ABSTRACT

Wastes containing phenolic compounds, including 2-chlorophenol and 4-chlorophenol at a threshold exceeding 50 mg / L, are very harmful to the environment. The processing of waste containing phenolic compounds using ozone and plasma technology is therefore an environmentally friendly and relatively inexpensive solution. The processing carried out in this study uses ozone plasma technology. Plasma is generated by high voltage transformer, which is fed into electrodes wound on a reactor made of quartz glass. The reactor type is dielectric barrier discharge (DBD) have the ability to degrade these waste, by producing reactive oxygen species, including •OH, •O₂⁻ and molecular species of O₃, H₂O₂. Subsequently, active species with high energy are transferred to the liquid phase, to react with chlorophenol compounds. According to the results, the dielectric barrier discharge plasma reactor using electrode coils was able to degrade waste containing 2-chlorophenol compounds by 70.96% and 79.41%, in acidic and alkaline conditions, respectively, while, 4-chlorophenol was degraded by 23.42% and 53.54%, in acidic and alkaline conditions, respectively.

Keywords: Dielectric barrier discharge, Plasma, 2-Chlorophenol, 4-Chlorophenol, Waste

ABSTRAK

Limbah yang mengandung senyawa fenol, seperti 2-klorofenol dan 4-klorofenol pada ambang batas melebihi 50 mg/L sangat berbahaya berada di lingkungan. Pengolahan limbah yang mengandung senyawa fenol menggunakan teknologi ozon dan plasma merupakan salah satu solusi yang ramah lingkungan dan relatif lebih murah. Proses
1. INTRODUCTION

Water contaminated with organic compounds for instance, chlorinated phenols, have been found to be very harmful to the environment (Aziz et al., 2018). Meanwhile, phenolic compounds are widely used for industrial processing, especially for fungicides, pesticides, wood processing, dyeing, pharmaceuticals, and herbicides industry (Li et al., 2002). Phenolic compounds widely used in industries include 2,4-dichlorophenol, 2-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol, p-nitrophenol, and pentachlorophenol. However, this study discussed 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol. Chlorophenol is an important intermediate compound in the synthesis of pesticides, herbicides, as well as dyes, and is also present chlorination process in water with high organic carbon concentrations (Dojčinović et al., 2008).

Chlorophenols contaminants constitute an important category of organic pollutants and some of them are identified as carcinogens and environmental endocrine disruptors. Chlorophenols are harmful to organism even at ppb levels and listed as priority pollutants by United State Environmental Protect Agency. Therefore, many attempts have been made to develop proper ways to remove these contaminants from contaminated water in recent years (Chen et al., 2013). This study therefore aims to discuss the
mechanism of 2-chlorophenol and 4-chlorophenol compound degradation, using a dielectric barrier discharge (DBD) plasma reactor. The DBD plasma reactor used functions as a direct ozonator, and the degradation dynamics’ result are shown directly in this test.

DBD is an application of non-thermal plasma technology, and the dielectric barrier discharge plasma generates high-energy electrons (1-10eV) initiating chemical reactions in ambient conditions. This is widely used as an ozone generator with oxygen or free air sources, and the performance depends on reactor configuration, injected gas, gas flow rate, packing material, as well as power supply (Ray et al., 2016). The main advantage of this electrical discharge type is the capacity to form an unbalanced plasma state in the atmospheric pressure gas, in an economical and reliable manner. In addition, the DBD reactor’s working principle is discharge occurrence. Gas ionization occurs in the gap between the gas phase and the high voltage plate, thus positive and negative ions are produced. Also, each ion produced goes to the appropriate electrode, therefore, the electric field is not homogeneous. The gas under an electric field’s effect is able to cause the movement of gaseous species, and high-energy electrons channel energy to the gas molecules through collisions, molecular excitation, electron dissociation, as well as ionization. Subsequently, the application of sufficiently high voltage between the electrodes, leads to an electrical disturbance and plasma formation. According to Figure 1, the high voltage is connected to the high voltage electrode while the other is the ground electrode.

