



## Degradation of methylene blue by radio frequency plasmas in water under ultraviolet irradiation

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### ABSTRACT

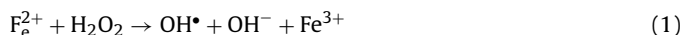
The degradation of methylene blue by radio frequency (RF) plasmas in water under ultraviolet (UV) irradiation was studied experimentally. When the methylene blue solution was exposed to RF plasma, UV irradiation from a mercury vapor lamp enhanced degradation significantly. A lamp without power supply also enhanced degradation since weak UV light was emitted weakly from the lamp due to the excitation of mercury vapor by stray RF power. Such an enhancement is explained by the fact that after hydrogen peroxide is produced via the recombination process of OH radicals around the plasma, OH radicals reproduced from hydrogen peroxide via the photolysis process degrade methylene blue.

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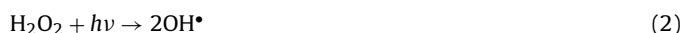
### 1. Introduction

Plasma in water can be used in advanced oxidation processes (AOPs) since it produces active species such as OH radicals. A number of studies have been conducted on pulsed streamer corona discharges generated in water [1–5]. Recently, the generation of radio frequency (RF) plasmas has been reported [6–9]. RF power is injected into water through an electrode. RF plasma is generated; it is surrounded by bubbles and is maintained locally on the electrode. According to Ref. [7], RF plasmas are used for the degradation of methylene blue dissolved in water. This degradation may be caused by the generation of OH radicals produced by the RF plasma. In Ref. [8], the formation of hydrogen peroxide has also been reported. Hydrogen peroxide is produced through the recombination of radicals in the bubble surrounding the plasma or in the aqueous neighborhood of the bubble. Hydrogen peroxide can degrade methylene blue gradually over a few weeks. This degradation may be due to chemical processes via hydrogen peroxide and tungsten powder from an electrode. Hydrogen peroxide alone can-

not contribute to rapid degradation since it is considerably more stable than OH radicals. Rapid degradation can be achieved by the reproduction of OH radicals from hydrogen peroxide via Fenton's reaction ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ), which is represented as



In Ref. [9], the addition of ferrous sulfate to the methylene blue solution enhanced the degradation rate of methylene blue. However, the solution appeared brownish after this process due to the presence of  $\text{Fe}^{3+}$  ions. Therefore,  $\text{Fe}^{3+}$  ions must be eliminated in order to obtain clear water. The other reaction for the formation of OH radicals from hydrogen peroxide is photolysis ( $\text{H}_2\text{O}_2/\text{UV}$ ):



In Ref. [10], the above mentioned reaction was made to occur using hydrogen peroxide and UV light (254 nm) emitted from a mercury vapor lamp. Recently, light-emitting diodes (LEDs) have been employed as UV sources [11]. Thus, the photolysis of hydrogen peroxide is useful for water treatment. These results suggest that UV irradiation is expected to enhance the degradation of methylene blue exposed to plasma. Since RF plasma in water is localized on the electrode, which is not the case in pulsed streamer discharge, it is easy to irradiate the solution with UV radiation from the mercury lamp submerged above the plasma. Such a system, which consists

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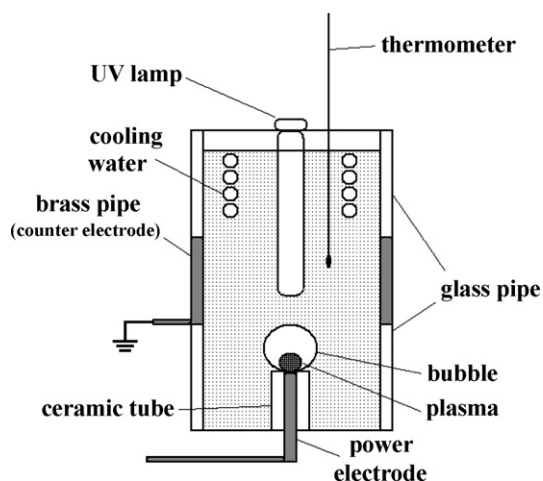


Fig. 1. Schematic view of experimental setup.

of UV and plasma, does not require the addition of chemicals to solution.

In this study, we compare the degradation of methylene blue and generation of hydrogen peroxide by RF plasma in water with and without UV irradiation. In addition, we compare these results with UV irradiation to the mixture of methylene blue solution and purchased hydrogen peroxide without exposure to plasma.

