

# Investigation of plasma-organic materials interaction in aqueous solution with atmospheric pressure plasmas

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**Abstract.** An investigation was carried out into the interaction of an atmospheric pressure plasma with an organic material in an aqueous solution. The degradation of methylene blue (MB) by plasma exposure through the gas/liquid interface was studied. In the optical emission spectrum of the plasma, in addition to strong He emission lines, emissions due to O and OH radicals formed by dissociation of water were present. The change in the absorbance of a MB aqueous solution during plasma exposure was measured using UV-Vis spectroscopy. The absorption peak intensity decreased with plasma exposure time and complete decolorization occurred after 10 min. Since plasma exposure was found to decrease the pH of water, the effect of changes in pH on MB degradation in the absence of a plasma was investigated using solutions with different pH values. However, varying the pH was found to have no influence on MB degradation. The results indicated that MB degradation occurred due to interactions between MB and radicals across the plasma/liquid interface.

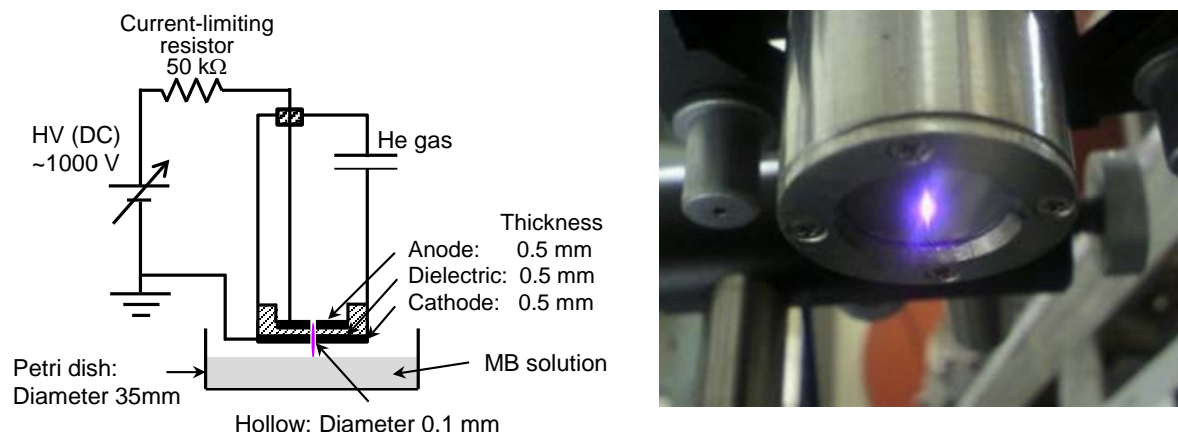
## 1. Introduction

There has been a remarkable increase in the number of medical and biological applications of plasmas [1-11]. In particular, high-pressure non-equilibrium plasmas, including atmospheric pressure plasma, are attractive in the field of medicine because thermal damage to cells is negligible if the plasma parameters and experimental setup are appropriately tuned. However, in order to fully understand the complex interactions of plasmas with biomolecules such as DNA, amino acids and proteins, which are the building blocks of cells and organs, it is essential to perform fundamental studies at the molecular or atomic level. In particular, it is important to understand plasma interactions with organic material through the plasma/liquid interface, because in many cases the active species interact with biomolecules through water. In the present study, the interaction of an atmospheric pressure He plasma with a methylene blue (MB) aqueous solution was investigated in order to determine the degradation effects of plasma exposure on such organic molecules.

## 2. Experimental

As shown in Figure 1, the atmospheric pressure He plasma was produced using a micro-hollow cathode plasma source, which operates at a low DC voltage of a few hundred volts, making it easy and efficient to apply to solutions. In the present experiment, a voltage of 800 V was used. He gas was supplied at a flow rate of 400 sccm. The plasma was used to irradiate a 10 mg/l aqueous solution of MB. The distance between the plasma source and the surface of the solution was 1 mm.



