

Comparison of Decolorization of Methylene Blue Aqueous Solutions Irradiated with Atmospheric-Pressure Plasma Jet in Air and in Argon Gas

by

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(Received on Mar. 30, 2018 and accepted on May 10, 2018)

Abstract

The decolorization of a methylene blue aqueous solution irradiated with an atmospheric-pressure argon (Ar) plasma jet in air was compared with that in Ar gas. The time required for decolorization of the methylene blue aqueous solution irradiated with a plasma jet in Ar gas was 10 min, which was half that required for decolorization in air. We suggest that this is caused by a high current of 60.8 mA flowing during plasma jet irradiation in Ar gas, which is ~1.6-fold higher than that in air. In addition, in the case of the plasma jet irradiation in Ar gas, neither nitrate ions (NO_3^-) nor nitrite ions (NO_2^-) were generated, but only hydrogen peroxide (H_2O_2) was generated, unlike the case of plasma jet irradiation in air. The results obtained in this study show that harmful organic compounds in wastewater can be decomposed quickly without generating nitrogen oxide ions (NO_x^-) by irradiating the solution with an atmospheric-pressure Ar plasma jet in Ar gas, compared with the case of irradiation in air.

Keywords: Atmospheric-pressure plasma, Methylene blue aqueous solution, Decolorization

1. Introduction

Research on wastewater treatment using discharge and plasma has been attracting attention: for example, wastewater treatment using surface pulse discharge¹⁻⁵⁾, surface creeping discharge⁶⁾, surface atmospheric-pressure plasma⁷⁻¹⁰⁾, underwater pulse discharge¹¹⁻¹³⁾, and underwater discharge inside bubbles¹⁴⁻¹⁷⁾ have been reported thus far. In these reports, methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$), a blue organic dye, has been frequently used as an indicator of decomposition^{4, 5, 7, 9, 15-17)}. Hydroxyl (OH) radicals generated by dissociation of water (H_2O) molecules as a result of collisions of high-energy electrons in the discharge and plasma with H_2O molecules are associated with the decomposition of organic compounds. OH radicals are reactive oxygen species (ROS), have a high oxidation potential (2.80 V)¹⁸⁻²⁰⁾, and oxidatively decompose organic compounds.

We previously reported that a methylene blue aqueous solution was decolorized when it was irradiated with an atmospheric-pressure argon (Ar) plasma jet in air for 20 min²¹⁾. We also found, on the basis of the results of nuclear magnetic resonance (NMR) and electrospray ionization mass spectroscopy (ESI-MS), that the decolorization is associated with the decomposition of the phenothiazine ($\text{C}_{13}\text{H}_9\text{NS}$) structure accompanied by the dissociation of a methyl (CH_3) group from a side chain of the methylene blue molecule²²⁾.

In the previous articles, we reported that when distilled water is irradiated with an Ar plasma jet, nitrate ions (NO_3^-) are generated in distilled water and the absorption spectrum has a peak at a wavelength of ~200 nm²³⁾. This NO_3^- is considered to be generated as follows: high-energy electrons in plasma collide with nitrogen (N_2) and oxygen (O_2) molecules in air, inducing dissociation to form nitrogen (N) and oxygen (O) atoms. Then, nitrogen oxide ion (NO_x^-) species are generated by the bonding of N and O atoms. When NO_x^- enters distilled water, nitric acid (HNO_3) is generated. Finally, HNO_3 is ionized to generate NO_3^- . We also found that the peak at a wavelength of ~200 nm

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corresponds to the presence of hydrogen peroxide (H_2O_2) and a small amount of nitrite ions (NO_2^-), from the results of high-performance liquid chromatography (HPLC) ²⁴. From these results, we considered that NO_3^- , NO_2^- , and H_2O_2 are generated in a methylene blue aqueous solution irradiated with an Ar plasma jet; consequently, a peak at a wavelength of ~ 200 nm should exist in the absorption spectra.

In this study, a methylene blue aqueous solution was irradiated with an Ar plasma jet and absorption spectroscopy was carried out. If there is a peak at a wavelength of ~ 200 nm in absorption spectra, then NO_3^- , NO_2^- , and H_2O_2 are present in the methylene blue aqueous solution. HPLC was carried out to confirm the generation of NO_3^- , NO_2^- , and H_2O_2 . If NO_3^- and NO_2^- are generated as a result of collisions between high-energy electrons in plasma with N_2 and O_2 molecules in air, NO_3^- and NO_2^- should not be generated in the absence of the contact between plasma and air during irradiation. On the basis of this idea, a methylene blue aqueous solution was irradiated with a plasma jet in Ar gas, instead of air, and absorption spectroscopy and HPLC were carried out on the resultant solutions. Emission spectroscopy of the Ar plasma jet was also carried out to confirm the absence of N_2 molecules during plasma irradiation in Ar gas. The times required for decolorization of the solution irradiated with a plasma jet in Ar gas and air were different, and the currents flowing during plasma jet irradiation in Ar gas and in air were compared.