## 2. Experimental apparatus

RF plasma was generated using a power electrode in water (Fig. 1). Two Pyrex glass pipes (ID: 75 mm, height: 90 mm) connected by a brass pipe (ID: 75 mm, height: 60 mm) were used as the vessel. During the degradation experiments, 950 mL of methylene blue solution was stored in this vessel. Since the brass pipe was connected to the ground line, it functioned as a counter electrode. For UV irradiation, we used a UV lamp containing low pressure of mercury vapor (TUV PL-L 18W, Philips). This lamp consists of twin glass tubes; the OD and length of each tube is 10 mm and 185 mm, respectively. It can emit UV light with the wavelength of 254 nm, and lamp glass filters out the 185 nm ozone-forming line. For 18 W of AC power supply, power of emitted UV light is 4.7 W. The twin tubes were submerged in water. Water flowing through a copper pipe was used to control the temperature of water in the vessel. The temperature of water was measured using a fiber optic thermometer (FL-2000, Anritsu Meter); this thermometer can measure the temperature of water without being affected by the interference caused by an electromagnetic oscillation, because it uses the concept of the dependence of reflection of light by luminophor on temperature. The methylene blue solution was warmed in hot water and maintained at 40 °C before being poured into the vessel. The temperature of water in the vessel was controlled to within  $\pm 3$  °C during exposure to plasma and/or UV irradiation.

The power electrode was a tungsten rod with a diameter and length of 2.8 mm and 20 mm, respectively. It was covered with a ceramic pipe (OD: 5 mm, ID: 3 mm). The electrodes were connected to a resonator by copper leads, and RF power was supplied to the resonator by means of a tuner from a power supply (T161-6013H, Thamway,  $f = 13.56$  MHz). Here, the net input power was fixed at 210 W.

RF plasma was produced on the electrode in water as follows. Keeping the RF power low (50 W), the reflected RF power was reduced by adjusting the tuner, then, the RF power was increased until breakdown. At approximately 600 W, breakdown occurred. After breakdown, it took a few seconds to decrease the RF power into approximately 300 W. Subsequently, it took approximately

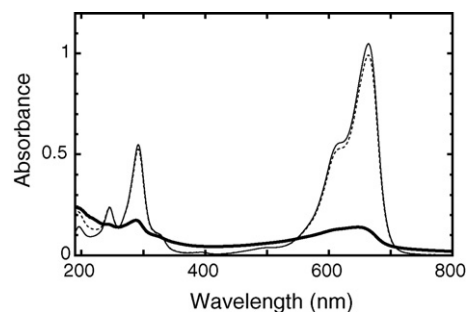


Fig. 2. Absorbance spectra of methylene blue solution before (solid line) and after exposure. The dotted and bold lines denote exposure to plasma with and without UV irradiation, respectively.

10 s to decrease the net RF power to 210 W while controlling the tuner to decrease the reflected power. The plasma was maintained stably until the RF power was turned off. The diameters of the RF plasma and surrounding bubble were approximately 3 mm and 6 mm, respectively.

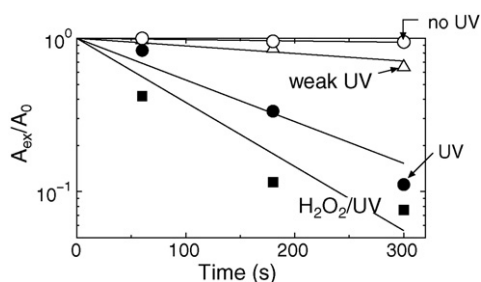
RF plasma in water can degrade methylene blue solution (5 mg/L). As compared with the solution before exposure, the solution after exposure lightened and its color tone varied. This variation is obvious from the absorbance spectrum. Absorbance  $A$  is defined as  $A(\lambda) \equiv \log I_0(\lambda)/I(\lambda)$ , where  $I_0(\lambda)$  and  $I(\lambda)$  are the intensity of light with wavelength ( $\lambda$ ) passing through the methylene blue solution, before and after transmission, respectively. A double-beam spectrophotometer (U-2810, Hitachi) was used for the measurement of the absorbance spectra.

There is no stirring system in our experimental apparatus. Water around the bottom was heated by plasma and water in the upper region was cooled by the cooling water. These effects lead convection effectively and then water in the vessel was mixed naturally. After exposure, difference of absorbance between the upper and bottom regions was less than one percent.

