Wastewater treatment based on remazol blue using DBD plasma reactor under acidic and basic conditions

Badzlina Khairunizzahrah¹, Setijo Bismo*¹
Chemical Engineering Department, Engineering Faculty, Universitas Indonesia

Email corresponding author: setijo.bismo@ui.ac.id

Abstract. Synthetic dyes are one of the most dangerous components of textile wastewater. Waste that contains various organic compounds, especially synthetic dyes, causes a high Chemical Oxygen Demand (COD) values. Remazol blue is a reactive dye that is widely used for the textile dyeing process. Therefore, water pollution occurs when the dye waste produced from textile activities is discharged into water bodies without prior treatment. In this study, innovation in waste treatment technology was applied in the Dielectric Barrier Discharge (DBD) plasma reactor. DBD are non-thermal plasma reactors designed to degrade organic and inorganic compounds in wastewater through oxidation process. This is carried out by active species, such as ozone (O3), hydrogen peroxide (H2O2) and hydroxyl radical (·OH), which are formed in the reactor. The study aims to evaluate the performance of non-thermal DBD plasma reactor in treating wastewater containing one of the textile dyes, namely remazol blue. The results showed that the percentage of degradation achieved was 98.43% within a process time of 120 minutes with a final concentration of 0.75mg/L. Furthermore, it showed that optimum conditions were obtained at pH value of 4, air flow rate of 2.5L/min, liquid flow rate of 50mL/min and a primary Neon sign transformer (NST) voltage of 19kV.

1. Introduction
The textile industry has developed rapidly in recent years and has become one of the most polluted industries in the world. The increase in textile production by this industry has resulted to a rise in wastewater. During its manufacturing processes, the textile industry consumes a substantial amount of water and produces wastewater which contains hazardous substances and chemical dyes. Therefore, the wastewater produced becomes very colourful and contains organic pollutants that are difficult to degrade. The wastewater from the textile industry has a concentrated colour generally derived from the dye remnants. They form complex aromatic compounds in the form of azo compounds and derivatives of benzene groups which are difficult to degrade [1].

Various conventional methods for dealing with textile waste such as biological oxidation, physical-chemical treatment and adsorption have been carried out. However, these methods are less effective because most dyes are soluble in water, have complex structures and are resistant to chemical and biological degradation [2]. In addition, they have a high operational cost and toxic by-products are formed during the process. Various modern methods have been carried out for the removal of dye pollutants from wastewater before its final disposal into water bodies. They include biodegradation, chlorination and ozonation methods. However, these methods do not provide satisfactory results and require a high operational cost which makes it less effective in Indonesia. Therefore, in this study the proposed waste treatment technology innovation was the use of a Dielectric Barrier Discharge (DBD) plasma reactor.
DBD are non-thermal plasma reactors designed to degrade organic and inorganic compounds in wastewater through oxidation process by active species, such as O$_3$, H$_2$O$_2$ and •OH, which are formed in the reactor. It also has advantages, which include low energy consumption to induce chemical reactions in gases at relatively low temperatures (T< 200°C), operates at room temperature and atmospheric pressure, the reactor design allows the process scale-up to operate with larger volumes of gas, exhibits high electron density and glow discharge extensions [3].

2. Material and Methods
The main tool used in this study was the Dielectric Barrier Discharge (DBD) plasma reactor with a spiral cylindrical coaxial pipe configuration. The unity series of the reactor system which show how the DBD plasma reactor is connected with other supporting components is illustrated below in figure 1.

![Figure 1. The schematic diagram of experimental setup for wastewater degradation.](image)

The synthetic wastewater which was degraded in this study was remazol blue. The initial concentration of remazol blue used was 50ppm. The total liquid volume used was 500mL. The test was carried out with an air flow rate of 2.5L/min, and an NST secondary voltage of 19kV with a processing time of 120 minutes by varying the pH of the solution i.e. pH 4 and 6 for acidic conditions pH 7 for neutral conditions and pH 10 for basic conditions.

3. Results and Discussion
The study began with a preparatory stage which included the reactor hydrodynamic and ozone solubility test. The number of hydroxyl radicals were quantified using two methods, iodometric and permanganometric titration, to find the optimum conditions. Furthermore, the degradation of remazol blue dye wastewater was carried out by varying the pH value at optimum conditions.

