A comparative study on the degradation of 2,4-dichlorophenol and 2,5-dichlorophenol using DBD non-thermal plasma reactor

Febri Monica Diristiani, Badzlina Khairunizzahra, Samantha Suryo and Setijo Bismo*

Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok, West Java, 16424, Indonesia.

*Corresponding author: setijo.bismo@ui.ac.id

Abstract. The dichlorophenol compound group (DCP) is one of the pollutants contained in industrial wastewater. This component is difficult to degrade in the environment, subsequently leading to hazards and a severe impact on human health. Based on the location of the chlorine atom in the aromatic ring, the variety present in some isomers ought to be removed from the water, in order to reduce the impact. Therefore, the technology adopted to eliminate the DCP concentration levels in wastewater includes the application of Dielectric Barrier Discharge (DBD) plasma reactor of high efficiency. This set up implements advanced oxidation processes (AOPs) by relying on highly active species, specifically \( \cdot \text{OH} \) and \( \text{O}_3 \). The aim of this study, therefore, is to compare the effectiveness of DBD reactors in the degradation activity on isomer 2,4-DCP and 2,5-DCP under acidic (pH 4) and alkaline (pH 10) conditions. The results showed the highest percentage removal (89.05%) after 120 minutes process of 2,5-DCP degradation, under the following conditions: pH 10; flow rate 50 mL/minute; airflow rate of 2.5 L / min; plasmatron voltage of 19 kV. Under similar circumstances, 2,4-DCP was reduced by 86.95%. In addition, the COD content in the waste material reached 46.88% and 46.14%, respectively.

1. Introduction
Water pollution instigated by industrial waste is one of the environmental problems requiring the development of law-compliant treatments. Moreover, one of the potential driving factors is the increasing number of industries, due to the elevation in life necessities. Based on various previous research, a number of contaminant phenolic compounds have been identified in production effluents, including dichlorophenol (DCP). In addition, several industries are known to generate the liquid-based variety as waste, comprising the pharmaceutical, pesticide, pulp and paper, petrochemical, plywood, and others. However, wastewaters based on DCP compounds are highly dangerous for living things and the environment.

These dichlorophenols have very low biodegradability, hence the possibility of sustained risk to living things with direct exposure. Moreover, the presence in wastes has been identified in several isomer forms, with the most common type being 2,4-dichlorophenol and 2,5-dichlorophenol, where each confers a different adverse effect on humans. Notably, a deposit of 2,4-dichlorophenol is able to damage the liver as well as kidneys and initiate blood circulation failures, while 2,5-dichlorophenol is an endocrine-disrupting chemical with the capacity to trigger obesity and instigate type 2 diabetes [1,2]. These potential impacts are to be eliminated by phenolic compound producing industries, through the
practice of proper waste treatment before disposal, with reference to waste quality standards. The
maximum content is estimated at 0.5 ppm, through PERMENLH No. 5/2014, although there is no
specific standard for the complete control, alongside the isomers. However, most industries in several
countries pay little attention to this aspect, particularly the compounds discharged into water [3].
Furthermore, advanced oxidation processes (AOPs) are one of the waste treatment methods
developed using hydroxyl radicals and ozone as active species, and dielectric barrier discharge (DBD)
plasma reactor is one of the technologies involved. Moreover, a non-thermal plasma reactor is able to
produce active species, including O₃ and H₂O₂ molecules, as well as hydroxyl radicals (·OH, H·, O·).
With the capacity to decompose phenolic compounds. The oxidation process with DBD has the
advantage of requiring only a short time, low operating temperature, high energy efficiency, and
compatibility with the environment, compared to other AOP implementations [4].
There has been extensive research on the degradation of 2,4-DCP isomers with AOP, but not with 2,5-
DCP [3], especially in terms of DBD plasma reactor applications. Meanwhile, degradation depends on
the chlorine atom position [5], and the entire process is determined by the solution pH, resulting from
the direct influence [6]. This study, therefore, examines the degradation ability of DBD plasma against
different DCP isomers, and dielectric barrier discharge (DBD) was used is the coaxial pipe configuration
of spiral cylinders. The initial pH of wastewater was conditioned according to the average value
stipulated in the industry.

2. Materials and Methods

2.1. Wastewater Materials
The experiments involved synthetic wastewater contaminated with DCP. Furthermore, 2,4-DCP (99%) was
obtained from Sigma-Aldrich, while 2,5-DCP (99%) was obtained from Merck, and the solutions
were prepared using distilled water. Also, all chemicals used in the study were of extra purity or
analytical grade.

