Degradation of 2-chlorophenol in dielectric barrier discharge reactor

Samantha Suryo\textsuperscript{a}, Febri Monica Diristiani, Badzlina Khairunizzahrah and Setijo Bismo\textsuperscript{b}

Department of Chemical Engineering, Universitas Indonesia, Indonesia

\textsuperscript{a})samantha.suryo@ui.ac.id
\textsuperscript{b})Corresponding author: setijo.bismo@ui.ac.id

Abstract. Liquid waste containing 2-chlorophenol compound has high toxicity, carcinogenic, and poor degradation properties, leading to bioaccumulation in the environment. It also considered as a primary chemical feedstock in the manufacture and widely used in various industry. Conventional methods such as chlorination, adsorption, liquid-liquid extraction, steam distillation, photocatalytic are inefficient and expensive. Plasma technology with a non-thermal dielectric barrier discharge (DBD) plasma reactor can efficiently degrade chlorophenol compounds without producing side effects. Various active species produced in the reactor are electrons and radical compounds •OH, O\textsubscript{3}, H\textsubscript{2}O\textsubscript{2}. This study aims to evaluate the degradation performance of DBD plasma reactors, namely the percentage of degradation, degradation concentrations of 2-chlorophenol, and chemical oxygen demand (COD). Variations were made with pH 4 and 10, while the fixed variables were waste flow rate 50 mL/min, air flow rate 2.5 L/min, and plasmatron voltage 19kV. It was found that degradation process of 2-chlorophenol with DBD reactor in pH 4 and 10 achieve 70.96% and 79.41%, respectively.

1. Introduction

Several industries such as pharmaceutical, coloring, agricultural and domestic release large amounts of toxic and dangerous pollutants into the environment. Most of these pollutants have xenobiotic and recalcitrant properties, which tend to be bioaccumulated and difficult to degrade in the environment. Increasing water pollution from industrial development and diminishing water resources lead to greater demand for clean water and various new regulations emerged \[1\]. One of the dangerous compounds contained in waste is chlorophenol. Chlorophenol is a serious problem if it is found in soil, sediments, and ground water. These pollutants and their derivatives are very mutagenic, carcinogenic, and immunogenic for humans and other organisms.

Many conventional waste treatment methods such as biological processes do not achieve high purification. The methods of chlorination, adsorption, liquid-liquid extraction, solid phase extraction, steam distillation, photocatalytic also have disadvantages, including slow reaction kinetics so that the degradation process is ineffective. Biological and classical physics-chemical processes are less effective in the processing of chlorophenol. The advanced oxidation process is an effective method for removing chlorophenol. In addition to the large number of AOPs studied, a very promising process is based on the use of electric discharge technology to remove hazardous compounds in wastewater, namely dielectric barrier discharge (DBD) \[2\].
Non-thermal plasma technology, namely the use of dielectric barrier discharge reactors, is a method of treating waste in an environmentally friendly manner. The process is simple, effective, low energy consumption, does not require the use of other chemicals, and does not produce by-product. The DBD reactor has the potential to decompose chlorophenol in liquid waste due to the production of active species such as O₃, •OH, •O, and H₂O₂ in the reactor so that it can decompose organic pollutants. Because it has a high level of oxidation, many complex compounds and toxic organic pollutants can be degraded into non-toxic products and completely degraded to CO₂ and H₂O or to become biodegradable and less toxic intermediates. Compared to other plasma technologies, DBD reactors have several advantages compared to other plasma technologies, including enabling scale-up processes to operate with larger volumes of gas and producing stable micro discharges [3].

This research used DBD plasma reactor with spiral cylinder configuration to degrade chlorophenol compounds contained in liquid waste. Chlorophenol compound has been able to be degraded by as much as 50% at pH 4 with oxidation of hydrogen peroxide [4]. This research was conducted to obtain more effective results in degrading chlorophenol. The effectiveness of the performance of the plasma DBD reactor system can be seen from the degradation of chlorophenol compounds by observing the pH value of the compound, especially in acidic and basic conditions. The influence of pH affects the reactivity of the compound since chlorophenol is dissociating compound. In addition, the effect of the pH value will have an impact on the production of hydroxyl and ozone radicals [5].