3.1. Hydrodynamic Testing
Hydrodynamic testing was carried out to determine the optimum residence time of the fluid in the DBD plasma reactor. With optimum residence time, the contact time between the feed gas fluid and plasma were optimal therefore, the reaction was effective. The calculation of the liquid phase residence time is shown in equation below.

$$\tau = \frac{V}{Q_L}$$  (1)

Where $\tau$ is the average residence time of the reactants in the reactor, $V$ is the reactor volume, and $Q_L$ is the flow rate of the liquid feed.
**Figure 2.** Effect of fluid flow rate on average residence time with a fixed air flow rate = 2.5 L/min.

Figure 2 shows that the higher the flow rate of liquid feed entering the DBD plasma reactor, the lower the residence time of the feed in the reactor. When the liquid flow rate was 50mL/min, residence time had its highest value. This was because at a low liquid flow rate not all parts of the space in the reactor were occupied by liquid therefore, the gas phase occupied the space that was not filled, which slightly compressed the liquid phase. Conversely, the liquid flow rate of 80mL/min had the smallest residence time value due to the flow being in the pulse regime (high interaction). Therefore, the liquid phase pressure was strong enough to withstand the gas phase pressure and the residence time was less influenced by the gas phase. Furthermore, based on the hydrodynamic test, it was predicted that the most optimum liquid feed flow rate to be operated in a non-thermal DBD plasma reactor was 50mL/min.

### 3.2. Hydroxyl Radical Quantification

The solution used in this study was aquades as a substitute for wastewater remazol blue compound with the aim that it does not affect the calculation of the quantity of •OH radicals formed. •OH radicals react with each other to form H₂O₂ (hydrogen peroxide) as shown in the equation below. H₂O₂ is a radical compound that is stable and has a long lifetime.

$$•\text{OH} + •\text{OH} \rightarrow \text{H}_2\text{O}_2$$

(2)

To determine the production of hydroxyl radicals, the amount of H₂O₂ formed was measured.

#### 3.2.1. Iodometric Titration Method

In the hydroxyl radical quantification of the iodometric titration method, the resulting •OH radical combined to produce H₂O₂, resulting in the addition of H₂O₂ to the KI used and iodine was produced as in the equation below [4].

$$\text{H}_2\text{O}_2 + 2\text{KI} + \text{H}_2\text{SO}_4 \leftrightarrow \text{I}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$$

(3)

$$\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \leftrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$$

(4)

From the above reaction, •OH radical calculation was compared with H₂O₂. KI solution produced other compounds besides iodine (I₂), which were basic in accordance with the oxidation reaction, as in the equation below:

$$2\text{KI} + 2•\text{OH} \rightarrow \text{I}_2 + 2\text{KOH}$$

(5)

From this reaction, if the KI was oxidized by •OH radical therefore, the iodine formed will be half the number of moles of the •OH radical.

The test was carried out with an air flow rate of 2.5L/min, and an NST secondary voltage of 19kV with a processing time of 120 minutes. Samples were taken at 15, 30, 45, 60, 75, 90, 105 and
120 minutes under optimum conditions i.e. when the air flow rate was 2.5L/min, liquid rate was 50mL/min and the NST secondary voltage was 19kV. This method was carried out by varying the pH of the solution i.e. pH 4 and 6 for acidic conditions pH 7 for neutral conditions and pH 9, 10 and 12 for basic conditions.

Figure 3 shows that the amount of H$_2$O$_2$ tends to rise with increasing pH. This was because the higher the pH, the faster the rate of ozone decomposition [5]. In basic conditions, ozone which is one of the active species produced in the discharge process was induced by the presence of hydroxide ions in solution. Therefore, it decomposed quickly into OH radicals [6].

The mechanism of ozone decomposition reaction into •OH radical is as follows [7; 8].

$$\text{O}_3 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{O}_2$$  \hspace{1cm} (6)

$$\text{HO}_2^- + \text{O}_3 \rightarrow \cdot\text{OH} + \cdot\text{HO}_2^- + \text{O}_2$$  \hspace{1cm} (7)

3.2.2. Permanganometric Titration Method. The principle of permanganometric titration is based on the reduction-oxidation process. It involves the use of potassium permanganate (KMnO$_4$) as a strong oxidizer which also acts as a titrant. The H$_2$O$_2$ oxidation process by KMnO$_4$ follows the equation below:

$$5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{O}_2 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O}$$  \hspace{1cm} (8)

The test was carried out with an optimized variable which was when the liquid flow rate was 50mL/min, air flow rate was 2.5L/min, and NST secondary voltage was 19kV with a processing time of 120 minutes. Samples were taken at 15, 30, 45, 60, 75, 90, 105 and 120 minutes. Production of hydroxyl radicals in DBD plasma reactors in this method was analyzed from the influence of pH values.