2.2. Experimental installation and procedure
The experimental setting comprised of a DBD non-thermal plasma reactor with a continuous system,
alongside cylinder-spiral configuration inner and outer electrodes, respectively. This possessed the
dimensions of 150 mL, 40 cm, and 22 mm for volume, height, and diameter. Figure 1 shows a diagram
of the experimental arrangement scheme for this study. This research was initiated with a pump and
compressor calibration to ensure precise fluid measurements. Subsequently, a reactor start-up test was
conducted to ascertain the possibility of operating the plasma generating systems without significant
complexities or problems. In addition, a leak test was performed by running distilled water from the
reservoir through the pump, as well as air feed from the compressor to the reactor. Therefore, the duct
tape is installed after a crack is detected, to prevent loss of water or injected air. The next step required
a physical plasma test, involving the observation of the plasma phenomenon, characterized by the
display of a purplish incandescent along the reactor. Furthermore, a hydrodynamic test was performed
to ensure the fluid flows as specified.

Some preliminary tests were conducted to quantify the hydroxyl radicals, and dissolved zone. Also,
hydroxyl radical analysis was performed using the iodometric titration method, based on some
experimental parameters, including liquid fluid flow rates of 50, 65, and 80 mL/min, plasmatron voltage
of 15, 17, and 19 kV, as well as solution pH of 4 and 10. Similarly, dissolved ozone concentration was
evaluated based on the pH parameters by an ozone test kit with spectrophotometric measurements at a
wavelength of 550nm. Therefore, DCP degradation was carried out with best-operating conditions
implemented from the preliminary test and other prerequisites.
Figure 1. The schematic diagram of the experimental setup for wastewater degradation.

The initial wastewater concentration was 50 mg/L, with pH of 4 and 10, while the process duration extended for 120 minutes, with sampling at intervals of 0, 5, 10, 15, 30, 45, 60, 75, 90, 105 and 120. The amount of dichlorophenol compounds were determined through spectrometry, 2,4-DCP and 2,5-DCP were identified at a wavelength of 513.8 and 505.6 nm, respectively. Furthermore, the COD levels were evaluated using similar method and recognized at 650 nm using COD HACH.

3. Result and Discussion

3.1. Quantification of Hydroxyl Radical and Dissolved Ozone Concentration

Hydroxyl radical quantification aimed to determine the performance of DBD plasma reactors in producing ·OH as an active species, with the intrinsic capacity to degrade phenolic compounds under certain conditions. Therefore, potassium iodide solution was used as a phenolic compound substitute to obtain an accurate measurement. Based on the high reactivity and non-selective nature of ·OH, the quantification process is represented by \( \text{H}_2\text{O}_2 \) concentrations, through the following reaction:

\[
\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2
\]

The oxidation of \( \text{H}_2\text{O}_2 \) by KI follows a reduction-oxidation principle, as formed in the reaction below:

\[
\begin{align*}
\text{H}_2\text{O}_2 + 2\text{KI} + \text{H}_2\text{SO}_4 & \leftrightarrow \text{I}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} \quad (2) \\
\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 & \leftrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \quad (3)
\end{align*}
\]

Figure 2. Quantity of (a) hydroxyl radicals at liquid flow rate variations (b) voltage variations.
Figure 3. Quantity of (a) hydroxyl radicals (b) Dissolved ozone concentrations at pH variations.

The Hydroxyl radical quantification was evaluated by varying the flow rate of the liquid fluid feed 50, 65 and 80 mL/minute, as well as the plasmatron input voltage 15, 17, 19 kV. Figure 2(a) shows more significant production of hydrogen peroxide in samples with slower rate. This phenomenon was due to the longer fluid residence time in the reactor, and the slower circulation of entry and exit materials. In addition, the reactants formed are expected to remain in the reactor plasma for a long time to achieve a complete treatment [8]. Therefore, higher contact time perfects the hydroxyl radical formation, despite the relatively low circulation. Figure 2(b) shows a directly proportional increase in hydrogen peroxide concentrations produced along with the elevated plasmatron voltage supply. Furthermore, higher electric field intensity facilitates higher energy generation for particles and electrons. This phenomenon leads to greater collisions and more significant ionization rates [7]. Therefore, elevated voltage increases the electric field intensity, and prompts the release of an extensive number of ionized, excited, as well as dissociated molecules, and further augments the formation of active species, including •OH.