2. Experimental Methods

Figure 1 shows a schematic of the experimental setup used in this study. In the unit used to generate the plasma jet, a copper tube (inner diameter, 4 mm; outer diameter, 6 mm), as the discharge electrode, was inserted into a dielectric quartz tube (length, 50 mm; inner diameter, 6 mm; outer diameter, 8 mm) around which copper foil (thickness, 0.05 mm; width, 10 mm) was wrapped as the ground electrode ²⁵. A high AC voltage was applied to induce dielectric barrier discharge inside the quartz tube between the electrodes and to convert the Ar gas to plasma that was then ejected into the air in the form of a jet. A high-voltage power supply (LHV-10AC, Logy Electric Co., Ltd.) was used to generate the Ar plasma jet (frequency, 10 kHz; applied voltage, 10 kV; Ar gas flow rate, 10 L/min). A methylene blue aqueous solution [10 mL of a 10 mg/L (10 ppm) solution] in a glass Petri dish (diameter, 60 mm) was irradiated with the Ar plasma jet in air for 1–20 min. The distance from the end of the quartz tube to the solution (irradiation distance) was 15 mm. Plasma jet irradiation in Ar gas was carried out after an acrylic resin container ($80 \times 80 \times 30$ mm³) was filled with

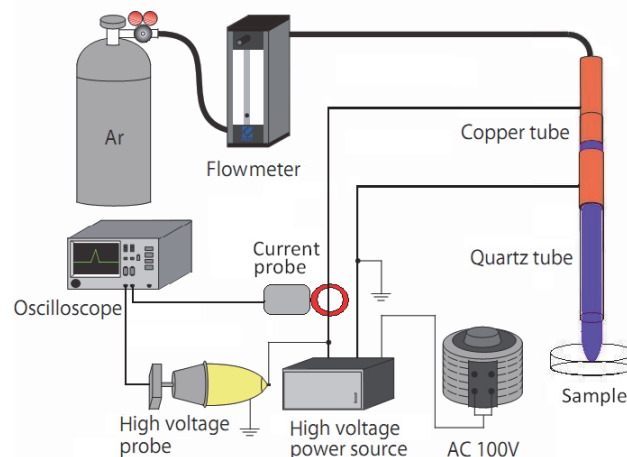


Fig. 1 Schematic of the experimental setup.

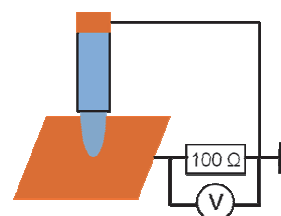


Fig. 2 Circuit used to measure current.

Ar gas. The voltage and current were measured using a high-voltage probe (P6015A, Tektronix, Inc.) and a current probe (A621, Tektronix, Inc.), respectively, which were both connected to a digital oscilloscope (TDS1001B, Tektronix, Inc.). The gas flow rate was adjusted using a gas flow meter (RK-1250, Kofloc Kyoto, Kojima Instruments Inc.).

Absorption spectra of the methylene blue aqueous solutions were obtained using a spectrophotometer (V-630, JASCO Corporation). For HPLC, a pump (PU-2080 Plus, JASCO Corporation), a UV detector (UV-2075 Plus, JASCO Corporation), and a column (Hydrosphere C18, YMC Co., Ltd.) were used. A 0.05% aqueous solution of phosphoric acid was used as the mobile phase at a flow rate of 1.0 mL/min. The UV wavelength of the detection unit was 210 nm. The amount of specimen used for the measurement was 20 μL . For emission spectroscopy of the plasma jet, a multichannel spectroscope (QE65000, Ocean Optics) was used. For emission spectroscopy in Ar gas, a quartz glass window was installed on the acrylic resin container to enable the observation of emissions inside the container. The quartz glass window has a transmittance of $\geq 85\%$ at wavelengths of 190–1100 nm.

Figure 2 shows the circuit used to measure current. To measure the current during plasma jet irradiation, copper foil was used as an electrode to which a 100 Ω resistor was connected. One end of the resistor was grounded. The

voltage between the two ends of the resistor was measured to obtain the current. In the case of plasma jet irradiation in Ar gas, this circuit was placed in the acrylic resin container.

