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A colorimetric method for comparison of oxidative strength of DBD plasma

Jiushan Cheng[a,b], Qiang Chen[b], Gregory Fridman[c], Hai-Feng Ji[a,*]

[a] Department of Chemistry, Drexel University, Philadelphia, PA 19104, USA
[b] Laboratory of Printing & Packaging Material and Technology, Beijing Institute of Graphic Communication, Beijing 102600, China
[c] C&J Nyheim Plasma Institute, Drexel University, Camden, NJ

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ABSTRACT

A preliminary study on plasma treatment of dye solutions and dyed paper strips is presented. The discoloration and degradation of all nine organic dyes upon exposure of plasma was observed. UV-vis spectra were used to quantitatively characterize the degradation efficiency of the plasma. Discoloration rates may be used as the parameter for comparison of the oxidation strength of plasma. The oxidation strength of plasma may also be empirically compared using the discoloration of the dyed papers.

1. Introduction

Recently, the development of plasma devices that generate non-thermal, dielectric-barrier discharge (DBD) plasma has extended their potential applications in the medical, environmental, agricultural, and industrial fields [1–3]. DBD plasma is generated by applying high voltage between two electrodes, where at least one electrode is insulated. DBD plasma can be generated in air or other gases at atmospheric pressure and room temperature [4,5]. DBD plasma is electrically safe to use and low-heating in nature [6,7], which makes the DBD an energy-saving approach for decomposing organic chemicals compared with thermal plasma, for example. However, it is usually difficult to compare the results obtained from different research labs since the DBD devices differ in their power, frequency, pulse shape, electrode morphology, etc. and no well-established method had yet been adopted to measure and compare the intensity of plasmas, generated using different plasma systems. In this work, we attempt to address this issue by developing a colorimetric method.

Plasma in air is an ionized gas composed of a variety of reactive oxygen and nitrogen species (ROS and RNS), including ozone (O_3), NO and ·OH radicals, superoxide radicals (O_2^-), H_2O_2, singlet oxygen ($^1O_2$), and UV photons [8,9]. Many of these short and long lived species, including ions, molecules, and atoms are chemically active. Others can be electronically excited and emit light as they relax to their natural state. The generated ROS from DBD plasma have been used to efficiently oxidize organic chemicals (including sugars, amino acids, and lipids) [10–15]. For most of the applications of DBD in the medical, environmental, and industrial fields, such as for waste and pollutants decomposition, the intensity of atmospheric DBD plasma from various devices is proportional to the concentration of these ROS and RNS species [16,17]. In fact, the major concern for researchers in this field is to be able to compare the concentration of the ROS and RNS species, in the solutions, i.e. the oxidative strength of the solutions [18–23], rather than the plasma intensity. Thus, our strategy to compare the oxidative strength of plasma generated from different devices is to measure and compare the concentrations of ROS and RNS generated from these plasma devices.

The oxidative degradation of organic chemicals by ROS and RNS led us to believe that dye molecules in solutions would change color exposed to DBD plasma, which may be used as an indication for the concentration of ROS and RNS in the solution. This may become a useful method of direct comparison of different plasma systems in their effect on the surface being processed.

2. Experimental

2.1. Dye solution

The nine dyes used in these experiments are phenol red (Fisher Scientific, Walthan MA, USA), methylene blue (Fisher Scientific), rhodamine 6G (Eastman, Kingsport, TN, USA), rhodamine B (Kodak, Rochester, NY, USA), brilliant blue R (Sigma-Aldrich, St. Louis, MO, USA), brilliant blue G (Aldrich), acridine orange (Applied Chemical, Florence, AL, USA), bromocresol green (Spectrum Chemical, New Brunswick, NJ, USA), and

* Corresponding author.
E-mail address: hj56@drexel.edu (H.-F. Ji).