The best conditions were selected based on the variables evaluated, including the fluid flow rate and plasmatron voltage applied to assess the hydroxyl radical quantification, as well as the ozone solubility tests with varied solution pH. Figure 3(a) shows the detection of \( \text{H}_2\text{O}_2 \) concentrations at acidic and basic pH. This base solution influences the dissociation into hydroxide anion (OH\(^-\)) and sodium cation (Na\(^+\)). Moreover, \( \text{H}_2\text{O}_2 \) concentration required to consume species concentration is relatively high because of the reactive and non-selective nature of •OH combined with fellow •OH and the slight decline over time due to oxidation processes. Figure 3(b) shows a decrease in ozone solubility with increasing pH, and the value recorded tends to fluctuate with time. This phenomenon is due to the shorter ozone half-life initiated in the water sample [10] and is also related to the presence of hydroxide ions (OH\(^-\)) at high pH, with the capacity to induce the ozone decomposition rate. Furthermore, this fluctuation in solubility is implicated in the formation of other compounds, through the interaction mechanism between molecules producing \( \text{H}_2\text{O}_2 \), \( \text{O}_2 \), \( \text{O}_3^- \), and •OH [11]. Also, water temperature is another influential parameter, as lower values are strongly associated with higher levels of ozone dissolution. It occurs because the ambient temperature is erratic, therefore causing the fluctuating concentration values.

3.2. The Effect of pH of the Solution on DCP Degradation

The effect of pH on the degradation of DCP isomer waste is evaluated based on the final concentration obtained under similar operating conditions. Figure 4 shows the final output in the form of percentage degradation with varied pH treatments.
Figure 4. Degradation of (a) 2,4-DCP and (b) 2,5-DCP at pH variations.

| Dichlorophenol (DCP) | pH  | Final Degradation (%) | Initial Conc. of DCP (mg/L) | Final Conc. of DCP (mg/L) |
|----------------------|-----|------------------------|----------------------------|---------------------------|
| 2,4-DCP              | 10  | 86.95                  | 49.8                       | 6.5                       |
|                      | 4   | 76.63                  | 50.5                       | 11.8                      |
| 2,5-DCP              | 10  | 89.05                  | 53.9                       | 5.9                       |
|                      | 4   | 78.06                  | 51.5                       | 11.3                      |

As seen in Figure 4 an increase in percentage degradation at the exponent of time, which shows pH influenced the entire process, as more significant extents were measured pH 10, compared to 4. This parameter is influential due to the presence of DCP in the form of either molecular or dichlorophenoxide ions [12]. The DCP compound molecule tends to dissociate into dichlorophenoxide ions at higher pH, therefore enhancing the ease to degrade. As previously explained, the presence of \( \cdot \)OH is higher as the pH of the solution increases while \( \mathrm{O}_3 \), which less oxidative to attack DCP molecule, is higher at lower pH. Furthermore, the degradation yield at pH 4 somewhat smaller than at pH 10. However, DBD plasma reactors have the advantage of being able to produce \( \cdot \)OH under both acidic and alkaline conditions. Thus, the presence of \( \cdot \)OH facilitates the vulnerability of DCP compounds in molecular form to attack [13].
Based on Table 1, the percentage of degradation of 2,5-DCP (89.05%) was slightly greater than 2,4-DCP (86.95%) over time. 2,5-DCP, due to the relatively faster polarization and dissociation to dichlorophenoxide ions. Furthermore, chlorine atom substituent in close proximity to the hydroxyl group instigate the effect of a steric hindrance [14] and further prevents the attack tendency of •OH against aromatic rings. The distance between each chlorine atom influences the steric hindrance strength, and the chlorination rate was determined to be more significant in 2,5-DCP, compared to 2,4 DCP [15]. Conversely, the degradation rate of 2,5-DCP was only slightly faster, although the final percentage showed no significant difference (<5%). This is because •OH and O₃ work synergistically and complementarily under certain conditions.

3.3. Changes in pH of the Solution
The pH of samples obtained from the reservoir during the treatment was evaluated. Figure 5 shows any changes detected pertaining to the degree of acidity.

![Figure 5. pH changes in degradation of 2,4-DCP and 2,5-DCP at pH variations.](image)

Figure 5 demonstrates the ability for DCP to lower the solution pH rapidly. The oxidation process modifies some of the molecules into organic acids, including muconic acid, malonaldehyde, maleic acid and others. These are further oxidized into simpler forms, comprising oxalic and formic acid [6] to ensure the final pH is acidic. However, DCP solutions in exhibit different phenomena of pH changes under alkaline conditions, where consistently decreasing values were recorded and acidic environment characterized by an increase in pH, particularly during the initial 10 minutes. This preliminary rise in possibly occurs due to the presence of organic compounds, including carbonates and hydroxides.

3.4. COD Removal
The COD removal analysis was conducted by measuring the concentration per sample at 0, 5, 60, and 120 minutes under best conditions at pH 10, and the results are shown in Figure 6.

