

# A Study on Dyeing Wastewater Treatment by Applying Pulsed Non-Thermal Plasma

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**Abstract-**Interest in pollution issues caused by synthetic dye wastewater is growing. For many years, researchers have attempted to develop more efficient treatment technology to solve this long-standing environmental problem. As many related studies have focused on advanced oxidation processes (AOPs), the plasma process is remarkable due to its high decolorization efficiency over a short time. This study applied a plasma process in the form of pulsed discharge to treat dye wastewater and to investigate the decolorization of dye wastewater over time by manipulating operation parameters. This method is expected to provide a rapid and highly efficient decolorization technology for wastewater treatment. The results indicate that 99%, 98%, 95% and 73% decolorization could be achieved for methylene blue solutions with initial concentrations of 1 ppm, 5 ppm, 10 ppm, and 20 ppm, respectively, after the experimental device was operated for one hour with operation parameters set at 100 mL min<sup>-1</sup> for air inflow, an initial pH of 2.5 for pollutants, and 10 KV for output voltage, while other parameters were fixed.

**Keywords-** Advanced Oxidation Processes (AOPs); Plasma Processes; Methylene Blue (MB); Decolorization

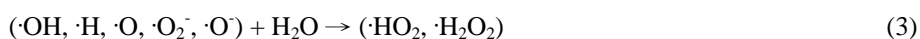
## I. INTRODUCTION

Currently, various synthetic dyestuffs composed of organic aromatic compounds are widely-used. Dyeing wastewater typically has properties of high degree-of-color, high alkalinity and low biodegradability [1, 2]. With the exception of some organic matter and suspended solids which can be removed by traditional wastewater treatment technologies, it is difficult to decompose most commercial synthetic organic dyes by biological treatment due to their toxicity to microorganisms in biological treatment processes. Additionally, the color of dyeing wastewater is very difficult to remove using traditional treatment methods. Therefore, when high color-degree wastewater drains into rivers or natural bodies of water, it not only pollutes the environment and affects water quality, but also forms a barrier to sunlight entering the water and obstructs the photosynthesis of aquatic plants, resulting in a shortage of dissolved oxygen in water and indirect damage to the ecological balance.

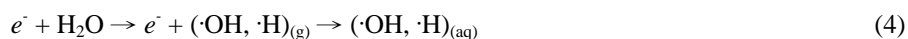
Therefore, it is of great importance to remove the color in dyeing wastewater. In the past, dyeing wastewater was typically treated with coagulation and sedimentation methods and/or biological treatment processes. As technology has advanced, Advanced Oxidation Processes (AOPs) including the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, UV/TiO<sub>2</sub>, Fenton and Plasma Methods, have been introduced [3-7]. In this study, a plasma process in the form of high voltage pulsed discharge was applied to decolorize dye in wastewater over a short time.

The plasma process applied in this study is classified as a non-thermal plasma technology, which is generated by high voltage discharge under one atmosphere. The test reactor utilized a pulsed corona discharge, a major corona discharge technology which offers the advantages of a simple structure, low radiation, low energy consumption, and high efficiency. The principle of a pulsed corona discharge is to provide pulsed high voltage between the anode and cathode of the reactor, thus creating a high electric field in order to agitate the discharge of electrodes and thus generate non-thermal plasma. The key reactions of the non-thermal plasma reactor occurring in the liquid and gas phases are shown as the following equations [8, 9].

Liquid phase:



Gas phase:



The electrons generated by the aquatic pulsed discharge collide with water molecules to yield hydroxyl radicals ( $\cdot\text{OH}$ ) and singlet hydrogen free radicals ( $\cdot\text{H}$ ). The hydroxyl radicals then react with water to produce peroxy radicals ( $\cdot\text{HO}_2$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). All of the radicals and substances described above are powerful oxidizers which are able to oxidize and remove organic matter from water.

