Decolorization of Methylene Blue Aqueous Solution by Atmospheric-Pressure Plasma Jet

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Decolorization of a methylene blue aqueous solution was carried out using an atmospheric-pressure plasma jet. When the plasma jet was directly irradiated onto a methylene blue aqueous solution, the blue solution was decolorized within 10 min. Owing to plasma jet irradiation, the maximum absorbance spectral peak of the methylene blue aqueous solution decreased, and its position shifted to the short-wavelength region. This result indicates that the lengths of conjugated systems in the molecular structure of methylene blue decreased, and that the methylene blue aqueous solution was decolorized as a result of the decomposition of methylene blue.

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I. INTRODUCTION

Research on water purification by the decomposition of harmful organic substances in water using discharges and plasma is ongoing [1–4]. Organic substances are decomposed by chemically active species with a high oxidative power, such as hydroxyl (OH) radicals generated in water using discharges and plasma. In such research, organic dyes such as methylene blue (C₁₆H₁₈ClN₃S₂), a blue pigment, and indigo carmine (C₁₆H₈N₂Na₃O₇S₂) are used as models of harmful organic substances. The results of the decolorization of organic dyes using plasma generated in bubbles in water have been reported [1, 2, 5]. However, there are few reports on the direct irradiation of plasma generated in air into water containing organic dyes [6]. In Ref. [6], it was reported that methylene blue was degraded owing to the atmospheric-pressure plasma generated above a methylene blue aqueous solution; however, the plasma generator used in this experiment required water to cool the metallic electrodes. It was also necessary to place the methylene blue aqueous solution between the electrodes in order to generate plasma between them. Moreover, a high voltage of 22 kV was required to generate the plasma because the gaseous layer in which the plasma was generated and the methylene blue aqueous solution layer existed between the electrodes in addition to two glass layers.

Ohyama, one of the authors of this paper, developed a pencil-shaped device that can generate a plasma jet under atmospheric pressure at an applied voltage of 10 kV or lower by dielectric barrier discharge using a low-frequency high-voltage power source [7]. This device is simple, small, and highly portable, and has no restriction on the position of the target of plasma irradiation, thus enabling the irradiation of a plasma jet without moving the target. The plasma jet generated from this device extends 2-3 cm into the atmosphere; therefore, it is possible to irradiate a plasma jet onto a target even in a concave region by inserting the pencil section of the device into the concave region. Moreover, no cooling system is required for this plasma generator because it generates a nonequilibrium low-temperature plasma in which the temperatures of the gas and ions are lower than that of electrons [8, 9].

In this letter, we report the decolorization of a methylene blue aqueous solution by direct irradiation of a plasma jet. The changes in the concentration and molecular structure of methylene blue are speculated from the change in the absorbance spectra in the wavelength range from ultraviolet to near-infrared light as a result of decolorization.

II. EXPERIMENTAL

Figure 1 shows a schematic of the atmospheric-pressure plasma jet generator. In this device, a copper tube (inner diameter, 4 mm; outer diameter, 6 mm) used as a discharge electrode is inserted into a dielectric quartz tube (length, 10 cm; inner diameter, 6 mm; outer diameter, 8 mm), around which a copper foil (thickness, 0.05 mm; width, 10 mm) is wrapped as a grounding electrode. When a high AC voltage is applied, dielectric barrier discharge is induced in the quartz tube between these electrodes (yellow in Fig. 1), and the inflow gas is excited to plasma, which is ejected into the atmosphere (blue in Fig. 1).

Argon gas was used in the experiment. A plasma jet was generated at an argon gas flow rate of 10 L/min using a high-voltage power source, LHV-10AC (Logy Electric Co., Ltd.), with a frequency of 9 kHz and an applied voltage of 7 kV. Under these conditions, the plasma jet extended into the atmosphere approximately 2 cm from the...
FIG. 2: Photograph of argon plasma jet.

FIG. 3: Change in color of methylene blue aqueous solution owing to plasma jet irradiation for different times: (a) Before, (b) 5 min, and (c) 10 min.

end of the quartz tube, as shown in Fig. 2, and its maximum diameter was approximately 6 mm. This plasma jet was directly irradiated onto 10 mL of methylene blue aqueous solution with a concentration of 10 mg/L in a 60-mm-diameter glass petri dish for 1-10 min. The distance between the end of the quartz tube and the surface of the methylene blue aqueous solution was approximately 10 mm. Absorbance spectra were measured using a spectrophotometer, V-630 (JASCO Corporation).

