

# INVESTIGATION OF PLASMA-INDUCED METHYLENE BLUE DEGRADATION USING DIELECTRIC BARRIER DISCHARGE

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## ABSTRACT

Non-thermal plasma can produce reactive species such as O, O<sub>3</sub> and OH to induce dye degradation in water. Many chemical reactions are known to occur at the plasma-water interface, but contributions from each reactive species for the degradation are still not clear. This research investigated the discoloration of methylene blue using a specially-configured dielectric barrier discharge reactor, where the plasma was injected into the methylene blue solution through micro-holes to initiate the oxidation reactions at different pH values of 2.9, 7.1 and 11. The degradation effects from hydroxyls and ozone were determined separately by using the radical scavenger Tert-butanol. The results demonstrate that methylene blue is degraded by both ozone and reactive hydroxyl radicals, with the latter contributing up to 30% of the discoloration effect depending on solution pH values. The yield of plasma-produced hydroxyl radicals up to 4.6 g/kWh was achieved and the efficiency was not affected by solution pH values; the corresponding methylene blue degradation efficiency is 184 g/kWh.

## 1. INTRODUCTION

Advanced oxidation processes (AOP) using O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, UV, or Fenton reactions have shown potential in treating hard degradation wastewater. Hydroxyl radicals produced in the process possess high oxidation ability and the reactions do not produce carcinogenic by-products [1]. They can react with substances without any selection and the general reaction constant is more than 10<sup>7</sup> [2]. As an alternative to the traditional AOP process, research in non-thermal plasma-induced AOPs has been extensively

investigated in the past decades. The reactions at the plasma-water interface lead to chemical activation by producing active species in-situ, including ions, reactive radicals, excited molecules and atoms, without the requirement for additional chemicals [3].

Different gas discharges have been investigated for the oxidation process including corona, glow, arcs and dielectric barrier discharge. Reddy investigated methylene blue degradation by dielectric barrier discharge with catalysts, and methylene blue degradation yield up to 67 g/kWh was achieved [4]. Jiang investigated the methyl orange degradation by corona discharge, 92% removal was achieved after 20 min at 11.7 g/kWh [5]. The present research attempts to separate the oxidation effects from different reactive species at the plasma-water interface, mainly ozone and hydroxyl radicals. A specially-configured discharge reactor has been developed to enhance the interface reactions and the degradation efficiency.

## 2. EXPERIMENTS

### 2.1 Experimental setup

The dielectric barrier discharge reactor is shown in Fig. 1. The PTFE test cell was used to hold the methylene blue solutions; its bottom is uniformly distributed with 400 micro-holes of 0.15 mm diameter. A PTFE layer of 1 mm thick and 50 mm diameter was used as the barrier next to the high-voltage electrode. The gap between the PTFE layer and the bottom of the test cell is 0.2 mm. The feed gas flows through the micro-holes into the methylene blue solution, which acts as ground electrode via a grounding wire placed in the solution.

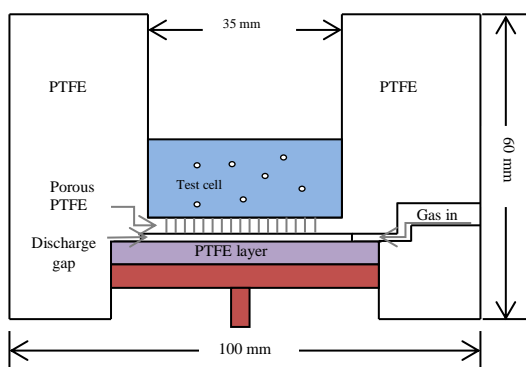


Fig. 1 Dielectric barrier discharge plasma reactor

The flow rate and pressure of pure oxygen were measured by a mass flow meter and pressure gauge (Alicat). The flow rate was set at 0.5 L/min and gauge pressure at 0.15 bar. An IGBT frequency inverter and  $L$ - $C$  resonant circuit were used to supply sinusoidal voltage of 10 kV and 7.7 kHz to the barrier discharge using pulse-density modulation (PDM) and pulse-width modulation (PWM) control.