## II. EXPERIMENTAL MATERIALS AND METHODS

### A. Target Dye and Analysis

In this study, methylene blue ( $\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS}$ ) was considered the pending target pollutant. Methylene blue, a basic dye, carries a positive charge after dissociation in the aqueous phase. A spectrophotometer was used for colorimetric assay to analyze the discoloration rate during the test. According to the result of the full wavelength scan test, the maximum absorbance wavelength of methylene blue is located at 664 nm. Thus, the dye discoloration rate was determined in this experiment by measuring the absorbance level under this wavelength after different reaction times.

### B. Plasma Generation Equipment

In this test, the primary body of the plasma reaction tank was an acrylic chamber (with an inner diameter of 50 mm), of 300 mL capacity. Inside the reaction tank, a fixed-point electrode (with an inner diameter of 0.5 mm and outer diameter of 0.7 mm) and a plane electrode (with a diameter of 30 mm) were placed at a distance of 47 mm. Air was injected through the point electrode into the reaction tank by an air pump. A circulation pump was connected to the outside of the plasma reaction tank, in order to continuously circulate the test flow. A high voltage pulse device provided electricity to generate a pulsed discharge at the point electrode. During the test, the sample solution was first pumped into the plasma reaction tank by a circulation pump, and the intake air flow was controlled by a rotameter. The high voltage pulse device was then turned on to control the voltage. The voltage output was fixed at 10 KV and the circulation rate was fixed by the circulation pump. The total volume of target dye solution was always 300 mL, and the process time was 1 hour.

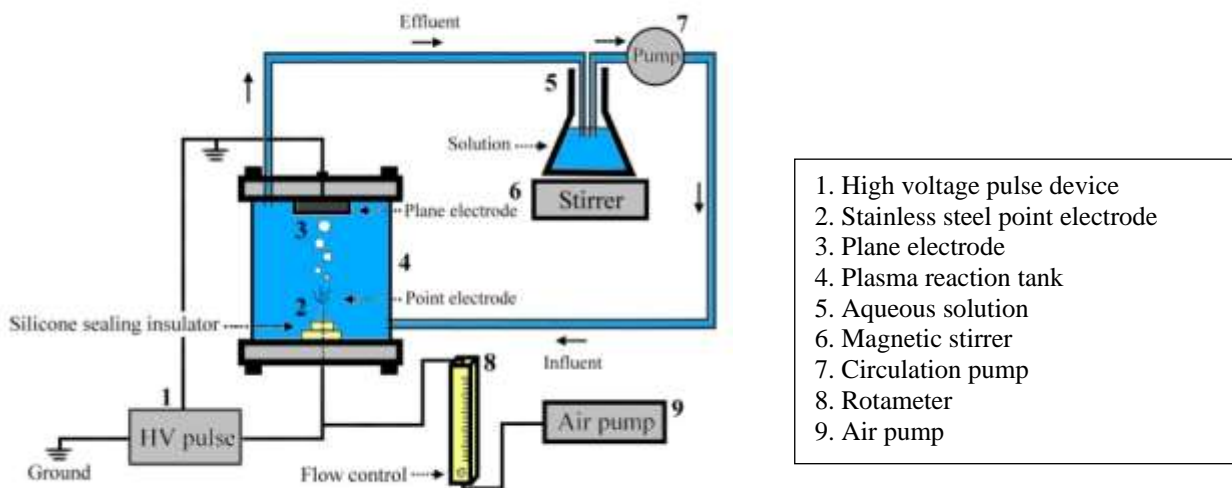


Fig. 1 Schematic diagram of the plasma test device

## III. RESULTS AND DISCUSSION

### A. Effect of Different Initial Dye Concentrations on Decoloration Rate

To determine the operation conditions of the test equipment and the different efficiencies under various dye concentrations, methylene blue solutions with initial concentrations of 1 ppm, 5 ppm, 10 ppm and 20 ppm were processed with plasma for one hour. The test parameters (distance between the point electrode and the plane electrode, circulation rate, output voltage) remained constant; the total volume of processing target pollutant solution was 300 mL; the initial pH and initial conductivity of the solution was not altered; and air was injected with a minimum air flowrate of  $40 \text{ mL min}^{-1}$  into the plasma reactor.