2. Materials and Methods

2.1. Materials
The synthetic effluent was prepared with distilled water and 2-chlorophenol. 2-chlorophenol was purchased from Sigma-Aldrich with concentration of 99% suitable for analysis. Solution of 50 mg/L concentration were prepared by adding synthetic effluent to distilled water. Sulfuric acid 2 M was used to make acid solution and natrium hydride 2 M was used to make basic solution.

2.2. Experimental design
2.2.1. Reactor. Figure 1 displays the reactor which consists of a high voltage power supply, DBD plasma reactor, pump, compressor, and many other instruments as shown in Table 1.

Figure 1. Overall DBD plasma reactor system.

The DBD reactor has a spiral cylindrical coaxial pipe configuration. The reactor has been designed to have several criteria, namely minimal power consumption and high productivity, easy operation and maintenance, and low operating and maintenance costs. The reactor was made of quartz glass as dielectric with a diameter of 22 mm and a length of 40 cm. The electrodes used are spiral-cylinder
configuration made of stainless steel (SS304). There are two electrodes which are inner and outer electrodes. The inner electrode functions as a high-voltage electrode, while the outer electrode functions as a low-voltage electrode. The inner electrode is a cylinder with a diameter of 9 mm, placed in the centre of the quartz tube and produces a discharge gap of 6.5 mm. The outer electrodes are stainless steel wires wrapped around the outer surface of the quartz tube with the number of turns (N) 30. Information of Figure 1 can be seen in the following Table 1.

| No. | Instrument                  | No. | Instrument                  |
|-----|-----------------------------|-----|-----------------------------|
| 1   | Power source                | 7   | Pump                        |
| 2   | Slide Regulator             | 8   | Reservoir                   |
| 3   | Transformer                 | 9   | DBD Plasma Reactor          |
| 4   | Voltmeter                   | 10  | Ozonator                    |
| 5   | Amperemeter                 | 11  | Flowmeter                   |
| 6   | NST (Neon Sign Transformer) | 12  | Compressor                  |

2.2.2. Procedure. The research carried out hydroxyl radical quantification and ozone solubility test before degradation process. Hydroxyl radical quantification used iodometric titration and ozone solubility test used ozone reagent. Chlorophenol solution was filled inside the reservoir. Air was fed to the discharging zone and gas flow meters were used to control the flow rate. Then, the high voltage was applied to produce the plasma between solution and quartz plate. The 500 mL 2-chlorophenol was treated for 120 minutes. The pH value was adjusted to 4 and 10. Degraded samples of 2-chlorophenol were measured with amino-antipyrine reagent. The chemical oxygen demand (COD) was measured with a COD HACH reagent. All experiments were performed at room temperature. All experiments carried out with the fixed variables are air flow rate 2.5 L/min, volume of liquid 500 mL, voltage 19kV, while the independent variables are pH 4 and pH 10. The pH values were chosen at those value because a lot of waste is also present at that pH so there is no need to adjust the pH first before it is degraded.

2.3. Analysis methods
The concentration of 2-chlorophenol was analyzed by spectrophotometer in the wavelength of 513.2 nm dan 510.3 nm respectively. The efficiency of degraded 2-chlorophenol was determined from the following equation:

\[
\%\text{degradation} = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \times 100\% \quad \text{(Eq. 1)}
\]

where \( C_{\text{inlet}} \) is the initial concentration of chlorophenol and \( C_{\text{outlet}} \) is the concentration of chlorophenol after 't' minutes.

The degradation reaction of 2-chlorophenol obeyed the apparent first order kinetic law. The equation could be expressed as follow:

\[
\ln \left( \frac{C_0}{C_t} \right) = k_{cp}t \quad \text{(Eq. 2)}
\]

where \( C_0 \) is the initial concentration of chlorophenol, \( C_t \) is the final concentration of chlorophenol after degradation, \( k_{cp} \) is rate constant, and \( t \) is degradation time.