3. Methylene Blue

Figures 3(a) and 3(b) show the molecular structures of methylene blue ($C_{16}H_{18}ClN_3S$) and phenothiazine ($C_{13}H_9NS$), respectively. As the name defined by the International Union of Pure and Applied Chemistry (IUPAC), i.e., 3,7-bis(dimethyl amino) phenothiazin-5-ium chloride, indicates, methylene blue is an organic compound having the basic structure of phenothiazine with side chains of dimethyl amino groups $[-N(CH_3)_2]$. The basic structure is a conjugated system, in which single bonds and double bonds are alternately connected. The π electrons in the conjugated system are delocalized²⁶⁾. The conjugated system of the phenothiazine structure is a chromophore and is the main cause of the color. The side-chain dimethyl amino groups are auxochromes. It is known that the bonding of an auxochrome (side chain) to a chromophore (conjugated system) increases the intensity of the absorption maximum and shifts its wavelength to the longer wavelength side²⁷⁾. This is considered to result from the delocalization of π electrons in the conjugated system, which leads to a decrease in the energy of the π electrons. Negatively charged chlorine ions (Cl^-) are bonded to positively charged sulfur ions (S^+) via Coulomb's force. In the methylene blue aqueous solution, methylene blue molecules are positively ionized and Cl^- is the counterion (separated from S^+ ions).

4. Results and Discussion

Figure 4 shows the plasma jet irradiating the surface of a methylene blue aqueous solution in (a) air and (b) Ar gas. In both cases, in the plasma, there are many streamers that reach the aqueous solution. Therefore, high-energy electrons in the streamers are considered to collide with H_2O molecules on the surface of the aqueous solution, inducing the dissociation of H_2O molecules and the generation of OH radicals and hydrogen (H) atoms. The OH radicals are considered to contribute to the decomposition of methylene blue molecules. The dissociation energy of H_2O molecules into H atoms and OH radicals is reported to be 5.1 eV^{28,29)}. Therefore, the energy of high-energy electrons in a plasma jet is considered to be at least 5.1 eV.

To confirm whether the acrylic resin container is filled with Ar gas instead of air during plasma jet irradiation in Ar gas, emission spectroscopy of the Ar plasma jet was performed. Figure 5 shows the emission spectra of the Ar

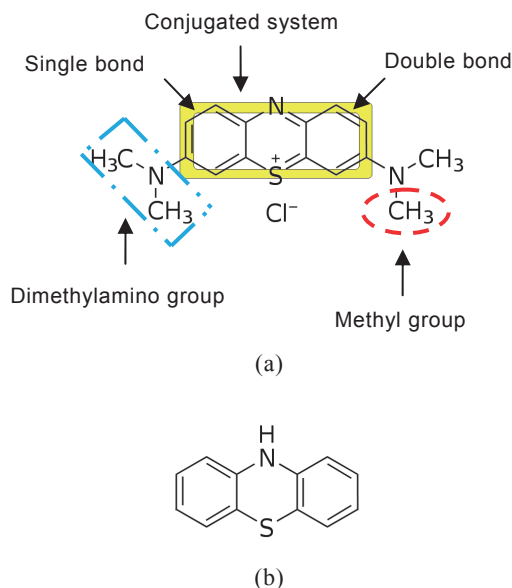
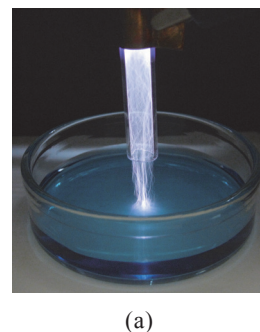
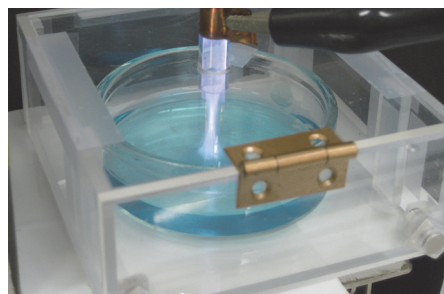


Fig. 3 Molecular structures.