Fig. 2 shows the decoloration rate change tendency over time for methylene blue with different initial concentrations. After

one hour of plasma processing, methylene blue with initial concentrations of 1 ppm, 5 ppm, 10 ppm and 20 ppm reached decoloration rates of 65 %, 64 %, 57 % and 31 %, respectively. Results indicate that the decoloration rate decreased as the initial concentration of methylene blue increased. This indicates that the intermediates generated by plasma processing increase as the initial concentration increases. Those intermediates compete with the active substances generated by the aquatic plasma, resulting in a low decoloration rate.

Furthermore, it was observed that the speed of decoloration was slow in the first 30 minutes and clearly increased after 30 minutes for different concentrations of methylene blue. This likely occurred because the gradually acidified solution accelerated the decoloration reaction. According to a previous study [10], the reason for the gradual acidification of the solution may be the generation of hydroxyl radicals, ozone and hydrogen peroxide during plasma processing. When these high-oxidizing substances react and directly or indirectly destroy the structure of organic dyes, the dye molecules are broken down into organic acids of small molecules, resulting in the gradual acidification of the solution. An acidic condition is of benefit to the decoloration reaction of plasma, because the hydrogen peroxide generated by the plasma process is stable in acidic solutions. Additionally, it could also react with ozone to accelerate the production of hydroxyl radicals, thus increasing the decoloration rate significantly. These results are in accordance with the results reported by a previous study [11].

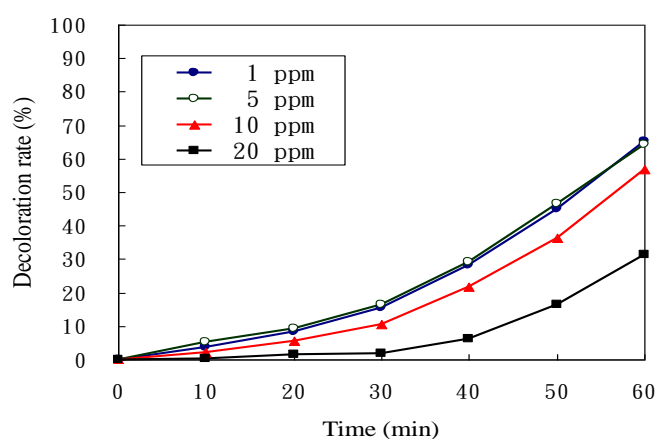


Fig. 2 The decoloration rates with different initial concentrations over time

#### B. Effect of Different Gas Flow Rates on Decoloration Rate

The influence of different gas flow rates on decoloration rate was investigated by using air as the injection gas and fixing the concentration of methylene blue at 1 ppm according to the above test result. The test parameters (distance between the point electrode and the plane electrode, circulation rate, output voltage) also remained constant; the total volume of the processed target pollutant solution was 300 mL; and the initial pH and initial conductivity of the solution were not altered.

Fig. 3 shows the change of methylene blue decoloration rate under different gas flow rates over time. After one hour of plasma processing, with  $40 \text{ mL min}^{-1}$ ,  $60 \text{ mL min}^{-1}$ ,  $80 \text{ mL min}^{-1}$  and  $100 \text{ mL min}^{-1}$  of gas flow, decoloration rates of 65%, 73%, 79% and 90% were observed, respectively. It was observed that the decoloration rate increased as the gas flow rate increased. This may be because the likelihood of aquatic pulsed discharge occurring in bubbles increased when the gas flow rate increased. According to a previous study [12], when an aquatic pulsed discharge occurs in bubbles rather than in solution, the average free path length of electrons is extended, thus producing high-energy electrons with greater speed. When these fast high-energy electrons occur, whether in bubbles or solution, more molecules are agitated and ionized to generate more high-oxidizing radicals, resulting in the acceleration of dye degradation and decoloration. Alternatively, the oxygen content in the reaction tank also increases as a result of the increased air flow rate, which is beneficial for ozone production [9]. By direct or indirect reactions, high concentrations of ozone could destroy the structure of dye molecules and increase the dye decoloration rate.