## 3. Experimental results and discussions

The absorbance before exposure is represented by the solid line in Fig. 2. The absorbance shows three spectral peaks (246 nm, 292 nm, and 664 nm). Absorbance of the solution after exposure to the RF plasma for 5 min is represented by the dotted line in Fig. 2. This shows that the peaks were somewhat diminished by the exposure. At the same time, the absorbance around 200 nm increased. This increase in the absorbance denotes generation of hydrogen peroxide [9]. These facts suggest that degradation of methylene blue and generation of hydrogen peroxide occurred simultaneously. When the solution was exposed to the RF plasma under UV irradiation, the solution lightened significantly. In this case, AC power (60 Hz, 18 W) was supplied to the UV lamp simultaneously with exposure to plasma for 5 min. The absorbance of the solution in this case is represented by the thick line in Fig. 2. All the peaks were flat, which implies that almost complete degradation was achieved.

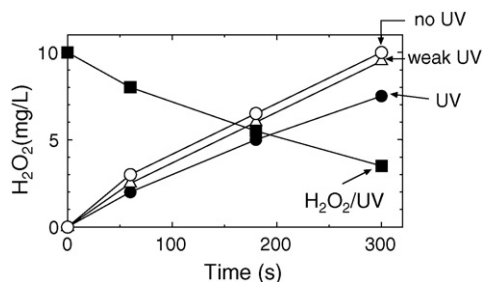
It is convenient to use the ratio  $A_{\text{ex}}/A_0$  for determining the index of degradation. Here,  $A_0$  and  $A_{\text{ex}}$  denote the absorbance values of at the main peak ( $\lambda = 664$  nm) before and after exposure, respectively. Fig. 3 shows the temporal evolution of the ratio  $A_{\text{ex}}/A_0$  under exposure and/or irradiation on a semi-logarithmic basis. Each point is the average of three experimental data. The error bars are almost the same size as the symbols. The open and closed circles denote exposure to plasma with and without UV irradiation, respectively. Here, AC power was supplied to the mercury vapor lamp for irradiation. After the exposure of the solution to plasma with UV irradiation for 300 s, the ratio  $A_{\text{ex}}/A_0$  became 0.14. Such a small value of the ratio is due to the fact that the color of the methylene



**Fig. 3.** Temporal evolution of absorbance ratio  $A_{ex}/A_0$ . The open circles labeled 'no UV' denote exposure to plasma without UV irradiation. The closed circles labeled 'UV' denote exposure to plasma under irradiation by 4.7 W-UV light from the lamp with AC power supply (18 W). The open triangles labeled 'weak UV' denote the exposure to plasma under irradiation by weak UV light from the submerged lamp without AC power supply. The closed squares labeled 'H<sub>2</sub>O<sub>2</sub>/UV' denote H<sub>2</sub>O<sub>2</sub>/UV photolysis.

blue solution was lightened to the extent that the degradation was visual. Without UV irradiation, wherein the mercury vapor lamp was not submerged, we could not observe the degradation visually, because the extent of degradation was small ( $A_{ex}/A_0 \approx 0.95$  on exposure for 5 min). It is important to supply UV light. In fact, when the solution is exposed to the RF plasma without UV irradiation, an additional RF power of 18 W, which implies a total RF power of 228 W, is not sufficient to change the absorbance ratio  $A_{ex}/A_0$ . Even if AC power is turned off, the submerged lamp can radiate UV light weakly because stray RF power excites the mercury vapor. The open triangles in Fig. 3 denote the exposure to the plasma maintained at 210 W under irradiation by weak UV light from the submerged lamp without AC power supply. The ratio  $A_{ex}/A_0$  after exposure with weak UV light for 300 s becomes 0.69.

We investigated the concentration of hydrogen peroxide under exposure and/or irradiation by using pure water instead of methylene blue solution. To measure the concentration, we use a colorimetric method, where 4-aminoantipyrine with an enzyme was used as a reagent for coloring (Kyoritsu Chemical-Check Lab, DPM-H<sub>2</sub>O<sub>2</sub>). Fig. 4 shows the temporal evolution of the concentration of hydrogen peroxide under exposure and/or irradiation. The open circles denote exposure to plasma without UV irradiation. Exposure to plasma leads to an increase in the concentration of hydrogen peroxide with exposure time. The concentration of hydrogen peroxide was  $\approx 10$  mg/L at 300 s. Under UV irradiation, increase in the concentration of hydrogen peroxide becomes smaller although it does increase with exposure time (see closed circles in Fig. 4). At 300 s, the concentration of hydrogen peroxide was 7.5 mg/L. The difference between the concentrations of hydrogen peroxide in both the cases is  $\approx 2.5$  mg/L. The open triangles