(a)



(b)

Fig. 4 Plasma jet irradiation in (a) air and (b) Ar gas on the surface of the methylene blue aqueous solution.

plasma jet for irradiation in (a) air and (b) Ar gas. In the spectrum shown in Fig. 5(a), peaks are observed at wavelengths of 300–400 and 700–950 nm. The peak at 309 nm is attributed to the presence of OH radicals³⁰⁻³²⁾, peaks at 310–400 nm are attributed to excited N_2 molecules of the 2nd positive system³³⁻³⁵⁾, and peaks at 700–950 nm are attributed to excited Ar atoms³⁶⁻³⁸⁾. In contrast, in the spectrum shown in Fig. 5(b), the peaks at 310–400 nm attributed to N_2

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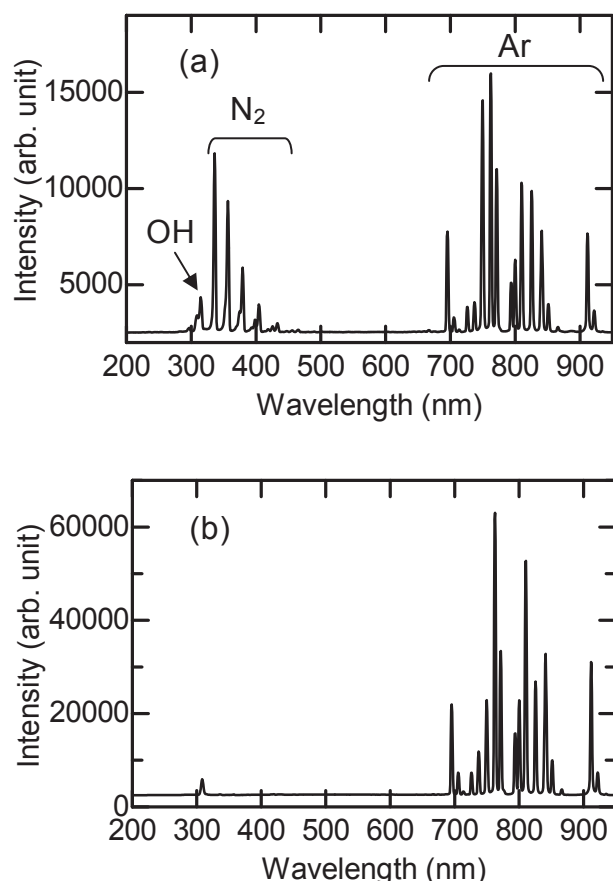


Fig. 5 Emission spectra of plasma jet for irradiation in (a) air and (b) Ar gas.

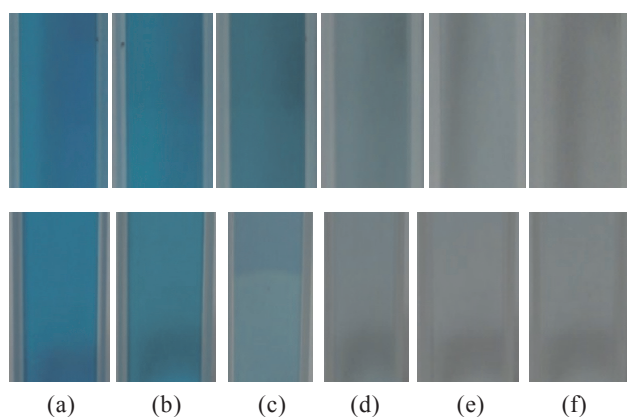


Fig. 6 Changes in color of methylene blue aqueous solutions irradiated with plasma jet in air (top) and in Ar gas (bottom): (a) before irradiation, (b) after 1 min of irradiation, (c) after 3 min of irradiation, (d) after 5 min of irradiation, (e) after 10 min of irradiation, and (f) after 20 min of irradiation.

molecules are not observed. This result indicates that there are no N_2 molecules in the acrylic resin container and thus no interaction between the plasma and N_2 molecules.

Therefore, it was confirmed that the air in the acrylic resin container was almost completely replaced with Ar gas. The maximum emission intensity of the excited Ar atoms for irradiation in Ar gas was ~ 60000 , which is approximately fourfold higher than that for irradiation in air (~ 15000). This finding indicates that the number of excited Ar atoms is higher when irradiation is carried out in Ar gas. In other words, the number of ionized Ar atoms is high and the quantity of electrons is also high when irradiation is carried out in Ar gas.

To compare the quantity of electrons that reached the surface of the methylene blue aqueous solutions, the current during plasma jet irradiation in air and in Ar gas was measured using the circuit shown in Fig. 2. The results of the measurements indicate that the current for irradiation in Ar gas is 60.8 mA, which is approximately 1.6-fold higher than that in air (37.6 mA). This finding indicates that the quantity of electrons generated for irradiation in Ar gas is approximately 1.6-fold higher than that in air and that more OH radicals are generated in the methylene blue aqueous solution irradiated with a plasma jet in Ar gas. Therefore, it is expected that decolorization of the methylene blue aqueous solution irradiated with a plasma jet in Ar gas will proceed faster than that of the solution irradiated with a plasma jet in air.

