Time dependence of the concentration of dissolved ozone in water generated by dielectric barrier discharge (DBD) plasma using atmospheric air

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Abstract. Ozone is one of the reactive oxygen species that can be produced from plasma. In this study, the ozone was generated by using a dielectric barrier discharge (DBD) plasma technology. DBD plasma was generated using two electrodes separated by a glass dielectric isolator and an alternating current (AC) voltage source of 5 kV with an airflow rate of 1 L/min at room temperature and atmospheric pressure. In this study, the ozone concentration was determined using the titration method. The ozone concentration was measured by varying the titration time between 0-10 minutes. The time dependence of ozone concentration in water tends to follow the polynomial trendline. The longer plasma treatment was performed, the higher ozone concentration was measured. The ozone significantly increased when the treatment was conducted for more than 6 min.

1. Introduction
Ozone has a triatomic form of oxygen, strong oxidants (much more than oxygen), and absorption cross-section in the 240-790 nm region [1]. Ozone has been used since the 19th century for disinfecting drinking water treatment. The other application of ozone includes wastewater and air treatment, and degradation of pharmaceuticals [2, 3]. Ozone has antimicrobial properties as an oxidant, with an oxidation potential of 2.07 V; therefore, it is useful in curing skin diseases and wounds [4, 5].

Many plasma generation techniques have been applied to produce ozone, such as corona discharge, electrohydraulic discharge, dielectric barrier discharge (DBD) [6]. Under certain conditions, ozone can generate hydroxyl radicals because it has a high oxidation potential [7]. Oxidation potential and high mass transfer efficiency are present in ozonation fine bubbles [8]. The most effective DBD method produces ozone because of its low power consumption and initial voltage [9]. DBD is known as ozone production resulting from the release of electricity between two electrodes separated by a dielectric...
barrier [10]. DBD plasma has shown good sterilization from the effects of ozone, UV, and reactive oxygen and nitrogen species (RONS) produced by the release of plasma [11]. The discharge results in low temperature, so there is no need for a cooling system, and homogeneous occurs throughout the reactor volume [12].

The determination of the concentration of ozone produced by DBD plasma can be used volumetric method and spectrophotometry method. Among these two methods, the most commonly used for ozone analysis is volumetric, and the volumetric method used for determining ozone concentration is iodometric titration [2]. Based on the previous work [13], low flow rates produce high concentrations, and the time required to determine the concentration of ozone titration unnecessarily long. Efforts can be made to increase ozone concentration by increasing the discharge equipment and adding a combination of equipment with a catalyst, a photocatalyst [14]. Ozone concentrations produced from plasma DBD are influenced by voltage, flow rate, gas input, and electrode configuration [4]. The study of the concentration trend of ozone dissolved in water at various times has not been explored. For instance, by the increasing of the treatment time, whether the increase of the ozone concentration follows linear or non-linear trends has not been investigated yet. Therefore, the present study aims to study the time dependence of the concentration of dissolved ozone in water produced by DBD plasma using atmospheric air.

2. Experimental Methods
2.1. Materials and equipment
The reagents potassium iodide (KI) 2%, H₂SO₄ 90%, starch 2%, and Na₂S₂O₅.5H₂O 0.2 N used in this study were supplied by Merck & Co., Inc. DBD plasma generator was set as shown in Fig. 1. The reactor of plasma DBD was made of a quartz tube with a length of 250 mm and an inner diameter of 40 mm in which there is a 5 mL measuring pipette with an outside diameter of 10 mm. This DBD reactor uses two electrodes of Cu wire and the stainless steel mesh, which is connected to the Cu foil. The DBD reactor used an AC high voltage source of 5 kV and airflow of 1 L/min.