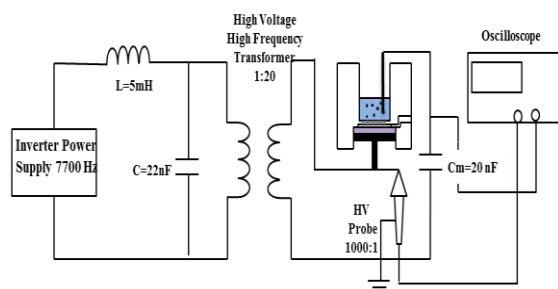


Fig. 2 Experimental set-up

The experimental set up is shown in Fig. 2. A Tektronix P6015A high-voltage probe (bandwidth 75 MHz) was employed to measure the voltage applied to the reactor. A measuring capacitor,  $C_m = 20$  nF, was connected to the reactor to plot the Lissajous figure. A Tektronix digital storage oscilloscope (TDS3054B) with a bandwidth of 500 MHz and sampling rate of 5 GS/s was used to record waveform data. An ozone analyser (BMT) was used to measure the ozone concentration.

## 2.2 Methylene blue and tert-butanol

High-purity methylene blue hydrate (95%, Acros organics) and deionised water ( $\sigma < 0.1$   $\mu\text{S}/\text{cm}$ ) were used to prepare the solution. The initial methylene blue concentration was prepared at 600 mg/L with an absorbance of 130. Several 10 ml samples were exposed to plasma for 1, 2, 3, 4 and 5 minutes at three different pH values of 2.9,

7.1 and 11, adjusted by 1 M HCl and 1 M NaOH. The absorbance at 665 nm was measured by a spectrophotometer (Thermal spectronic). The Beer-Lambert law was used to determine the treated sample concentrations. Tert-butanol (ACS reagent  $\geq 99.0\%$ , Sigma-Aldrich) was used as a scavenger to absorb hydroxyl radicals in the solutions and to inhibit ozone decomposition into hydroxyls. A dose of 1  $\mu\text{mol}$  was applied in each sample solution.

## 2.3 Dielectric barrier discharge

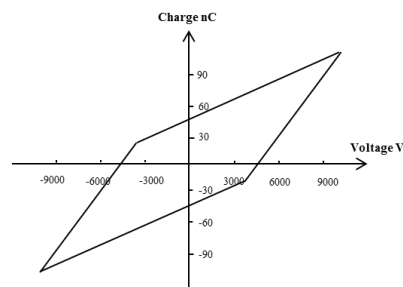


Fig. 3 Lissajous figure of dielectric barrier discharge

Ozone is produced in the barrier discharge. To determine the methylene blue discoloration from ozone and separate the effect from that of other reactive species, it is necessary to measure the amount of ozone diffused into the solution during each treatment. A sample of 10 ml deionised water in the test cell was exposed to plasma treatment and the ozone off-gas from the water was measured. The barrier discharge power was 0.6 W, calculated from the Lissajous figure, and the corresponding ozone production was 3.5  $\text{g}/\text{m}^3$  and 1.75  $\text{mg}/\text{min}$ .

## 3. EXPERIMENTAL RESULTS

### 3.1 Ozone degradation

#### 3.1.1 pH effects

Fig. 4 presents the methylene blue degradation by ozone at different pH values. After 1 minute treatment, the methylene blue concentration was reduced by 50%, 59% and 68% at pH values of 2.9, 7.1 and 11, respectively. This corresponds to the reacted methylene blue of 9.7, 10.9 and 12.7  $\mu\text{mol}$ , respectively.

After 5 minutes treatment, the methylene blue concentration was reduced by 93%, 97.3% and 99%, which corresponds to 17.1, 18.4, and 19.2

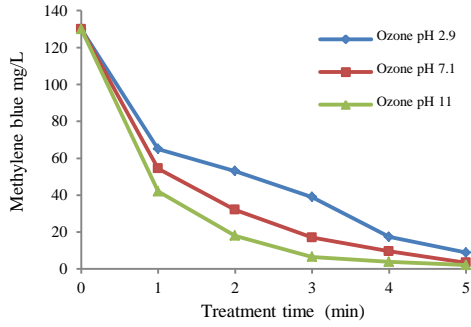


Fig. 4 Ozone degradation of methylene blue

$\mu\text{mol}$ , respectively. The methylene blue degradation rate increases at higher pH value. This may be due to slower ozone decomposition into hydroxyl radical in acidic solution ( $\text{pH} < 4$ ).