![Figure 1. Mechanism of DBD Plasma Reactor](image)

Meanwhile, a dielectric as a barrier was used to regulate the number of electrons flowing through the discharge gap, and consequently, colliding with the molecules. These molecules are effectively untied, and the main active species resulting from the electron energy transfer are ions, radicals, and excited atoms. Subsequently, DBD produces reactive oxygen species (ROS) including ($\bullet\text{OH}$, $\bullet\text{O}_2^-$) and molecular species ($\text{O}_3$, $\text{H}_2\text{O}_2$) (Saraslifah et al., 2016). Active species with high energy are then injected into the liquid phase to
react with chlorophenol compounds. In the industry, DBD reactor is used to produce ozone, deodorize, surface treatment, and other processes (Schiorlin et al., 2015).

2. MATERIALS AND METHODS

2.1. Experimental Set-Up

The dielectric barrier discharge plasma used in this study is a plug flow reactor type made from borosilicate glass. Figure 2 shows this material has high heat resistance at a relatively low price, and is referred to as the first DBD reactor. This reactor is a glass tube with a 24 cm length, a 2 cm tube diameter, 0.1 cm thickness, and is equipped with a threaded cap as a support for a high voltage electrode, with a hole for injecting air or a mixture of ozone as well as O\textsubscript{2} gas to ensure direct contact with the waste stream. The waste stream with the predetermined discharge is expected to mix homogeneously with oxygen gas. Also, the small hole where waste exits has a diameter of 0.3 cm and is 3 cm away from the dielectric glass tube’s top end.

Meanwhile, the electrodes in the tube are also dielectric media, and the high-voltage electrodes were arranged on one axis and in the reactant gas as well as waste products’ direction of flow. The reactor is also designed to enable oxygen gas use as a reactant or feed, while the feed stream passes through the high voltage electrode chamber, and reverses direction through the dielectric medium’s inside, then exits at the output hole. In the electrode room, a plasmanization process occurs, where the exposure process to feed gas in a high-voltage electric field occurs. This in turn experiences ozone formation, and this dissolves in water forming *OH, to degrade the waste.

![Figure 2. Dielectric Barrier Discharge Plasma Reactor First Type](image-url)

This plasma reactor is generated using a high voltage of 12 kV, a current of 0.015A, and a power of 1 watt. Plasma formation occurs at the positive electrode, from an ozone generator with a free air source coming from the compressor and meeting in this reactor.
Meanwhile, the solution enters the liquid inlet and meets the radicals formed, thus, the degradation process occurs in this plasma DBD reactor.

The reactor is made of quartz glass as a dielectric, with a 22 mm diameter and 40 cm length. In addition, the two electrodes used, are a cylinder-spiral configuration made of stainless steel (SS316). The inner electrode functions as a high voltage, is a cylinder with a 9 mm diameter, placed in the center of the quartz tube and produces a discharge gap of 6.5 mm. Meanwhile, the outer counterpart functions as a ground, and is a stainless steel wire coiled around the quartz tube’s outer surface, with a total coil (N) of 30.

The alternative process used in the study related to the degradation of phenol compounds involves modifying the dielectric barrier discharge plasma reactor, using a different electrode coil, referred to as the second type DBD reactor. This reactor has a spiral cylindrical coaxial pipe configuration, and has been designed to have several criteria. These are minimal power consumption and high productivity, easy operation and maintenance, as well as low operation.

![Diagram of the reactor](image)

**Figure 3.** Dielectric Barrier Discharge Plasma Reactor Second Type

Based on the two reactors, the mechanism of degradation process for wastes containing phenol compounds is seen. Figure 3 shows the use of a change in the reactor model, expected to produce an even higher waste degradation process.

**Material and Reagents**

For this reaction, distilled water was used to make synthetic phenol waste compounds as a solvent. In addition, the process utilized 2-chlorophenol and 4-dichlorophenol treated solutions with an initial concentration of 50 mg/L because maximum concentration permitted at this level, as well as pH of 4 and 10, and a 2 ppm ozone dose.