![Figure 1. DBD plasma reactor setup.](image-url)
2.2. Methods
The DBD plasma was generated at various treatment times of 0, 2, 4, 6, 8, and 10 min produced ozone dissolved in 25 mL distilled water. The ozone concentration produced was estimated by the iodometric method with slight modification. 2 mL of KI solution and 0.1 mL of H2SO4 2 N was added into 2 mL water contained ozone until the solution turned yellow. This color change was produced by an oxidation reaction forming I2. Then, one drop of starch was added until the color of the solution changes to dark blue. The solution was then titrated by Na2S2O3.5H2O 0.2 N until the solution turns clear. The number of moles of ozone is equivalent to the number of moles of I2. Thus, the ozone concentration was estimated using the number of moles of I2, which was determined from the moles of Na2S2O3.5H2O. The ozone concentration resulting from DBD plasma treatment was calculated using the equation (Eq. 1) [15].

\[
C = \frac{R \times V \times N}{V_{gas}} \quad \text{(Eq. 1)}
\]

where C is the concentration of ozone (gram/L), R is the analytic mole ratio, V is the volume of the standard solution (L), N is the normality of Na2S2O3.5H2O (mol/L), and V gas is the volume of the gas used (L). The iodometric titration sequence technique to determine ozone concentration can be seen in Fig. 2.

![Iodometric titration mechanism to determine ozone concentration.](image)

3. Results and Discussion
3.1. Mechanism of ozone formation in DBD plasma
DBD plasma results in electrical discharges between two separate electrodes and a dielectric isolator from the Cu wire electrode (active electrode) and the stainless steel mesh and Cu foil (passive electrode). The discharge occurs from the flow of electrons around the active electrode, the dielectric quartz tube, and stacking [10].

The BD plasma discharge generates a non-uniform magnetic field in the area around the active electrode, which enables ionization and formation of high-energy electrons in the area producing ozone. The ozone is produced in the plasma discharge when the atmospheric air passes through the gap between the two electrodes. The oxygen molecules contained in the atmospheric air were dissociated due to the influence of high-energy electrons in the gap between the electrodes producing ozone. The formation of ozone involves O, O2, and O* leads to the formation of the O3 molecule [16]. The reactions of the ozone formation from oxygen are presented in reaction (1-2) [6].

\[
e^- + O_2 \rightarrow e + O + O^* \quad (1)
\]
\[
O^* + O_2 \rightarrow O_3 \quad (2)
\]

Following these reactions, the decomposition reaction that is triggered by O3 produces hydroxyl radicals. The hydroxyl radical has the potential ability to produce greater oxidation than O3 through reactions (3)
and (4). The high oxidative potential of hydroxyl radicals makes it usable for purifying other organic molecules through reactions (5).

\[
\begin{align*}
\text{OH}^- + \text{O}_3 &\rightarrow \text{O}_2^+ + \text{HO}_2^+ \quad (3) \\
\text{O}_3 + 3 \text{HO}_2^+ &\rightarrow 3\text{OH}^+ + 3\text{O}_2 \quad (4) \\
3\text{O}_3 + \text{H}_2\text{O} &\rightarrow 2\text{OH}^+ + 4\text{O}_2 \quad (5)
\end{align*}
\]

Moreover, the oxygen can absorb UV light between 240 nm-320 nm generated from the plasma discharge. The ultraviolet radiation then breaks down oxygen gas in free air into two oxygen atoms called the photolysis process. The oxygen atom naturally collides with oxygen gas molecules around it, forming ozone molecules. The ozone decomposes back into an oxygen molecule and one oxygen atom if the photon is re-absorbed by ozone. The sequence process is shown respectively in the reaction (6-7) [2].

\[
\begin{align*}
\text{O}_2 + h\nu &\rightarrow \text{O} + \text{O} \quad (6) \\
\text{O}_2 + \text{O} &\rightarrow \text{O}_3 \quad (7) \\
\text{O}_3 + h\nu &\rightarrow \text{O}_2 + \text{O} \quad (8)
\end{align*}
\]