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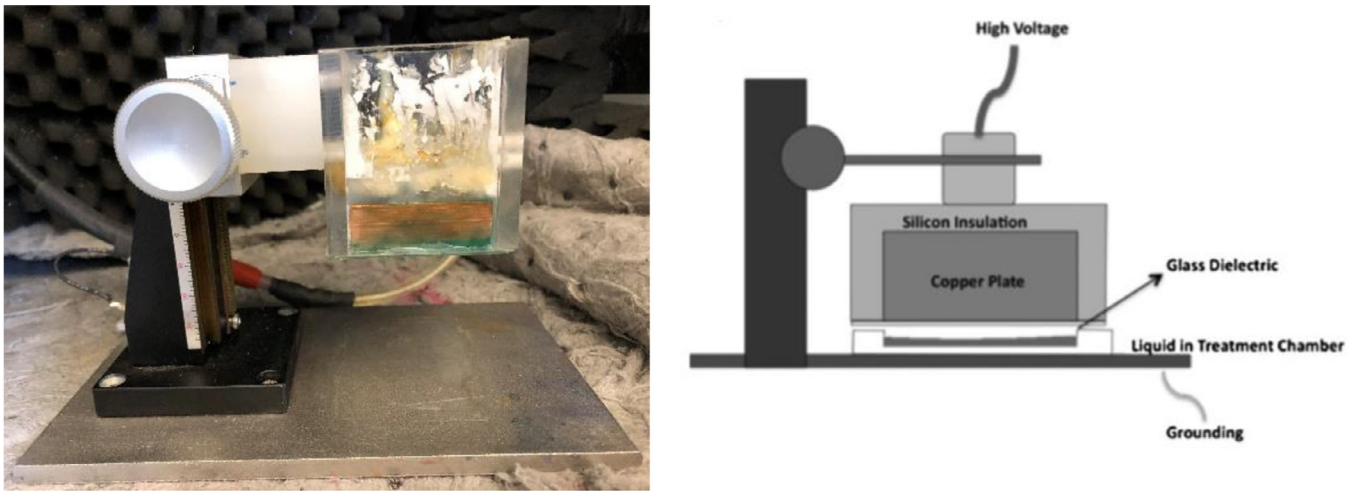


Fig. 1. A picture (Left) and scheme (right) of the DBD electrode used in this work.

direct red 80 (Aldrich) were used as received. Deionized water was used for preparation of the solutions. The concentration of each dye solutions was 10 mg L^{-1} in a 1 M phosphate buffer at pH7.00±0.10. The temperature for conducting all the experiments in the lab was maintained at 20–25 °C.

2.2. Plasma setup

The DBD Plasma was generated using a microsecond-pulsed power supply and an electrode-dielectric barrier discharge setup reported previously [12] (Fig. 1). The DBD electrode was made of a 38 mm × 64 mm copper plate covered with 1 mm-thick glass slide. The resistance, dielectric constant, and dielectric strength of glass are 10^{15} Ω, 4.6, and 30 kV/mm, respectively. The input energy was 10 mJ/pulse. The plasma is in the streamer regime [14]. The frequency of discharge and waveform were reported in our recent publication [15]. A custom-designed quartz fluid holder that can maintain 1 mL of liquid was placed on top of the second metal electrode. The discharge gap (difference between the two electrodes) for plasma was < 1 cm. One mL of each dye solution was treated individually at different time points and collected immediately (typically less than 15 s) after plasma treatment to measure its UV-Vis absorption using a Hewlett Packard 8453 UV–Vis spectrophotometer (Palo Alto, CA, USA). The HP 8453 allows scanning of a sample to finish within 10 s. Samples were treated under ambient atmospheric condition. A pH ultrasensitive probe attached to a Thermo Orion Research Digital pH meter (Thermo Fisher Scientific, Waltham, MA) was used to measure plasma treatment-associated pH changes in fluid over time.

3. Results and discussion

Nine dyes were used for the tests. It was well known that the aqueous solutions became acidic after an atmospheric plasma treatment [5]. To avoid the change of the color due to the pH, the dyes were dissolved in 1 M pH7.00±0.10 phosphate buffer solutions. After the plasma treatment, the pH of the solutions remained around pH 7 (<0.1 pH change).

UV–Vis spectra of the dye solutions before and after the plasma treatment are shown in Fig. 2. Discolorations of the dyes (shown in the insert figures) were observed for all nine dye solutions due to the degradation of the dye molecules. Among these, methylene blue, rhodamine B, brilliant Blue R, brilliant blue G, and Bromocresol Green showed the most significant changes and are the top candidates as the indicator for the oxidation power of plasma. Some dyes (such as Acridine Orange and Bromocresol Green) changed their colors quickly in 20 s so they may be used for lower dose of plasma. It is noted that a higher baseline throughout the wavelength range with an absorption intensity of around 0.15 a.u. was observed in all 9 insert figures in Fig. 1. This baseline shift was not observed in solutions of these dyes in pure water (figures omitted due to peak shifts when the pH changes), so the baseline shift appeared to be related to the change of the phosphate buffer when treated with plasma. However, to the best of our knowledge, such baseline shift was not observed before, and a stable baseline was reported in a similar study [24]. We are unable to understand this at this moment and the phenomenon may merit further studies in the future.