**Analytical Methods**
Furthermore, degradation pollutants measured with a Hack Brand UV/Vis spectrophotometer, at 250 nm. The degradation of chlorophenol wastewater in the DBD plasma reactor was performed by varying time variables to obtain the optimum operating conditions. Subsequently, the sample was analyzed by the degradation percentage of 2-chlorophenol and 4-chlorophenol, as well as the resulting degradation products.

### 3. RESULT AND DISCUSSION
#### 3.1. Evaluation of degradation efficiency

During the quantification of hydroxyl radicals, distilled water is used to determine the number of hydroxyl radicals formed without reaction with chlorophenol solution. The OH radicals have a short residence time of $3.7 \times 10^{-9}$ seconds (Jiang et al., 2014), thus, difficulty is faced while measuring the radicals’ presence. However, •OH recombine to become H$_2$O$_2$, thus, the radical quantity is measured by hydrogen peroxide formation. The reaction to the H$_2$O$_2$ formation is shown in the equation below.

$$2 \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad [1]$$

The hydroxyl radical quantification was performed with the iodometric titration method based on the oxidation-reduction reaction. In this case, the amount of iodine released is equivalent to an oxidizing agent’s counterpart. In addition, the sample is to be titrated with sodium thiosulfate, while amylum indicator is also used to show the titration’s endpoint. This is obtained quantitatively because the dark blue color changes to clear at the end point. Equations 2 and 3 show the determination of the number of • OH moles, the oxidizing agent, determined from the amount of H$_2$O$_2$ produced:

$$\text{H}_2\text{O}_2 + 2 \text{KI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} \quad [2]$$

$$\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \quad [3]$$

This quantification aims to determine the best-operating conditions to show ozone productivity, and is carried out in order to measure the amount of dissolved ozone in a liquid at acidic and alkaline pH. At acidic pH, ozone works simply as ozone, but often works in the form of OH radicals at high pH. This study used an output voltage, liquid volume, and airflow rate of 19 kV, 5000 ml, and 2.5 L/min, respectively. The data obtained shows the amount of radicals in the type 1 reactor is 0.0576 mg/hour with the dissolved ozone of 0.008 mg/L, while the type 2 reactor produced 0.4025 mg/hour and 0.221 mg/L, respectively. Based on the radicals
produced, the type 2 DBD reactor is better, compared to type 1, therefore, the research was continued using type 2. This reactor type is better at producing OH radicals because the coaxial electrode type used has a larger cross-sectional area, compared to the rod electrodes. In addition, the length of contact time also significantly influences the production of hydroxyl radicals.

3.2. 2-Chlorophenol Degradation

Mechanism

Figure 4 shows the 2-chlorophenol waste treatment process with a 50 mL/minute liquid flow rate, a 2.5 L/minute airflow rate, a 19 kV voltage, and an initial pH of 4.

![Figure 4](image)

**Figure 4.** Graph degradation of 2-chlorophenol with voltage = 19kV, waste flowrate 50 mL/minute, air flowrate = 2.5 mL/minute

Based on the DBD type 2 reactor test results, the highest degradation was 79.41% at pH 10, while the degradation at pH 4 was 70.96%, at a 120 minute exposure time. Thus, an increase in pH causes an increase in processing, because the existing ozone produces more OH radicals.

Furthermore, there is a mechanism of 2-chlorophenol degradation by •OH and ozone. According to Figure 5, the decomposition of 2-chlorophenol with •OH radicals has two possible routes, para-hydroxylation or ortho-hydroxylation.

![Figure 5](image)

**Figure 5.** Degradation mechanism 2-chlorophenol by radicals (JiaDe et al., 2008).

Chlorinated dihydroxybenzenes chlorohydroquinone (CHQ), chlorobenzoquinone (CBQ), and 3-chlorocatechol (3-CCC)) are the main intermediates from the oxidation of 2-chlorophenol by •OH, while catechol (CC) is an aromatic byproduct without chlorine groups. Figure 6 shows the intermediate experiencing further
decomposition to form aliphatic and dechlorination products.