3.2. Determination of ozone concentration

The ozone concentrations dissolved in distilled water samples treated with DBD plasma for 0, 2, 4, 6, 8, and 10 minutes were determined using iodometric titration. Before the titration begins, the distilled water sample was added with KI and H$_2$SO$_4$. The purpose of adding KI is as a donor of iodide that will react with O$_3$ to form iodine. H$_2$SO$_4$ solution was added to provide an acidic atmosphere so that the sample did not react with hydroxide. When adding KI and H$_2$SO$_4$, the sample changes color from clear to yellow. Furthermore, the solution was added starch, which serves as an indicator showing a change in color to dark blue, and at the end of the titration, the dark blue color changed to a colorless solution [17]. The addition of a starch indicator before the endpoint of the titration aims to avoid the formation of the iod-starch complex so that it is difficult to be titrated by sodium thiosulfate [18]. The reaction when adding KI and H$_2$SO$_4$ is shown in reaction (9).

\[
\text{O}_3 + 2 \text{KI} + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{I}_2 + 2 \text{KOH} \quad (9)
\]

The higher ozone concentrations by the increasing of the treatment time are caused by accelerated electron movements leading to a higher chance of collisions. The color of the solution changed from dark blue to clear when the resulting iodine was titrated by a standard solution of Na$_2$S$_2$O$_3$.5H$_2$O. The reaction during titration with Na$_2$S$_2$O$_3$.5H$_2$O is shown in reaction (10).

\[
\text{I}_2 + 2 \text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2 \text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \quad (10)
\]

The concentration of ozone formed is determined from the number of mol I$_2$ from the titration results. Triiodide ion (I$_3^-$) is formed when excess iodine is present. The reaction when I$_3^-$ formed is shown in reaction (11).

\[
\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^- \quad (11)
\]

The yellow and dark blue color would be more intense along with the longer treatment time, indicating more ozone was produced by the increasing treatment time. The calculated ozone concentration at each time variation of 0, 2, 4, 6, 8, and 10 min are listed in Table 1. Table 1 and Fig. 3 show that the treatment
time of DBD plasma affects the ozone concentration. The longer the DBD plasma treatment time causes the concentration of ozone produced increases. The relationship graph of ozone concentration against treatment time is drawn in Fig. 3.

Table 1. Determination of ozone concentration data at each time variation

| Time (minute) | Titrant volume (mL) | Ozone Concentration (ppm) |
|--------------|---------------------|---------------------------|
| 0            | 0                   | 0                         |
| 2            | 0.20                | 0.960                     |
| 4            | 0.43                | 2.064                     |
| 6            | 0.63                | 3.024                     |
| 8            | 2.46                | 11.808                    |
| 10           | 5.76                | 27.679                    |

Figure 3 shows that the highest ozone concentration reached 25 ppm for 10 min treatment. The ozone significantly increased when the treatment was conducted for more than 6 min. The plot of the concentration of the ozone dissolved in water at various times does not follow a linear line but follows a polynomial trend. The polynomial line equation obtained is \( y = 0.4701x^2 - 2.2425x + 1.5737 \), with determination coefficient \( R^2 \) of 0.965. The ozone produced is affected by the number of oxygen molecules passing in the DBD reactor. Inside the plasma reactor, the oxygen molecules result in dissociation, ionization, or recombination of electrons, which further induce the relatively large ozone concentrations [13]. Therefore, the longer plasma generated, the higher the ozone concentration was estimated in this study.

Figure 3. The influence of treatment time DBD plasma on ozone concentration.

4. Conclusions
DBD plasma generated in this study successfully produced ozone in a significant amount. The time dependence of ozone concentration in water tends to follow the polynomial line. Moreover, the DBD plasma treatment time greatly influences the results of ozone concentration measurements, in which the ozone significantly increased when the treatment was conducted for more than 6 min. The longer plasma treatment was performed, the higher the ozone concentration was measured.

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