Fig. 3 shows intensity of the maximum absorption peak of each dye molecule vs the exposure time of the dye solution. In these experiments, 10 mg/L of dye fresh stock solutions were made with 1 mL aliquots pulled for each sample treatment at different time as those in Fig. 2 insert pictures. The slight volume changes within 4 min plasma treatments at room temperature were normalized when calculating the concentrations of dyes using the UV method. The peak intensities were reduced with increased time upon exposure to the plasma. All the dyes decomposed faster in the first 30 s and continue to decompose at a slower rate until reaching its plateau [25,26].

These result suggest that the dye solutions and their discoloration upon exposure to plasma can be used for the measurement of ROS and RNS concentrations generated from plasma, as expected [27–29]. Based on the results obtained from the solutions, we further tested the discoloration of dyes on a wet filter paper, which may be used similar to that of a pH paper. In these experiments, a strip of a filter paper was dipped into and pulled out of a 1 M dye solution, the wet strip was then exposed to plasma to observe the discoloration of the strip at various times. Brilliant blue G was used for these tests. Fig. 4a shows that the strips dyed with Brilliant blue G gradually discolored upon exposure to DBD plasma in 20 min, suggesting the dyed paper can indeed be used for testing the plasma oxidative strength. We used the wet paper strips to test the oxidative strength of a plasma at different gap distances and plasma frequencies. In these tests, the results from two frequencies, 1.5 kHz and 2 kHz (both at 9 μs pulse duration), and two distances between the electrode and the samples, 5 mm and 6 mm, were compared.

Fig. 4a–c shows that the discoloration rate is higher when the frequency was higher or the distance is shorter. This results clearly demonstrated that even for the same plasma device, a change of the distance between samples and electrodes or a change of the plasma frequency resulted in different oxidative strength of the solutions, which strongly suggested that a comparison of the oxidative capability of the