Meanwhile, Figure 6 path A shows chlorodihydroxycyclohexadienyl radical (•CDHCD) first produced as a temporary product, after the OH radical reacts with aromatic hydrocarbons (electrophilic addition) on the C=C bond in the aromatic ring. CDHCD radicals react with oxides to form organoperoxyl radicals, and this in turn reacts with •HO₂ to produce chlorodihydroxybenzenes (Wang, J., et al., 2008).

Furthermore, chlorobenzoquinone is formed, and this undergoes oxidation into organic acids for instance, metacetonic acid, oxalic acid, acetic acid, and formic acid [9]. Meanwhile, the •OH attack the Cl group in 2-chlorophenol to produce catechol (the compound’s Cl group has already escaped). Figure 6 path B shows the process of attacking OH radical to form catechol (Lukes et al., 2003).

At an alkaline pH, 2-chlorophenol is in an ionic state, with OH and the chlorophenol anion as the main anions. OH becomes OH radicals as a result of electron loss, and reacts with chlorophenol anions to form chlorophenoxy radicals. Subsequently, these are oxidized to chlorobenzoquinone. Meanwhile, at acidic pH, 2-chlorophenol exists in the molecular state, and reacts with •H to form chlorophenoxyl radical as well as Cl⁻. The Cl ion changes to Cl₂, ClO⁻, and HClO, with the ability to oxidize the organic, although not as strongly as •OH (JiaDe et al., 2008). Figure 7 shows the decomposition of 2-chlorophenol with ozone. This reaction produces aromatic intermediates in the form of 3-chlorocatechol and chlorohydroquinone, and some of the organic acids produced are acetic, valeric, 2-propenoic, maleic, succinic, propionic, dihydroxymaleic, malonic, hydroxymalonic, muconic, oxalic, tartaric, as well as phthalic acids (Sung et al., 2007).

**Figure 6.** Degradation Mechanism 2-chlorofenol by hydroxyl radicals (Lukes et al., 2003).
3.3. 4-Chlorophenol Degradation Mechanism

Figure 8 shows the data obtained from the 4-chlorophenol waste treatment process with a 50 mL/minute liquid flow rate, 2.5 L/minute airflow rate, 19 kV voltage, and an initial pH of 4. The results obtained a percentage degradation of 53.54% at pH 10, and 23.42 at pH 4. Thus, at acidic pH, ozone acts to degrade, and radicals are not formed.

In the first 4-chlorophenol degradation to hydroquinone, 4-chlororesorcinol, and 4-chlorocatechol were obtained from the hydroxylation reaction. The opened ring becomes organic acids, for instance, formic, acetic, oxalic, malonic, maleic, and malic acids. Furthermore, 4-chlorophenol is easily broken down by breaking the C1-C2 or C5-C6 bonds, forming 4-chloro-2,4-hexadien-1-ol. Meanwhile, further breakdown of 4-chlorocatechol or hydroquinone produces 3-hydroxybutyraldehyde. Figure 9 shows the degradation mechanism for 4-chlorophenol. This reaction is better in alkaline conditions, because optimal formation of hydroxyl radicals occurs optimally.

**Figure 7.** Degradation of 2-chlorophenol by ozone (Sung et al., 2007).

**Figure 8.** Graph of degradation 4-chlorophenol with voltage = 19kV, waste flow rate 50 mL/min, air flow rate = 2.5 mL/min.