3. Result and Discussion

3.1. Hydroxyl radical quantification
The pH condition is very influential in the formation of hydroxyl radicals because it can affect the kinetics and reaction path. At alkaline pH, the formation of hydroxyl radicals increases significantly,
while the pH of acid, ozone remains in the molecular form so that the formation of hydroxyl radicals at acidic pH is very much different. Figure 2 the amount of H$_2$O$_2$ produced at pH 10 is 0.1 mmol while pH 4 is only 0.00125 mmol in 120 minutes. This proves that the more alkaline pH will produce high hydroxyl radicals. This indicate the hydroxyl radical generation is highly related to pH. At high pH, the transfer of one electron directly occurs according to equations (3) and (4) [6].

\[
\begin{align*}
O_3 + OH^- &\rightarrow \cdot O_3^- + \cdot OH \quad \text{(Eq. 3)} \\
\cdot O_3^- + H_2O &\rightarrow OH + O_2 + OH^- \quad \text{(Eq. 4)}
\end{align*}
\]

![Figure 2](image)

**Figure 2.** The effect of pH 4 and 10 on the amount of H$_2$O$_2$ formed.

3.2. **Ozone solubility test**

From Figure 3, the concentration of dissolved ozone is strongly influenced by pH. The highest dissolved ozone concentration is found at pH 4. At pH 10, ozone undergoes auto-decomposition to form OH radicals (7). This happens because pH 4 slows the rate of ozone decomposition so that molecular ozone is found. Conversely, the rate of ozone decomposition at pH 10 increases significantly. Alkaline pH There are many hydroxyl ions and hydroxide ions act as initiators in ozone decomposition. There are two possible reaction pathways, equation (5) shows ozone reaction with OH’ and equation (6) shows ozone reaction with HO$_2^-$. These both anions can lead ozone decomposition to hydroxyl radical production. The reaction can be seen in the equation below [8]:

\[
\begin{align*}
O_3 + OH^- &\rightarrow HO_2^- + O_2 \quad \text{(Eq. 5)} \\
O_3 + HO_2^- &\rightarrow \cdot OH + \cdot O_2^- + O_2 \quad \text{(Eq. 6)} \\
O_3 + \cdot O_2^- &\rightarrow O_3^{-} + O_2 \quad \text{(Eq. 7)} \\
\cdot O_3^- &\leftrightarrow O^- + O_2 (pH \geq 8) \quad \text{(Eq. 8)} \\
\cdot O^- + H_2O &\rightarrow \cdot OH + OH^- (pH \geq 8) \quad \text{(Eq. 9)} \\
\cdot OH + O_3 &\rightarrow HO_4 \cdot \quad \text{(Eq. 10)} \\
HO_4 \cdot &\rightarrow O_2 + HO_2 \quad \text{(Eq. 11)}
\end{align*}
\]
3.3. Degradation of 2-chlorophenol in DBD reactor

The degradation of the compound was carried out using a DBD reactor. This section will provide an analysis of the effect of pH with the flow rate of liquid 50 mL/min, air flow rate 2.5 L/min, and plasmatron voltage 19kV.

3.3.1. Effects of pH. From Figure 4, 2-chlorophenol degradation meets first-order kinetics as shown in equation (2). The highest decrease in concentration occurs in the 5th minute. This is because at the beginning of the reaction, the reactant concentration is still high so that many collisions occur between the active species and organic molecules. After the chlorophenol compound is degraded, direct collisions between active species and chlorophenol are reduced [7].

The degradation mechanism of chlorophenol compound is different under acidic and basic conditions. Ozonation at acidic pH is dominated by reactions with ozone molecules, whereas at alkaline pH it is dominated by OH radicals. Degradation at pH 10 is better than pH 4 as shown in Figure 4 for 2-chlorophenol compounds because of the higher degradation rate at alkaline condition. Degradation at pH 10 occurs faster due to dissociation of chlorophenol to chlorophenolate ions, which then tend to react with ozone and hydroxyl radical. When ozone is transferred from the discharge area to the liquid phase, it will react with 2-chlorophenol. A solution with a pH of 10 makes it easy to dissociate 2-chlorophenol into 2-chlorophenolate ions, which has a higher reaction rate with ozone so that at pH 10 ozone can be consumed at a higher rate. In other words, alkaline pH makes 2-chlorophenol ionized and supports ionic reactions. As a result, at pH 10, 2-chlorophenol experienced a degradation of 79.4% to 10.4 ppm, while pH 4 experienced a degradation of 70.96% to 14.2 ppm.