**Fig. 4.** Temporal evolution of concentration of hydrogen peroxide. The open circles labeled 'no UV' denote exposure to plasma without UV irradiation. The closed circles labeled 'UV' denote exposure to plasma under irradiation by 4.7 W-UV light from the lamp with AC power supply (18 W). The open triangles labeled 'weak UV' denote the exposure to plasma under irradiation by weak UV light from the submerged lamp without AC power supply. The closed squares labeled 'H<sub>2</sub>O<sub>2</sub>/UV' denote H<sub>2</sub>O<sub>2</sub>/UV photolysis.

denote the exposure to the plasma under irradiation by weak UV light from the submerged lamp without AC power supply. In this plot, the triangles appear somewhat lower than the open circles. This shows that only a small amount of hydrogen peroxide was decomposed.

For comparison, UV irradiation was carried out in the same vessel in the absence of plasma. The temperature of water was maintained at  $40 \pm 3$  °C. Since UV irradiation can break the bonds in methylene blue molecules directly, the irradiation may lead to the degradation of a small amount of methylene blue. When methylene blue solution without hydrogen peroxide was subjected to irradiation, the ratio  $A_{ex}/A_0$  decreased with irradiation time. After irradiation for 300 s, the ratio became 0.97. This implies that direct degradation occurred under UV irradiation, albeit to a small extent. The UV irradiation of methylene blue solution containing hydrogen peroxide is expected to degrade methylene blue via the H<sub>2</sub>O<sub>2</sub>/UV photolysis process. In order to investigate the role of hydrogen peroxide, we mixed methylene blue solution (10 mg/L) with the same volume of hydrogen peroxide solution (20 mg/L). Here, the hydrogen peroxide solutions used were dilutions of the 30% aqueous solution (Santoku Chemical Industry) purchased for the experiment. In the mixture, the initial concentration of hydrogen peroxide was approximately 10 mg/L. The concentration of methylene blue was 5 mg/L. The results of the irradiation are denoted by closed squares in Fig. 4. As expected, degradation progressed with irradiation time and the absorbance ratio became  $A_{ex}/A_0 \approx 0.075$  after irradiation for 300 s. In the H<sub>2</sub>O<sub>2</sub>/UV photolysis process without exposure to plasma, the concentration of hydrogen peroxide decreased with an irradiation time due to the lack of a generation process. From the initial concentration (10 mg/L), the concentration decreased to 3.5 mg/L for 300 s.

As shown in Figs. 3 and 4, UV irradiation for exposure to plasma enhances the degradation of methylene blue and suppresses the generation of hydrogen peroxide. When the solution containing hydrogen peroxide and methylene blue is subjected to the H<sub>2</sub>O<sub>2</sub>/UV photolysis process, UV irradiation not only decomposes hydrogen peroxide but also degrades methylene blue. These facts suggest that the degradation process under exposure to plasma with UV irradiation is as follows. (1) OH radicals are produced in the plasma via the decomposition of water molecules as  $H_2O \rightarrow H^\bullet + OH^\bullet$ . (2) Hydrogen peroxide is generated around the plasma through a recombination process as  $2OH^\bullet \rightarrow H_2O_2$ . (3) Hydrogen peroxide is diffused all over the solution. (4) Some amount of hydrogen peroxide is decomposed into OH radicals via the photolysis process as  $H_2O_2 + h\nu \rightarrow 2OH^\bullet$ . (5) Finally, these OH radicals degrade methylene blue. This series of reactions can explain the enhancement qualitatively. If quantitative discussions are required, it is necessary to consider some other reactions. Here, we point out only the fact that OH radical or hydrogen peroxide can react with active species like  $H^\bullet$ ,  $HO_2^\bullet$  and aqueous electron [3].