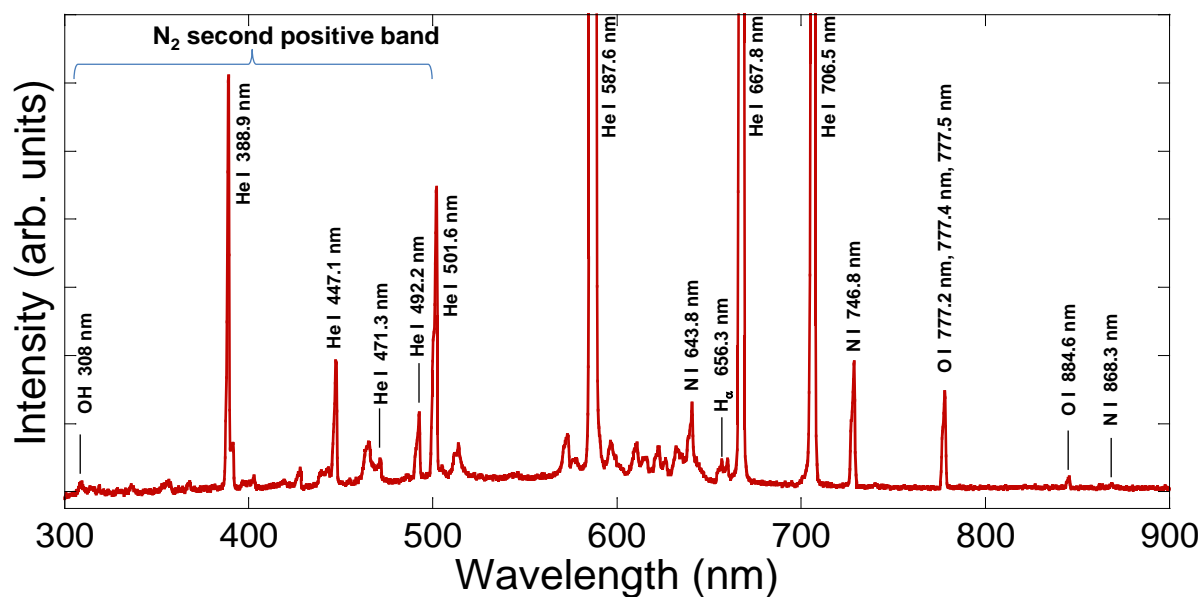


**Figure 1.** Schematic diagram and photograph of micro-hollow cathode plasma

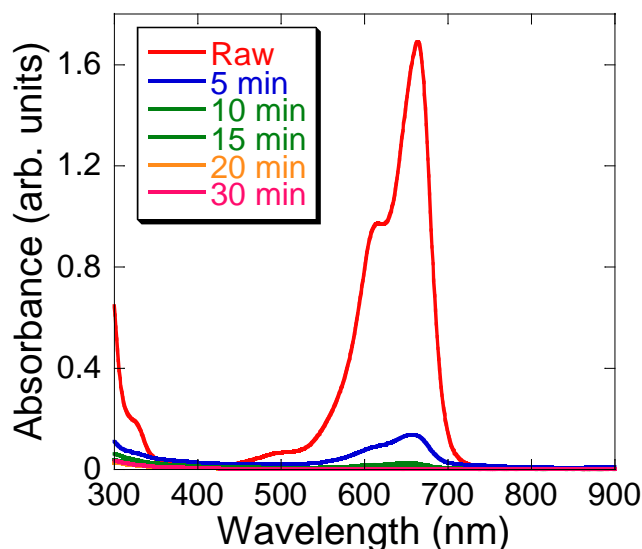
Optical emission spectroscopy (OES) was carried out on the plasma using a high-resolution fiber-optic spectrometer (HR-4000, Ocean Optics). The absorbance of the MB solution was measured by using an ultraviolet-visible (UV-vis) spectrophotometer (UV-2450, Shimadzu). The pH of the aqueous solutions was measured using a pH meter (HM-25G, DKK-TOA Corporation) with pH electrodes (ELP-036, DKK-TOA Corporation).

### 3. Results

Figure 2 shows a typical OES spectrum for the atmospheric pressure He plasma. In addition to strong He emission lines, emissions due to O and OH radicals formed by dissociation of water are seen. Furthermore, a broad peak attributed to NO<sub>x</sub> is observed from 400 nm to 700 nm. The hydroxyl radical (OH) has a higher oxidation reduction potential (ORP = 2.85 V) than ozone (2.07 V), hydrogen peroxide (1.78 V) or hypochlorous acid (1.63 V), and is environmentally friendly because its lifetime is only around 10<sup>-6</sup> sec [12,13]. Therefore, the use of an atmospheric pressure