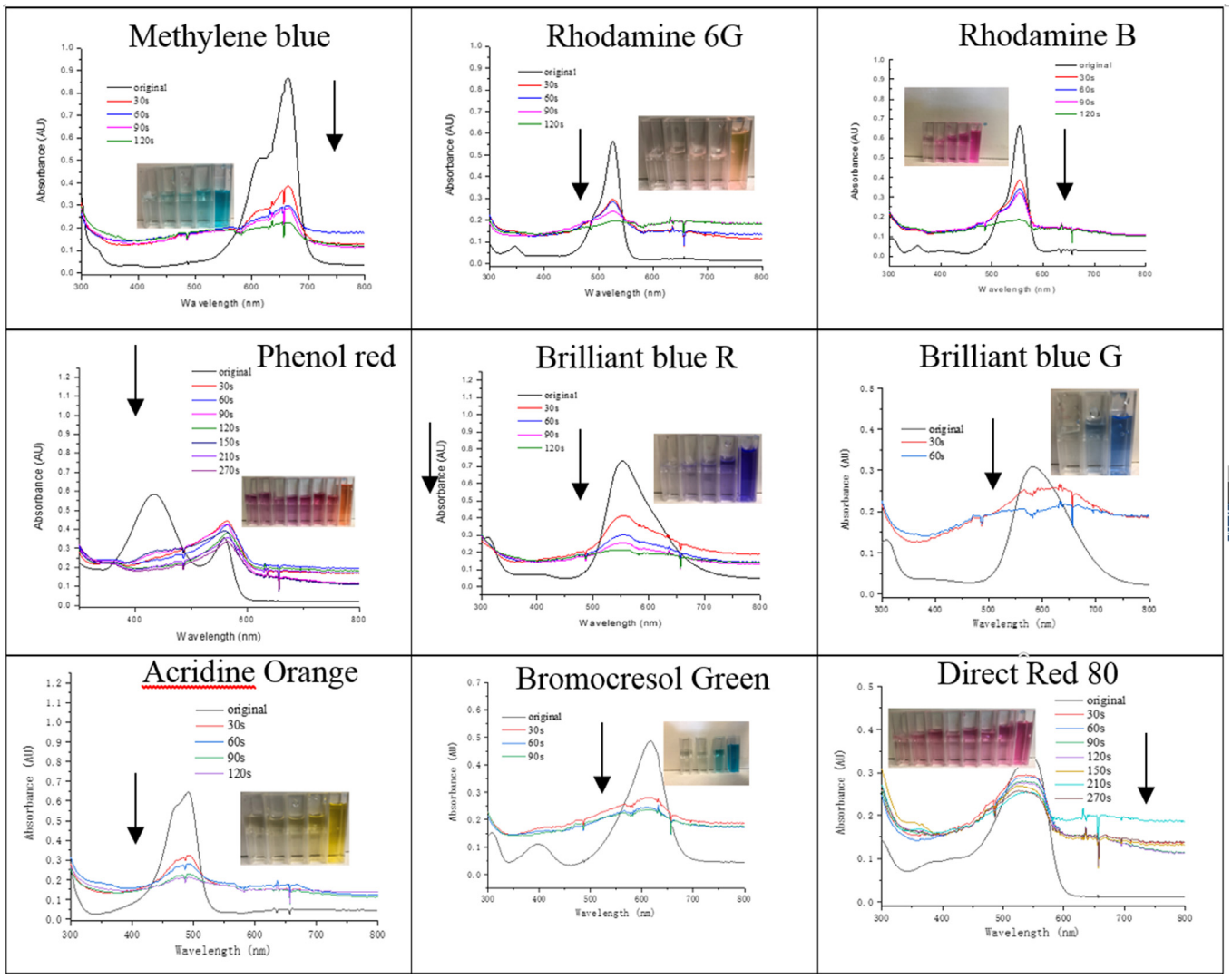


Fig. 2. UV–Vis spectra of the dye solutions before and after plasma treatments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

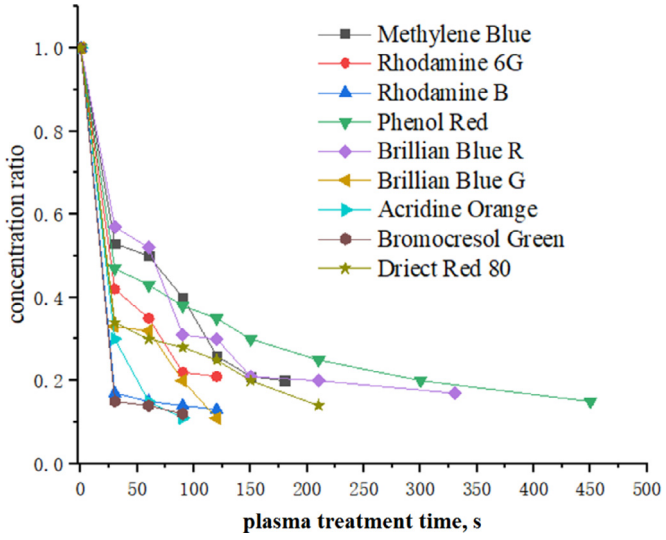


Fig. 3. Intensity of the maximum absorption peak of each dye molecule vs the exposure time of the dye solution.

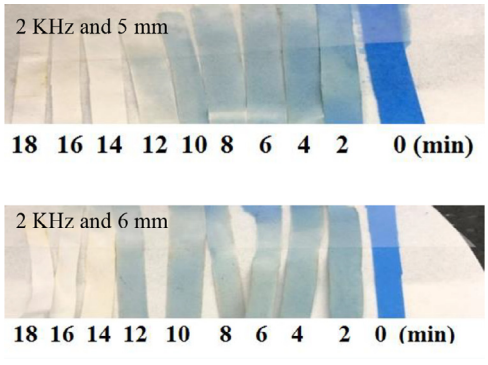


Fig. 4. The discoloration of a filter paper dyed with brilliant blue G at different exposure time under 1.5 KHz and 2 KHz and 5 mm and 6 mm distance between the electrode and the trips. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

plasma-treated solution, other than the power of the plasma, is a better parameter for comparison from labs to labs.

4. Conclusion

The aim of the work was to investigate how a colorimetric method may be used for the evaluation of the concentration of plasma-generated ROS and RNS, which is proportional, but not necessarily directly proportional, to the oxidation strength of atmospheric DBD plasma. The method may be able to compare the oxidative strength of DBD plasmas that are generated in different labs, and also possibly the efficiency and efficacy of their biological functions, such as inactivation of pathogens.

The results of this work are preliminary and more experiments will be needed in order to determine whether such a method can be adopted in the field, including: which dye molecule can be generally used for various plasmas; which parameter, such as half life time or kinetic data, could be used for the comparison; how widely can it be used for comparison for different systems, such as N_2 DBD plasma, O_2 DBD plasma, and non-DBD plasma, for example. These are under investigation in our lab.

Declaration of Competing Interest

No conflict of interests for all authors.

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