Figure 6 shows the changes in color of methylene blue aqueous solutions irradiated with a plasma jet in air and in Ar gas. Before irradiation, the color of the solution was blue in both cases. With increasing plasma irradiation time, the color gradually changed to lighter blue. The solutions became colorless after 20 and 10 min of irradiation in air and in Ar gas, respectively. The results of emission spectroscopy and current measurements demonstrate that the decolorization of the methylene blue aqueous solution irradiated with a plasma jet in Ar gas would proceed faster than that of the solution irradiated with a plasma jet in air, as we predicted.

The following redox reaction of methylene blue is known: when protons associate with methylene blue molecules in a methylene blue aqueous solution (i.e., methylene blue is reduced), methylene blue becomes the colorless leucomethylene blue. In contrast, when protons are dissociated from leucomethylene blue (i.e., methylene blue is oxidized), leucomethylene blue becomes methylene blue³⁹⁾. In this study, when the methylene blue aqueous solution that was decolorized by plasma jet irradiation was stirred, bringing it into contact with air for oxidation, the color of the solution did not return to blue. This finding indicates that the decolorization of the methylene blue aqueous solution upon plasma jet irradiation is not related to the leucomethylene

blue obtained by the reduction of methylene blue. Therefore, the decolorization of the methylene blue aqueous solution irradiated with a plasma jet is related to the decomposition of methylene blue molecules.

Figure 7 shows absorption spectra of methylene blue aqueous solutions irradiated with a plasma jet in (a) air and (b) Ar gas. In the absorption spectra obtained before irradiation, peaks were observed at wavelengths of 246, 291, 614, and 664 nm. In both Figs. 7(a) and 7(b), the absorbance at these peaks decreased with increasing plasma irradiation time. The decrease in absorbance indicates a decrease in the methylene blue concentration because the absorbance is proportional to the methylene blue concentration. This also indicates that the phenothiazine structure is decomposed because the phenothiazine structure in methylene blue is a chromophore.

In our previous studies, we reported that the decomposition of methylene blue molecules is caused by the dissociation of the bonds of the N and sulfur (S) atoms in the phenothiazine structure in the methylene blue aqueous solution irradiated with an Ar plasma jet, on the basis of the results of NMR and ESI-MS²²⁾.

In the absorption spectra obtained after irradiation in air, a new peak at a wavelength of approximately 200 nm was observed [Fig. 7(a)]. We have predicted that a new peak should be generated at a wavelength of approximately 200 nm in the absorption spectra of the methylene blue aqueous solution irradiated with a plasma jet in air, similar to the case of plasma jet irradiation onto distilled water, as explained in the Introduction. This prediction was demonstrated to be correct from our findings. This peak is attributed to the presence of NO_3^- , NO_2^- , and H_2O_2 . In contrast, in the absorption spectra obtained after irradiation in Ar gas, a small peak was observed at a wavelength of approximately 200 nm, as shown in Fig. 7(b). The plasma did not come into contact with air; therefore, the peak is not attributed to the presence of NO_3^- or NO_2^- ; rather, it is attributed to the presence of H_2O_2 . Absorption spectra similar to those in Fig. 7(b) are also obtained by underwater discharge inside bubbles in a methylene blue aqueous solution^{15, 17)}.

Figure 8 shows the dependence of absorbance at a wavelength of 664 nm on plasma irradiation time. The absorbance at 664 nm is proportional to the methylene blue concentration. The methylene blue concentration in the solution decreases with increasing plasma irradiation time. The absorbance becomes almost zero after 20 min of irradiation in air and 10 min of irradiation in Ar gas. Therefore, the time required for decolorization of the methylene blue aqueous solution irradiated with the plasma jet in Ar gas was half that required for irradiation in air. A