### 3.1.2 Tert-butanol effect

In order to investigate the decomposition of ozone into hydroxyl radicals, tert-butanol was used as a radical scavenger. The experimental results are presented in Fig. 5.

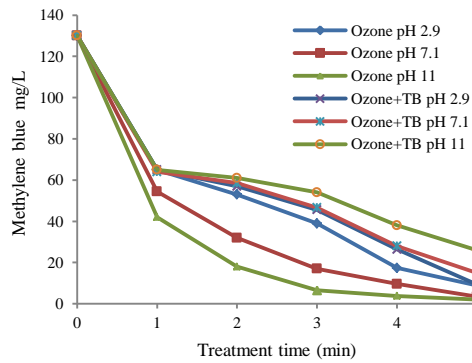


Fig. 5 Ozone degradation of Methylene blue with tert-butanol

The kinetic rate of tert-butanol reaction with hydroxyl radicals is  $6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  [6]. If any ozone is converted into hydroxyl radicals, they will be absorbed quickly by tert-butanol. As shown in Fig. 5, the degradation of methylene blue remains the same independent of the pH value when tert-butanol is applied, indicating that the radical scavenger inhibits the ozone decomposition into hydroxyl radicals and the degradation is due to ozone alone. Without tert-butanol, the degradation in basic solution is higher due to ozone decomposition into hydroxyl radicals, up to 35% at pH 11 after the first minute of treatment. The decomposition into

hydroxyl radicals is shown in the following reactions:

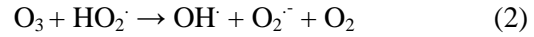
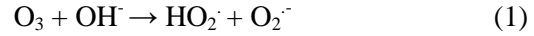


Fig. 6 presents the pH variation after ozone treatment for solutions of different pH values with and without tert-butanol. The pH reduction in basic solution is much higher than the acid.

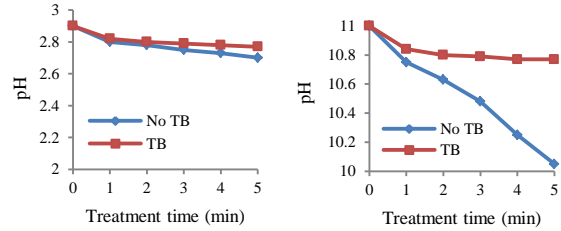


Fig. 6 pH variation with and without tert-butanol

Ozone decomposition can induce pH reduction by the reaction:



Tert-butanol controls pH reduction during the oxidation processes by reacting with hydroxyl radicals. This suggests that ozone decomposition in acid solution is very limited, which agrees with the research in [7].

### 3.2 Plasma treatment

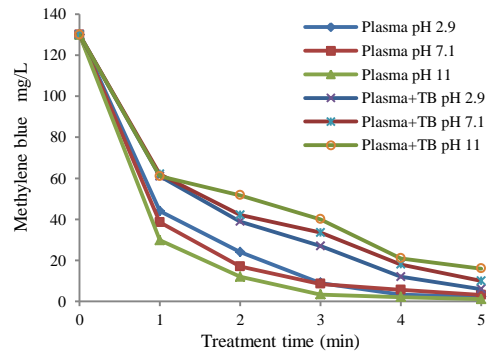
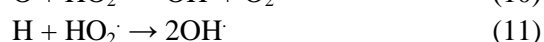
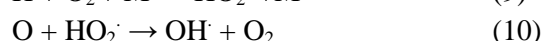
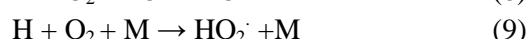
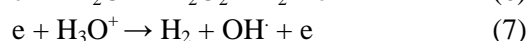
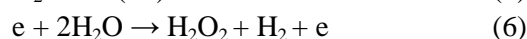
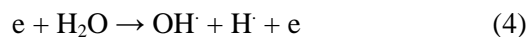


Fig.7 Plasma degradation of Methylene blue

Fig. 7 presents the results of methylene blue degradation following plasma treatment. The degradation without application of tert-butanol was 12.4, 13.8, and 15.4  $\mu\text{mol}$  for the first minute at the three pH values investigated. The level of degradation is reduced when tert-butanol is applied. The methylene blue is almost completely degraded within 5 minutes of plasma treatment.