The difference on the degradation of 2-chlorophenol at pH 10 and pH 4 is possibly due to the reaction between chlorophenol and number of hydroxyl radical and ozone produced under certain pH. The degree of dissociation of chlorophenol to pH that affects the overall reaction. Dissociation increases with increasing pH and deprotonated compounds are easier to oxidize. At pH 10, 2-chlorophenol is in a more deprotonated state than at pH 4. The pKa value of a compound is related to the pH of the solution. When pKa < pH, more compounds are turned into deprotonated states. This is due to the value of pKa 2-chlorophenol which is 8.52. Therefore, 2-chlorophenol at pH 10 is more in a deprotonation state and causes 2-chlorophenol more easily attacked by OH radicals. Likewise, at pH 4, 2-chlorophenol is more abundant in the protonated state or in the molecular form. At pH 4, the reaction is dominated by ozone and there are only a few OH radicals so that the 2-chlorophenol degradation yield at pH 4 is smaller than pH 10.
Figure 4. Degradation of 2-chlorophenol.

3.4. COD
After degradation, the next step is the analysis of COD of 2-chlorophenol. The compound was analysed at liquid flow rate of 50 mL/minute and air flow rate of 2.5 L/minute at reaction time of 0, 5, 60, and 120 minutes.

3.4.1. Analysis. COD analysis is carried out with the aim of assessing the total amount of oxygen needed to oxidize organic compounds. The percentage of mineralization of 2-chlorophenol at pH 4 is 38.82% while the pH of 10 removal occurs 44.04%. This is consistent with the results that have been obtained previously that at pH 10 the removal percentage is greater than pH 4. According to the Minister of Environment regulation No. 5 of 2014, waste to be discharged into the environment must meet the COD content standard, which is 100 mg / L (class I) and 300 mg / L (class II) as a standard quality requirement for industrial liquid waste so that it can be declared safe to be disposed. It was found that the processed waste has not met the Ministry of Environment regulation No. 5 of 2014.

4. Summary
Based on the result of the research, the study has shown that the degradation percentage of 2-chlorophenol is greater in pH 10 than pH 4. In alkaline condition, chlorophenols are easily to degrade than in acidic condition. At pH 10 the yield of 2-chlorophenol degradation reached 79.4%. At pH 4 the result of degradation of 2-chlorophenol only reached 70.96%. The difference in degradation yield of 2-chlorophenol is also strongly influenced by reaction mechanism according to the condition of the solution. The slightly degradation differences between pH 4 and 10 indicate that the DBD reactor can successfully degrade 2-chlorophenol compound under acidic and alkaline condition.

Acknowledgements
This work was supported by the PUTI Prosiding (Publikasi Terindeks Internasional Prosiding) No. PENG-1/UN2.RST/PPM.00.00/2020, Universitas Indonesia. The authors stated that there were no competing conflicts of financial interests.

References
[1] Van Aken P, Lambert N, Van den Broeck R, Degrève J and Dewil R 2019 Advances in ozonation and biodegradation processes to enhance chlorophenol abatement in multisubstrate wastewaters: a review. *Environ. Sci. Water Res. Technol.* 5(3) 444-81
[2] Marković M D, Dojčinović B P, Obradović B M, Nešić J, Natić M M, Tosti T B, et al. 2015 Degradation and detoxification of the 4-chlorophenol by non-thermal plasma-influence of homogeneous catalysts Sep. Purif. Technol. 154 246-54

[3] Nawaz M I, Yi C, Asilevi P J, Geng T, Aleem M, Zafar A M, et al. 2019 A study of the Performance of dielectric barrier discharge under different conditions for nitrobenzene degradation Water 11 4

[4] De A, Chaudhuri B and Bhattacharjee S 1999 A kinetic study of the oxidation of phenol, o-chlorophenol, and catechol by hydrogen peroxide between 298K and 333K J. Chem. Technol. Biotechnol. 74 162-8

[5] Zhang H, Liu Y, Cheng X, Zhang A, Li X, Liu J, et al. 2018 Degradation of phenol in water using a novel gas-liquid two-phase dielectric barrier discharge plasma reactor Water Air Soil Pollut. 229 10

[6] Wang J L and Xu L J 2012 Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application Crit. Rev. Environ. Sci. Technol. 42(3) 251-325

[7] Poznyak T, Tapia R, Vivero J and Chairez I 2006 Effect of pH to the decomposition of aqueous phenols mixture by ozone Sociedad Química de México 23-35

[8] Von Gunten U 2003 Ozonation of drinking water: Part I. Oxidation kinetics and product formation Water Res. 37(7) 1443-67