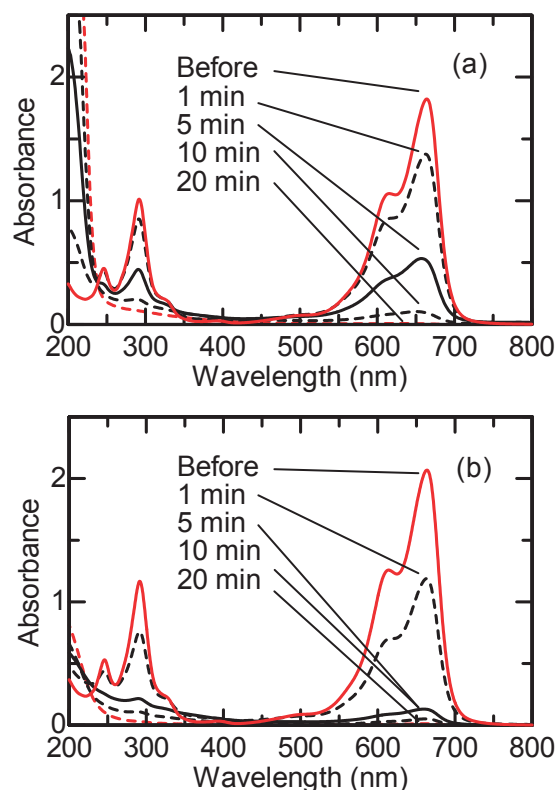


Fig. 7 Absorption spectra of methylene blue aqueous solutions irradiated with plasma jet in (a) air and (b) Ar gas.

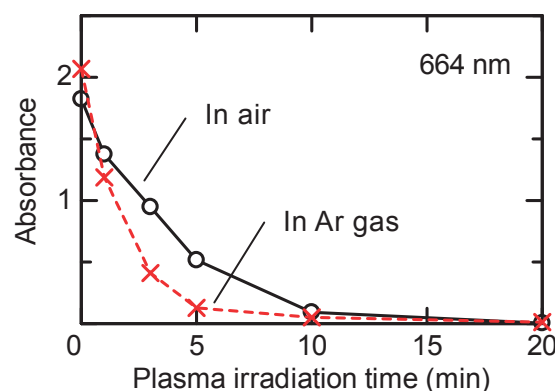


Fig. 8 Dependence of absorbance at wavelength of 664 nm on plasma irradiation time.

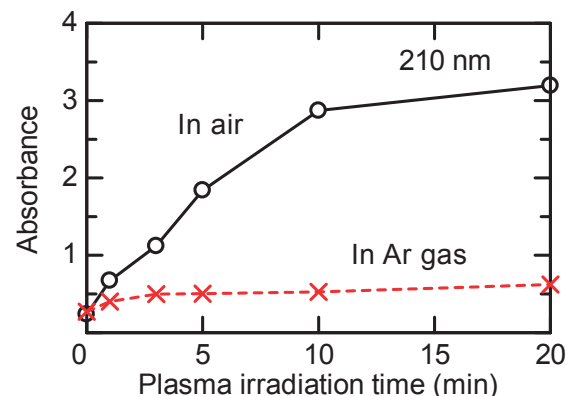


Fig. 9 Dependence of absorbance at wavelength of 210 nm on plasma irradiation time.