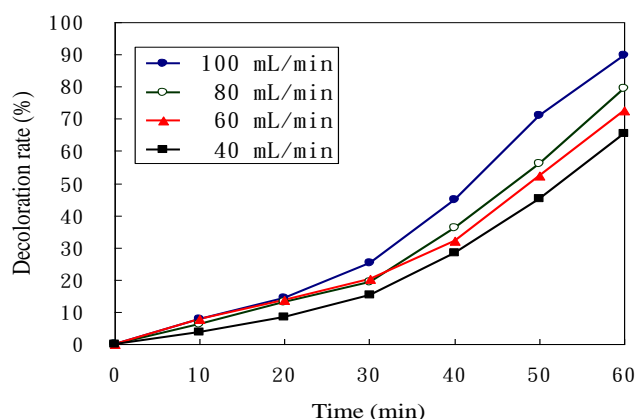


Fig. 3 The decoloration rate in different gas flow rates over time

### C. Effect of Initial pH to Decoloration Rate

The influence of different gas flow rates on decoloration rate was investigated by using air as the injection gas and fixing the concentration of methylene blue at 1 ppm. The test parameters (distance between the point electrode and the plane electrode, circulation rate, output voltage) also remained constant; the total volume of the processed target pollutant solution was 300 mL; the initial pH and initial conductivity of the solution were not altered.

Fig. 4 shows the change of methylene blue decoloration rate at different initial pH values over time. After one hour of plasma processing at pH values of 2.5 (acid), 6.5 (neutral) and 10.5 (alkaline), decoloration of 99%, 90% and 79%, were achieved, respectively. Results indicate that the decoloration rate was greatest under acidic conditions, second under neutral conditions and lowest under alkaline conditions. However, during the process, the alkaline solution reached its maximum decoloration rate of 90 % after ten minutes of plasma processing. After the process proceeded for one hour, its color degree gradually reached equilibrium and even slightly increased. This indicates that the plasma process made the alkaline solution gradually become neutral and then acidic. A change in pH caused not only a decrease in the decoloration rate but also induced a slight increase of the light absorbance of the dye, as shown in Fig. 5, resulting in a decreased decoloration rate. At the beginning of the reaction, however, the decoloration rate was higher under alkaline conditions than under neutral and acidic conditions. This may be due to the two reaction mechanisms of ozone. According to a previous study [13], ozone can destroy dye molecules directly under acidic conditions, and reacts indirectly under alkaline conditions where hydroxyl ions dominate. When ozone reacts indirectly, it forms hydroxyl radicals with hydroxyl ions. The hydroxyl radicals then destroy dye molecules. Because hydroxyl radicals have higher oxidation reduction potential ( $E^0 = 2.70 \text{ V}$ ) than ozone ( $E^0 = 2.07 \text{ V}$ ), the indirect reaction resulting from the hydroxyl radicals formed by ozone under alkaline conditions could remove dye at a faster rate than the direct reaction of ozone under acidic conditions, resulting in better a decoloration rate at the beginning of the reaction for an alkaline solution. In the end, among the three initial pH conditions, the acidic condition achieved the best decoloration rate after one hour of processing, achieving decoloration of 55% and 95% after 10 minutes and 20 minutes of plasma processing, respectively. Additionally, its decoloration rate steadily increased in the subsequent 60-minute processing period, and no color increase occurred.