The amount of methylene blue (320 g/mol) in the vessel was 15  $\mu$ mol. The difference between the concentrations of hydrogen peroxide in the solutions exposed to plasma with and without UV irradiation at 300 s was  $\approx 2.5$  mg/L (Fig. 4), which corresponds to a value of 70  $\mu$ mol. If all of the 70  $\mu$ mol hydrogen peroxide molecules were changed into OH radicals via Eq. (2), the amount of radicals was 140  $\mu$ mol. However, since hydrogen peroxide can be decomposed via some other reactions [3,12], the amount of the reproduced OH radicals is not clear. At present, we can mention only that amount of the reproduced radicals may be large enough to degrade 15  $\mu$ mol methylene blue. On the other hand, during the exposure of methylene blue to RF plasma without UV irradiation, although the same number of OH radicals were generated in the plasma, hydrogen peroxide generated via the recombination of OH radicals could not contribute to degradation; therefore the extent of degradation was small.

For discussing the degradation rate, it is convenient to consider reaction rate constants under the assumption that the degradation process follows pseudo-first-order reaction kinetics for degradation. The rate constant can be determined from the slope of concentration vs. time plot on semi-logarithmic basis:

$$\ln \frac{A_{\text{ex}}}{A_0} = -\beta t$$

where  $\beta$  is the observed first order rate constant ( $\text{s}^{-1}$ ),  $t$  is exposure and/or irradiation time, and  $A_{\text{ex}}$  is a function of  $t$ . The rate constant  $\beta$  can be evaluated by fitting the data as shown in Fig. 3. The fitted lines are also shown in Fig. 3. The rate constants for exposure with and without UV irradiation are evaluated to be  $6.3 \times 10^{-3} \text{ s}^{-1}$  and  $2.0 \times 10^{-4} \text{ s}^{-1}$ , respectively. This shows that UV irradiation enhances the rate constant by a factor of approximately 30.

As shown in Fig. 3, there is some discrepancy between the experimental data and the fitted line; that is, at 60 s experimental data is obviously larger than the fitted line. This suggests that the degradation rate is small due to the low concentration of hydrogen peroxide at an early time ( $\approx 60$  s) and increases with an increase in the concentration of hydrogen peroxide. Therefore, the assumption of first-order reaction kinetics for the degradation process may be somewhat unsuitable for the present case, although the rate constant  $\beta$  is convenient for comparing the degradation rates. In the  $\text{H}_2\text{O}_2/\text{UV}$  photolysis process without exposure to plasma, some discrepancy is observed; at 300 s experimental data is obviously larger than the fitted line. This is also explained by the decrease in the concentration of hydrogen peroxide.

In this paper, the temperature of water was maintained at  $40 \pm 3^\circ\text{C}$ . This temperature was selected because it was easy to maintain RF plasma stably. In Ref. [9], RF plasmas in water were generated under three temperature ranges ( $20^\circ\text{C}$ ,  $30^\circ\text{C}$ , and  $70^\circ\text{C}$ ). Concentrations of hydrogen peroxide generated by plasma increased with decrease in temperature of water. This suggests that UV can enhance degradation more effectively at room temperature. We will investigate dependence on temperature of water in the near future.

Weak UV light generated due to stray RF power reduces the concentration of hydrogen peroxide by around  $0.5 \text{ mg/L}$ , which corresponds to the generation of  $25 \mu\text{mol}$  of OH radical (similar amount of methylene blue). Although the number of OH radicals is insufficient, degradation is obviously enhanced. The rate constant for exposure under irradiation by the weak UV light is estimated to be  $1.1 \times 10^{-3} \text{ s}^{-1}$ . In this case, the UV light enhances the rate constant by a factor of approximately 5. This shows that even the weak UV light is effective for degradation. Emission of UV light due to stray RF power implies that it is possible to eliminate the filament from the mercury vapor lamp, resulting in a considerably longer lifetime of the lamp because deterioration of the filament determines the life of the lamp. Although we have utilized stray RF power in this paper, we can supply RF power to the UV lamp more effectively. Therefore, a filament-free lamp with long lifetime is expected to enable the enhancement of the degradation by exposure to plasma.

#### 4. Summary

Degradation of methylene blue by RF plasmas in water was studied experimentally. When the methylene blue solution was exposed to RF plasma under UV irradiation, the first-order rate constant increased by a factor of approximately 30. The use of a mercury lamp without power supply also caused an increase in the first order rate constant by a factor of approximately 5 since weak UV light was emitted from the lamp due to the excitation of mercury vapor by stray RF power. The rapid degradation of methylene blue may be attributed to the fact that after hydrogen peroxide is generated via a recombination process of OH radicals around the plasma, OH radicals reproduced from hydrogen peroxide via the photolysis process degrades methylene blue.

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