**Figure 2.** Optical emission spectra of atmospheric pressure He plasma.

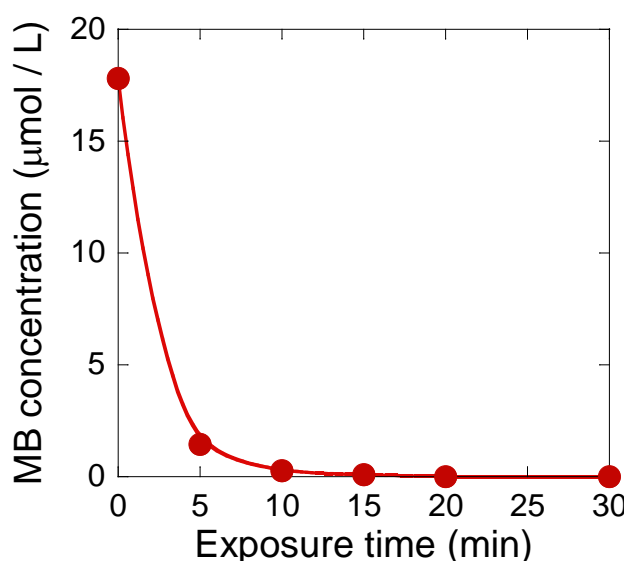


**Figure 3.** Time evolution of absorbance spectrum of MB solution during plasma treatment.

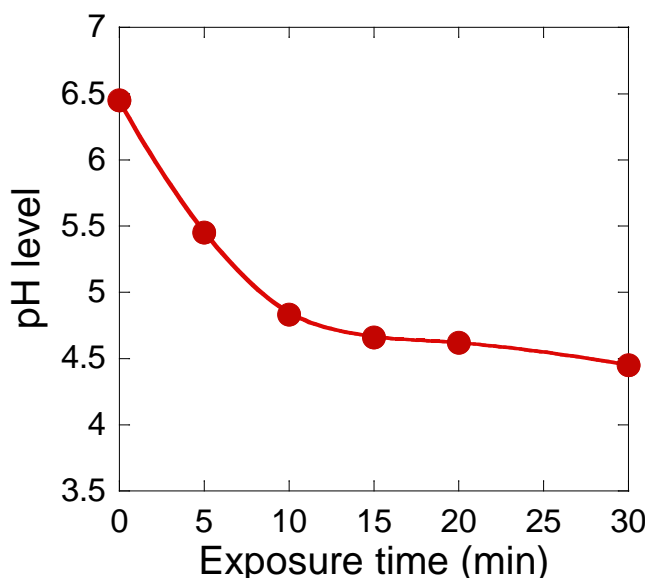
He plasma is a promising method for fluid sterilization, removal of discoloration, and oxidative dissolution.

Figure 3 shows the time evolution of the UV-Vis absorbance spectrum of the MB aqueous solution during exposure to the plasma. The absorbance peak intensity, which reflects the concentration of MB molecules, decreased with increasing plasma exposure time. Following plasma exposure for 10 min, the solution became completely colorless. Figure 4 shows the change in the estimated MB concentration with plasma exposure time. A large reduction is seen during the first 5 min.

One of the most notable chemical effects that plasmas have on solutions is acidification. To investigate whether this has some influence on the reduction of the MB concentration, deionized water was first exposed to the same plasma for varying lengths of time, and its pH was measured. Figure 5 shows the change in pH with plasma exposure time. The initial pH was about 6.4, and it decreased during the first 10 min of exposure and then became almost constant. The reason for the reduction in pH is considered to be the formation of nitric acid ( $\text{HNO}_3$ ) by dissolution of the NO generated in the plasma,



**Figure 4.** Variation of concentration of MB solution with plasma exposure time.



**Figure 5.** Variation of pH level of solution irradiated with atmospheric pressure He plasma.

as shown in the OES spectrum in Figure 2 [15]. To investigate whether the formation of  $\text{HNO}_3$  had some influence on the degradation of the MB, aqueous MB solutions with pH values of 2.4 and 5.6 were prepared and their absorbance spectrum was measured (not shown here). It was found that the solution pH had no effect on MB degradation. Therefore, it can be concluded that the decrease in the MB concentration during plasma exposure is due to radicals entering the solution from the plasma.

#### 4. Summary

An investigation has been carried out into the effect of an atmospheric pressure He plasma on the degradation of an aqueous solution of methylene blue (MB). In the optical emission spectrum of the plasma, in addition to strong He emission peaks, emissions due to O and OH radicals produced by dissociation of water were present. When the MB solution was exposed to the plasma, UV-Vis spectroscopy determined that the MB concentration decreased with exposure time, with the solution becoming completely colorless after 10 min. To determine whether this was the effect of changing pH, the absorbance was measured for MB solutions with different pH values. However, the pH was found to have no influence on MB degradation. The results indicated that MB degradation occurred due to interactions between MB and radicals across the plasma/liquid interface.

#### Acknowledgments

This work was partly supported by The Grant-in-Aid for Scientific Research on Innovative Areas “Plasma Medical Innovation” (24108003) from The Ministry of Education, Culture, Sports, Science and Technology (MEXT) and The Grant-in-Aid for Young Scientists (B) (24760597) from the Japan Society for the Promotion of Science (JSPS).

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