The degradation rate is faster in basic solution due to ozone decomposition into hydroxyl radicals. The plasma treatment enhances the oxidation rate by producing hydroxyl radicals through ions and electrons reactions shown below:



### 3.3 Hydroxyl radical production

The reaction ratio between methylene blue and ozone is 1:3. Based on the amount of ozone produced in the first minute, the methylene blue degradation should be 9.7  $\mu\text{mol}$ . However, the measured degradation by ozone is 9.7, 10.9 and 12.7  $\mu\text{mol}$  at pH values of 2.9, 7.1 and 11; for plasma treatment, it is 12.4, 13.8, and 15.4  $\mu\text{mol}$ ; the difference is due to the hydroxyl radicals produced by plasma. According to the reaction ratio between methylene blue and hydroxyl radicals which is 1:1 [8], the amount of hydroxyl radicals can be determined, which are 2.7, 2.9 and 2.7  $\mu\text{mol}$  per minute for the three pH values investigated.

## 4. CONCLUSION

This paper determined the ozone and plasma effects on methylene blue degradation. In ozone treatment, methylene blue degradation is higher in basic solution due to ozone decomposition. The results indicate that hydroxyl radicals produced by plasma make an important contribution to the degradation. The amount of hydroxyl radicals produced is independent on the solution pH values and its conversion efficiency could reach 4.6 g/kWh; the corresponding methylene blue degradation is 184 g/kWh. Although the contribution from plasma-induced hydroxyl radicals has been determined, the kinetics of hydroxyls production at the plasma-water interface is still not clear. It is necessary to determine whether the hydroxyls are produced

directly by electron effects or other reactive species produced in the plasma such as oxygen atoms in order to improve the conversion efficiency.

## REFERENCE

- [1] Y.S. Mok, J.O. Jo, H.J. Lee, H.T. Ahn, J.T. Kim, "Application of dielectric barrier discharge reactor immersed in wastewater to the oxidative degradation of organic contaminant", *Plasma Chem. Plasma Process.* 27 (2007) 51–64.
- [2] Kristin Kutschera, Hilmar Börnigk and Eckhard Worch, "Photo-initiated oxidation of geosmin and 2-methylisoborneol by irradiation with 254 nm and 185 nm UV light", *Water Research* 43 (2009) 2224–2232.
- [3] L. O. de B. Benetolia, B. M. Cadorina, V. Z. Baldissarelli a "Pyrite-enhanced methylene blue degradation in non-thermal plasma water treatment reactor", *Journal of Hazardous Materials* 237–238 (2012) 55–62.
- [4] P. Manoj Kumar Reddy, B. Rama Raju, J. Karupiah, E. Linga Reddy, Ch. Subrahmanya, "Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor", *Chemical Engineering Journal* 217 (2013) 41–47.
- [5] Bo Jiang, Jingtang Zheng, Qian Liu, Mingbo Wu, "Degradation of azo dye using non-thermal plasma advanced oxidation process in a circulatory airtight reactor system", *Chemical Engineering Journal* 204–206 (2012) 32–39.
- [6] A. López, J.-S. Pic, H. Benbelkacem, H. Debellefontaine, "Influence of *t*-butanol and of pH on hydrodynamic and mass transfer parameters in an ozonation process", *Chemical Engineering and Processing* 46 (2007) 649–655.
- [7] M. Ismail, Hasan M. Khan, Murtaza Sayed, William J. Cooper, "Advanced oxidation for the treatment of chlorpyrifos in aqueous solution", *Chemosphere* 93 (2013) 645–651.
- [8] Chen-Ju Liang and Shun-Chin Huang, "Kinetic model for sulfate/hydroxyl radical oxidation of methylene blue in a thermally activated persulfate system at various pH and temperatures", *Sustain. Environ. Research* 22 (2012) 199–208.