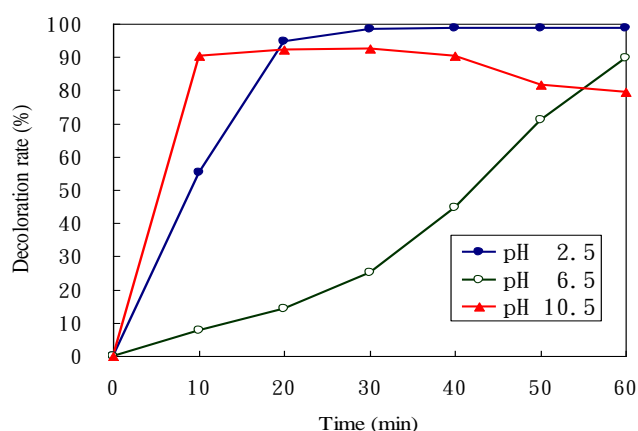


Fig. 4 The decoloration rate for different pH values over time

#### D. Optimum Operation Conditions

According to the test results described above, the optimum operation conditions were as follows: air was the injected gas with a flow rate fixed at  $100 \text{ mL min}^{-1}$ ; the pH of the solution was adjusted to pH 2.5 using  $\text{HNO}_3$ ; the solution conductivity was not adjusted; the test parameters (distance between the point electrode and the plane electrode, circulation rate, output voltage) all remained constant; and the total volume of the processed target pollutant solution was 300 mL. The concentration of methylene blue, the target pollutant, was increased to investigate the change of decoloration rate after one hour of plasma processing.

Fig. 5 shows the change of methylene blue decoloration rate in different initial concentrations over time. Results indicate that decoloration rates of 98%, 74%, 54% and 12% were achieved for methylene blue solutions with initial concentrations of 1 ppm, 5 ppm, 10 ppm and 20 ppm after 30 minutes of plasma processing, respectively, and decoloration rates of 99%, 98%, 95% and 73% were achieved after plasma processing for one hour. The above results indicate that the decoloration rate of methylene blue is still influenced by the initial concentration; higher methylene blue concentrations result in lower decoloration rates. However, the test result under optimum conditions was effectively improved, compared to the slow decoloration rate within a reaction time of 30 minutes mentioned above. It is concluded that plasma processing of methylene blue under optimum conditions can effectively increase decoloration rate and significantly accelerate the process.

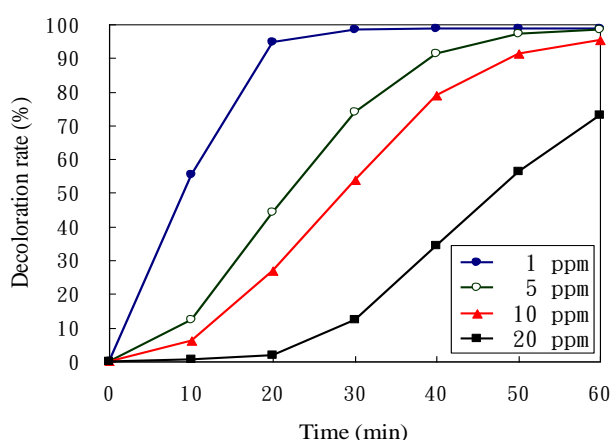


Fig. 5 Decoloration rate at optimum operation conditions over time

#### IV. CONCLUSIONS

Comparing the plasma processing of methylene blue at various pH values, the decoloration rate reached a maximum at pH 2.5 (acid), was second at pH 6.5 (neutral) and was lowest at pH 10.5 (alkaline). The reason for the high decoloration rate under acidic conditions may be because the hydrogen peroxide generated was relatively stable in acid. It was able to react rapidly with ozone to produce hydroxyl radicals, resulting in an increased methylene blue decoloration rate. Under alkaline conditions, the decoloration rate also increased because most of the ozone reacted indirectly. Ozone reacted with numerous hydroxyl radicals in the solution to yield hydroxyl radicals, resulting in a higher decoloration rate. Under neutral conditions, the decoloration rate increased slowly after the solution was acidified by the plasma process. Plasma processing of methylene blue under the optimum operation conditions can improve the slow decoloration rate caused by the concentration effect and can also significantly increase and accelerate the decoloration rate.

#### ACKNOWLEDGMENT

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