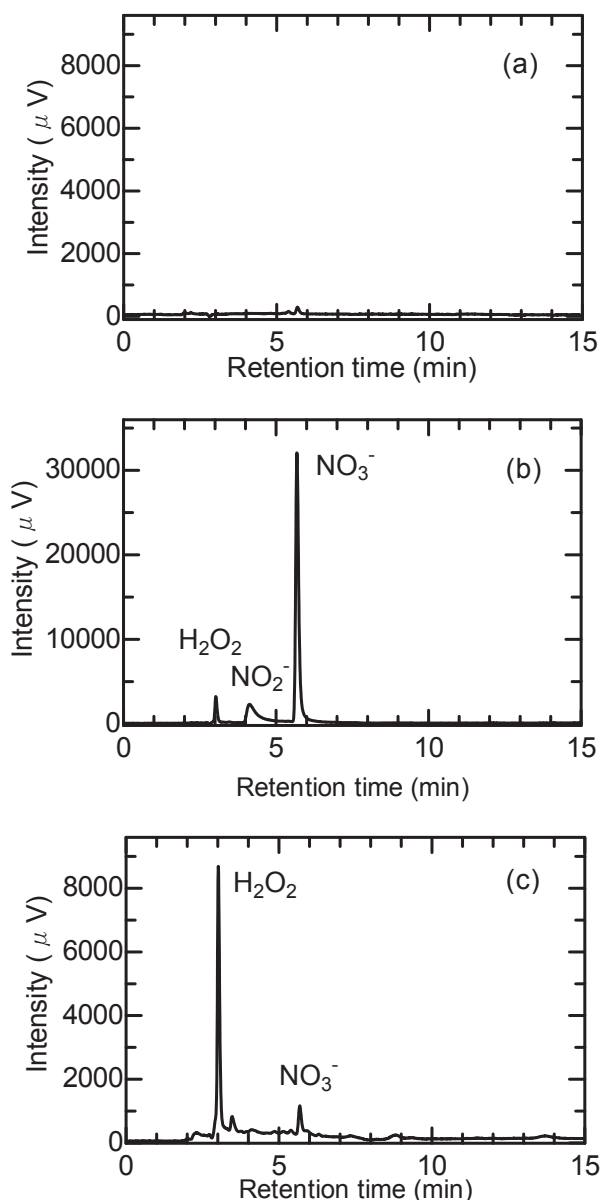


Fig. 10 HPLC chromatograms of methylene blue aqueous solution: (a) before irradiation, and irradiated with plasma jet for 1 min in (b) air and (c) Ar gas.

decrease in the methylene blue concentration with increasing plasma irradiation time has also been reported for atmospheric-pressure plasma irradiation on the surface of a methylene blue aqueous solution⁷⁾ and for plasma discharge inside bubbles in a methylene blue aqueous solution¹⁶⁾.

Figure 9 shows the dependence of absorbance on plasma irradiation time at a wavelength of 210 nm. The wavelength of 210 nm matches the wavelength used in HPLC measurement discussed later. The absorbance at this wavelength is considered to be linear with the total amount of $\text{NO}_3^- + \text{NO}_2^- + \text{H}_2\text{O}_2$. The absorbance at this wavelength increases linearly for 10 min of plasma irradiation, after

which it saturates. In contrast, the absorbance negligibly increases with plasma irradiation in Ar gas. This finding indicates that little NO_3^- , NO_2^- , or H_2O_2 is generated upon plasma irradiation in Ar gas.

Figure 10 shows HPLC chromatograms of methylene blue aqueous solutions irradiated with a plasma jet for 1 min. As shown in Fig. 10(a), no peaks were observed in the chromatogram before irradiation. In the chromatogram of the methylene blue aqueous solution irradiated with a plasma jet in air [Fig. 10(b)], peaks were observed at retention times of 3.0, 4.1, and 5.7 min. From the results of our previous study, these peaks were identified as H_2O_2 , NO_2^- , and NO_3^- , respectively²⁴⁾. From the findings of this study, H_2O_2 , NO_2^- , and NO_3^- were confirmed to be generated in the methylene blue aqueous solution irradiated with a plasma jet in air. From the results of comparisons of peak intensity, the proportion of the absorbance of NO_3^- among the total absorbance at 210 nm was the highest, followed by those of H_2O_2 and NO_2^- in that order. Most of the absorbance was attributable to NO_3^- . In the chromatogram of the methylene blue aqueous solution irradiated with a plasma jet in Ar gas [Fig. 10(c)], peaks were observed at retention times of 3.0 and 5.7 min; however, no peak was observed at 4.1 min. This finding indicates that in the methylene blue aqueous solution irradiated with plasma jet in Ar gas, H_2O_2 and a small amount of NO_3^- were generated; however, no NO_2^- was generated.

Figure 11 shows the dependence of the H_2O_2 concentration obtained using HPLC in the methylene blue aqueous solution irradiated with a plasma jet on plasma irradiation time. The H_2O_2 concentration was determined from the intensity of the H_2O_2 peak in chromatograms using a calibration curve. The H_2O_2 concentration increased linearly with increasing plasma irradiation time for irradiation in air and in Ar gas. The H_2O_2 concentration in methylene blue aqueous solution after 20 min of irradiation in Ar gas was 70 mg/L, which is ~1.4-fold higher than that in air (51 mg/L). This finding suggests that ~1.4-fold more OH radicals were generated in the solution irradiated with a plasma jet in Ar gas than that in air. This value is close to the ~1.6-fold higher current flowing during plasma jet irradiation in Ar gas compared with that in air. Therefore, we suggest that high-energy electrons in plasma were mostly used for the generation of OH radicals in solutions irradiated with a plasma jet in Ar gas. Similarly, an increase in the H_2O_2 concentration with increasing plasma irradiation time and discharge time was reported for surface atmospheric-pressure plasma irradiation^{40, 41)} and underwater pulse discharge^{12, 31, 42)}.

