases is shown in Table 2.

Table 2. The degradation efficiencies of the three different case studies are shown in Table 1.

	Case A	Case B	Case C
Efficiency (%)	95.4%	61.3%	94.8%

The decomposition efficiency from BGP to phosphates by plasma treatment was as high as 95.4% in the open atmosphere condition, whereas the efficiency was only 61.3% in the closed atmosphere. In the closed atmosphere, since the plasma was maintained using confined air defined by the reactor volume, lower nitrogen peaks were observed and decomposition efficiency was lower than in the case of the open atmosphere. In the closed atmosphere with air flow, the intensity of the nitrogen peaks more increased than in the case of the closed atmosphere, and the decomposition efficiency also increased to 94.8%, which is almost equal to the open atmosphere condition.

4. Conclusions

In this study, we proposed a pin-to-liquid DBD structure that used a water-containing vessel body as a dielectric barrier for the effective treatment of aqueous solutions. Since the proposed pin-to-liquid DBD structure does not use any additional discharge gas except for the atmosphere, the generated reactive nitrogen species originates from the atmosphere and its amount also varies with atmospheric air conditions. As a result, we observed that the water treatment efficiencies were different under three different atmospheric air conditions by comparing the decomposition properties of phosphorus compounds. In addition, we demonstrate that the decomposition performance of phosphorus compounds comparable to that of an open atmosphere can be obtained by circulating a few air flows in a closed atmosphere.

5. References

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