**Figure 9.** Degradation mechanism of 4-chlorophenol (Bian et al., 2011).
4. SUMMARY

Based on the research and analysis conducted, the plasma dielectric barrier discharge reactor using electrode coils was proven to be able to degrade waste containing 2-chlorophenol compounds by 70.96% and 79.41% in acidic and alkaline conditions, respectively. Meanwhile, the percentage degradation for 4-chlorophenol was 23.42% and 53.54% in acidic and alkaline conditions, respectively. By investigating the degradation of phenol waste in the plasma barrier discharge dielectric reactor, the solution’s condition was concluded to greatly affect the performance of ozone and working plasma. Also, the coaxial electrode type is very influential in hydroxyl radical formation within the DBD plasma reactor, as well as the dimensions of the reactor and the electrical power supplied. Therefore, as a development of the DBD plasma reactor model using electrode coils, this is proven to environmentally friendly, and able to properly degrade waste, however, further refinement is required.

Acknowledgment
The authors are grateful to the financial support provided for this research by the Universitas Indonesia. And also grateful to Samantha for assistance to collect data at Intensifikasi Proses Laboratory.

References
Aziz, K. H. H., Miessner, H., Mueller, S., Mahyar, A., Kalass, D., Moeller, D., . . . Rashid, M. A. M. (2018). Comparative study on 2, 4-dichlorophenoxyacetic acid and 2, 4-dichlorophenol removal from aqueous solutions via ozonation, photocatalysis and non-thermal plasma using a planar falling film reactor. *Journal of hazardous materials, 343*, 107-115.

Bian, W., Song, X., Liu, D., Zhang, J., & Chen, X. (2011). The intermediate products in the degradation of 4-chlorophenol by pulsed high voltage discharge in water. *Journal of hazardous materials, 192*(3), 1330-1339.

Chen, X., Bian, W., Song, X., Liu, D., & Zhang, J. (2013). Degradation of 4-chlorophenol in a dielectric barrier discharge system. *Separation and Purification Technology, 120*, 102-109.

Dojčinović, B. P., Manojlović, D., Roglić, G. M., Obradović, B. M., Kuraica, M. M., & Purić, J. (2008). Plasma assisted
degradation of phenol solutions. *Vacuum, 83*(1), 234-237.

JiaDe, W., RunYe, Z., Xia, C., & JianMeng, C. (2008). Mechanism and kinetics of 2-chlorophenol decomposition using coupled ultrasound and electrocatalysis. *SCIENCE IN CHINA SERIES B-CHEMISTRY, 51*(6), 577-585.

Jiang, B., Zheng, J., Qiu, S., Wu, M., Zhang, Q., Yan, Z., & Xue, Q. (2014). Review on electrical discharge plasma technology for wastewater remediation. *Chemical Engineering Journal, 236*, 348-368.

Li, C.-Q., Trudel, L. J., & Wogan, G. N. (2002). Genotoxicity, mitochondrial damage, and apoptosis in human lymphoblastoid cells exposed to peroxynitrite generated from SIN-1. *Chemical research in toxicology, 15*(4), 527-535.

Lukes, P., Clupek, M., Babicky, V., Sunka, P., Winterova, G., & Janda, V. (2003). Non-thermal plasma induced decomposition of 2-chlorophenol in water. *Acta Physica Slovaca, 53*(6), 423-428.

Ray, D., & Subrahmanyam, C. (2016). CO2 decomposition in a packed DBD plasma reactor: influence of packing materials. *Rsc Advances, 6*(45), 39492-39499.

Sarasrifah, S., Nur, M., & Arianto, F. (2016). Pengaruh Ozon yang Dibangkitkan Melalui Reaktor Plasma Berpenghalang Dielektrik Elektroda Silinder Spiral Terhadap Pengawetan Cabai. *Youngster Physics Journal, 5*(4), 319-326.

Schiorlin, M., Paradisi, C., Brandenburg, R., Schmidt, M., Marotta, E., Giardina, A., & Basner, R. (2015). Pollutant degradation in gas streams by means of non-thermal plasmas. In *Current air quality issues*: IntechOpen.

Sung, M., & Huang, C. P. (2007). Kinetics of the degradation of 2-chlorophenol by ozonation at pH 3. *Journal of hazardous materials, 141*(1), 140-147.