III. RESULTS AND DISCUSSION

Figure 3 shows the change in the color of the methylene blue aqueous solution as a result of plasma jet irradiation. The solution was blue before irradiation, lightened after 5 min of irradiation, and became almost transparent after 10 min of irradiation, indicating that the methylene blue aqueous solution was decolorized upon plasma jet irradiation. Huang et al. reported the decolorization of methylene blue using atmospheric-pressure dielectric barrier discharge plasma generated above a methylene blue aqueous solution [6]. They irradiated plasma onto 25 mL of methylene blue aqueous solution with a concentration of 100 mg/L and observed that the methylene blue aqueous solution was decolorized after 40 min of irradiation. It is known that there is a reduction-oxidation reaction in which an aqueous solution of methylene blue becomes transparent when methylene blue is reduced by hydrogen (H) in the aqueous solution to become leucomethylene blue, and the solution returns to blue when the leucomethylene blue is oxidized by oxygen (O) in the aqueous solution or air. In our experiment, the aqueous solution decolorized by plasma jet irradiation did not return to blue even when it was stirred and exposed to air to promote oxidation. This result indicates that methylene blue in the aqueous solution was not reduced to leucomethylene blue during decolorization by plasma jet irradiation.

Figure 4 shows the dependence of the absorbance spectrum of the methylene blue aqueous solution on plasma jet irradiation time. In the absorbance spectrum obtained before irradiation, peaks were observed at 246, 291, 614, and 664 nm. The absorbance of each peak decreased with increasing plasma jet irradiation time. Because absorbance is proportional to methylene blue concentration, the decrease in the absorbance indicates a decrease in methylene blue concentration, suggesting the decomposition of methylene blue. It has already been reported by Machara et al. that a similar change in the absorbance spectrum of the methylene blue aqueous solution was observed when using plasma in water [5, 10].

Figure 5 shows a change in the peak wavelength observed at approximately 664 nm with respect to plasma jet irradiation time. The peak shifted to the short-wavelength region as the plasma jet irradiation time increased. It is known that the position of an absorbance peak is related to the lengths of conjugated systems in the molecular structure; a peak shifts to the long-wavelength region when the lengths of conjugated systems increase, whereas it shifts to the short-wavelength region when the lengths decrease [11]. Figure 6 shows the molecular structure of methylene blue. As indicated by the red circle in the figure, a conjugated double bond is the one at which single and double bonds are alternately connected. Therefore, the shift of the absorbance peak towards the short-wavelength region owing to plasma jet irradiation indicates that the lengths of the conjugated double bonds
of methylene blue molecules in the aqueous solution decreased. This may be because the bonds of the methylene blue molecules broke, which suggests the decomposition of methylene blue molecules. Accordingly, the decolorization of the methylene blue aqueous solution by plasma jet irradiation was considered to be a result of the decomposition of methylene blue molecules.

Similar to experiments using plasma in water, OH radicals (·OH) are considered to contribute to the decolorization of the methylene blue aqueous solution in this experiment [5, 12]. Our plasma jet comprises argon ions (Ar⁺) and electrons (e⁻). The electrons directly impinge on water molecules (H₂O) in the aqueous solution to induce reaction (1) and generate ·OH.

\[ \text{H}_2\text{O} + e^- \rightarrow \cdot\text{OH} + \cdot\text{H} + e^- . \]  

IV. CONCLUSIONS

We carried out an experiment in which an aqueous solution of methylene blue was decolorized using atmospheric-pressure plasma jet generated at a frequency of 9 kHz, an applied voltage of 7 kV, and an argon gas flow rate of 10 L/min. When an argon plasma jet was directly irradiated onto 10 mL of methylene blue aqueous solution, the blue solution gradually lightened, became transparent within 10 min, and was thus decolorized. The maximum absorbance spectral peak of the methylene blue aqueous solution in the wavelength range from ultraviolet to near-infrared light decreased, and its position shifted to the short-wavelength region. This result indicates that the lengths of conjugated systems of methylene blue molecules in the aqueous solution decreased. This may be because the bonds of the methylene blue molecules broke, which suggests the decomposition of methylene blue molecules. Our atmospheric-pressure argon plasma jet is considered to be capable of decomposing methylene blue in aqueous solutions, and can also be used to decompose other organic substances in water. Thus, plasma jet irradiation can be applied to water purification.