Figure 12 shows the dependences of the NO_3^-

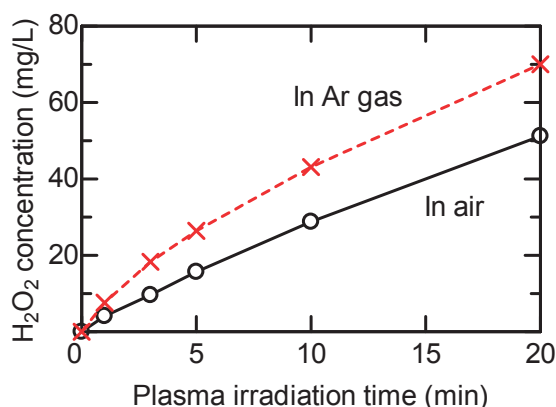


Fig. 11 Dependence of H₂O₂ concentration obtained by HPLC in methylene blue aqueous solutions irradiated with plasma jet on plasma irradiation time.

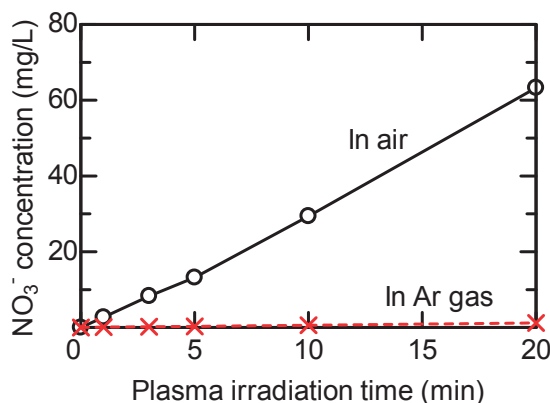


Fig. 12 Dependence of NO₃⁻ concentration obtained by HPLC in methylene blue aqueous solutions irradiated with plasma jet on plasma irradiation time.

concentration obtained by HPLC in methylene blue aqueous solutions irradiated with a plasma jet on plasma irradiation time. The NO₃⁻ concentration was obtained from the intensity of the NO₃⁻ peak in chromatograms using a calibration curve. The NO₃⁻ concentration increased linearly with increasing plasma irradiation time for irradiation in air; however, it rarely increased for irradiation in Ar gas. This finding indicates that the plasma did not come into contact with N₂ or O₂ molecules in Ar gas owing to the absence of air.

On the basis of the results from ion chromatography, Hunag *et al.* reported that NO₃⁻ is generated in pure water irradiated with a dielectric barrier discharge in air and that the NO₃⁻ concentration increases with increasing discharge time⁹⁾. Also, on the basis of the results of ion chromatography, Ikawa *et al.* reported that NO₃⁻ and NO₂⁻ are generated in distilled water irradiated with an atmospheric-pressure helium (He) plasma jet and that the

NO₃⁻ + NO₂⁻ concentration linearly increases with increasing plasma irradiation time⁴³⁾. Our results are in good agreement with their results.

The NO₃⁻ concentrations in the methylene blue aqueous solutions after 20 min of plasma irradiation in Ar gas and in air were 1.2 and 63.3 mg/L, respectively. Very little NO₃⁻ was generated in the solution irradiated with a plasma jet in Ar gas, approximately ~2% of the amount generated in air.

5. Conclusions

Decolorization of methylene blue aqueous solutions irradiated with an atmospheric-pressure Ar plasma jet in air was compared with that in Ar gas. The time required for decolorization of the methylene blue aqueous solution irradiated with a plasma jet in Ar gas was 10 min, which was half that required in air (20 min) because the current for irradiation in Ar gas was 60.8 mA, which was approximately 1.6-fold higher than that in air (37.6 mA). In addition, in the case of plasma jet irradiation in Ar gas, neither NO₃⁻ nor NO₂⁻ was generated and only H₂O₂ was generated in the methylene blue aqueous solution, unlike the case of plasma jet irradiation in air. The H₂O₂ concentration in the methylene blue aqueous solution after 20 min of irradiation in Ar gas was 70 mg/L, which was ~1.4-fold higher than that in air (51 mg/L).

The amount of OH radicals generated is large with plasma irradiation in Ar gas because the number of high-energy electrons that collide with H₂O molecules on the surface of the aqueous solution is high. The reason for the halving of the time required for the decolorization of methylene blue aqueous solution is considered to be the presence of a large amount of OH radicals that contribute to the degradation of methylene blue molecules.

In this study, the irradiation distance was 15 mm. The irradiation distance is considered to be a parameter that limits decolorization. We will carry out experiments with various irradiation distances in Ar gas in the future.

On the basis the results obtained in this study, we hypothesize that harmful organic compounds in wastewater can be decomposed in a shorter time without generating NO_x⁻ by atmospheric-pressure Ar plasma jet irradiation in Ar gas than that in air.

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