From figure 4, it is seen that at higher pH, ozone showed more stable results, while at lower pH the amount of hydroxyl radicals fluctuated. Ozone stability was strongly influenced by the water matrix, specifically pH, Natural Organic Matter (NOM) and alkalinity. The pH value was used as an indication of the activity of hydrogen ions [9]. High pH made the formation of OH radicals easier due to the presence of OH ions, which initiated the decomposition of ozone as the first step in producing OH radicals.
3.3. Ozone Solubility Test

To carry out the ozone solubility test in water, aquades was used at an acidic, neutral and basic pH (pH of the solution = 4, 6, 7, and 10) under optimum conditions. It was used as a substitute for remazol blue to measure the solubility of ozone in water. The solution was treated for 120 minutes and the ozone levels were checked periodically at 15, 30, 45, 60, 75, 90, 105 and 120 minutes. The concentration of dissolved ozone in water was determined using a spectrophotometer. Furthermore, the sample was reacted with a reagent ozone kit, before it was measured with a spectrophotometer.

From figure 5, it is seen that the concentration of dissolved ozone fluctuated due to the short lifetime it possesses when dissolved in water. Therefore, the dissolved ozone reacted with water molecules and decomposed easily into oxygen as in the equation below [10].

\[ O_3 + H_2O + 2e \rightarrow O_2 + 2OH^- \]  \hspace{1cm} (9)

In addition, the radicals formed in the DBD plasma reactor were reactive and interacted with ozone as shown by the following equations:

\[ O_3 + \cdot HO_2 \rightarrow \cdot OH + 2O_2 \]  \hspace{1cm} (10)

\[ O_3 + \cdot O_2^- \rightarrow \cdot O_3^- + O_2 \]  \hspace{1cm} (11)

Based on equation 10 and 11, it is seen that dissolved ozone returned to oxygen in the gas phase due to interactions with radicals. In addition, the fluctuation in the ozone solubility values was caused by unstable temperatures because, it was carried out at room temperature [11].
3.4. Degradation of Remazol Blue Compounds
In this study, the degradation of wastewater dyes was carried out using synthetic waste in the form of a remazol blue dye, which had an initial concentration of ≈ 50ppm. At this stage, the effect of the initial pH of wastewater on the percentage of degradation of remazol blue compounds was evaluated. This was carried out with variables that have been optimized at the quantification stage of hydroxyl radicals, namely at a liquid flow rate of 50mL/min, an air flow rate of 2.5L/min and a secondary NST voltage of 19kV. The results of the percentage degradation of remazol blue with variations in pH are shown in figure 6.

![Figure 6. Effect of pH on percentage of remazol blue degradation.](image)

**Table 1. Remazol blue concentration in waste after degradation process.**

| pH | Initial concentration (mg/L) | Final degradation (%) | Final concentration (mg/L) |
|----|-----------------------------|----------------------|---------------------------|
| 4  | 48.03                       | 98.4397753           | 0.75                      |

Figure 6 and table 1 show that the pH value affected the rate of degradation of the dye. The ability of ozone to degrade dyes was higher at low pH for certain dyes [12]. In remazol blue dye, its molecules oxidized specific chromophore molecules more effectively than hydroxyl radicals. In general, ozone oxidation pathways include direct oxidation by it or radical oxidation by OH. Direct oxidation by ozone molecules is more selective and dominates under acidic conditions, while radical oxidation by hydroxyl is less selective and dominates under basic conditions [13].

There are three possible reasons that may help to explain the above statement: 1) Anthraquinone dyes contain rigid structures that are not sensitive to oxidation reactions therefore, the ozonation mechanism may not be the dominant process for dye decomposition. 2) Anthraquinone may be transformed into leuko-forms (less colored) in acidic media, which reduces the colour content. 3) Amine group (-NH₂) in anthraquinone dye may be ionized to (-NH₃⁺) at low pH, which increases the solubility of the dye [13].

4. Conclusion
Wastewater treatment on remazol blue compound using a non-thermal DBD plasma reactor was carried out with a degradation percentage of 98.43% and a final concentration of 0.75mg/L. The lower the pH, the higher the percentage of degradation. The optimum operating conditions for remazol blue compound degradation were obtained at pH 4, air flow rate 2.5L/min, liquid flow rate 50mL/min, secondary voltage NST 19kV, liquid volume 500mL, and waste concentration 50mg/L in 120 minutes processing time.
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