![Figure 6. COD Removal at 2,4-DCP and 2,5-DCP.](image)
Based on Figure 6, the DCP degradation process in the DBD plasma reactor was consistently able to reduce COD levels over time by 46.88% (201.14 mg / L) and 46.14% (190.46 mg / L) for 2,5-DCP and 2,4-DCP, respectively. Correspondingly, the amount removed within the initial 5 minutes was relatively low with reference to the preliminary degradation mechanisms by active species. The intermediate compound manifested in the form of an aromatic degradation ring, as indicated by the consistently high oxygen content requirement. In addition, there was a continuous decline in the degradation levels at the exponent of time. This indicates to the phenomenon of declination or aromatic ring termination, caused by further oxidation by active species. The procedure leads to the production of simpler intermediate compounds and carboxylic acid. Based on the final percentage of COD, the removal rate was determined to be slower compared to the DCP degradation rate. The treatment result for both isomers shows high final COD levels, indicating a large number of intermediate compounds were formed [13]. These composites had not reached the end of mineralization to become CO₂ and H₂O.

4. Conclusion

DBD plasma reactors are able to degrade 2,4-DCP and 2,5-DCP isomers into simpler compounds effectively, and a final percentage of 86.95% and 89.05% were respectively recorded after a 120 minutes process. In addition, there was a simultaneous decline in the pH of the solution following the generation of acidic compounds in the final product. This elevation in the Ph of the solution increases the productivity of ·OH as the strongest oxidant. Therefore, the removal efficiency is improved to achieve lower DCP concentrations in wastewater. The COD content of the 2,5-DCP and 2,4-DCP isomers after treatment through the DBD decreased by 46.88% and 46.14%, respectively. Meanwhile, the best-operating degradation conditions include a wastewater and airflow rate of 50 mL/minute, and 2.5 L / min, correspondingly, with a plasmatron voltage of 19 kV. The results show the absence of any significant differences regarding the location of chlorine in the DCP isomer while using the DBD plasma reactor. However, the final yield was unable to attain the quality standards issued by the government PERMENLH No. 5/2014; hence there is a need for additional processes.

Acknowledgments

The authors are grateful to the PUTI Prosiding 2020 (The Grants of International Indexed Publication for the lecturers of Universitas Indonesia) No. PENG–1/UN2.RST/PPM.00.00/2020. This was organized by the Directorate of Research and Community Service (DRPM) – Universitas Indonesia. Also, there are no competing or conflicting financial interests.

References

[1] Melanie B, H Murray, and Franco S 2014 Association of urinary phenols with increased body Weight Measures and Obesity in Children and Adolescents. J. of Pediatr 165 744-9.
[2] Wei Y and J Zhu 2015 Urinary concentrations of 2,5-dichlorophenol and diabetes in US adult J. Expo. Sci. Environ. Epidemiol 1-5
[3] Alexander J and Clementina R 2015 A comparative study: degradation of 2,5-dichlorophenol in wastewater and distilled water by ozone and ozone-UV Ozone-Sci Eng, 38 181-93
[4] Li L, Zhang H and Huang Q 2015 New insight into the residual inactivation of Microcystis aeruginosa by dielectric barrier discharge Sci. Rep. 5 13683
[5] Song-hu Y and L. Xiao-hua 2005 Comparison treatment of various chlorophenols by electro-fenton method: relationship between chlorine content and degradation J. Hazard. Mater. 118 85–92
[6] Poznyak T and Vivero J 2005 Degradation of aqueous phenol and chlorinated phenols by ozone. J. Ozone-Sci Eng, 27 447-58
[7] Setyaningrum D, et al 2007 Aplikasi plasma lucutan penghalang dielektrik dengan reaktor berkonfigurasi spiral-silinder menggunakan gas sumber oksigen (O₂) murni untuk enghasilkan gas ozon (O₃)
[8] Wang J and Jiang X 2009 Unusual catalytic effects of iron salts on phenol degradation by glow
discharge plasma in aqueous solution *J. of Hazard Mater* **161** 926-32

[9] Hoigne J and Bader H 1975 Ozonation of water: role of hydroxyl radicals as oxidizing intermediates *Sci* **190**(4216) 782-4

[10] Gardoni D, Vailati A and Canziani R 2012 Decay of ozone in water: a review *Ozone Sci. Eng.* **34** 233-42

[11] Ershov B and Morozov P 2009 The kinetics of ozone decomposition in water: the influence of pH and temperature *Russ. J. Phys. Chem.* **83** 1457-62

[12] Hoigne J and Bader H 1983 Rate Constant of Reactions of Ozone with Organic and Inorganic Compounds in Water: Dissociating Organic Compounds *Water Res.* **17** 185-94

[13] Zhang H, Zhang Q, Miao C and Huang Q 2018 Degradation of 2,4-dichlorophenol in aqueous solution by dielectric barrier discharge: effects of plasma-working gases, degradation pathways, and toxicity assessment *Chemosphere* **204** 351-8

[14] Tang W and C P Huang 1996 Effect of chlorine content of chlorinated phenols on their oxidation kinetics by fenton’s reagent *Chemosphere* **33** (8) 1621-35

[15] Tang W 2003 *Physicochemical Treatment of Hazardous Wastes* (New York: Taylor & Francis Group) pp 182