Characteristic of phenol and 2,4-dichlorophenol synthetic wastewater degradation in a DBD (dielectric barrier discharge) reactor

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Abstract. In this study the content of phenol and 2,4-DCP (2,4-dichlorophenol) in synthetic wastewater was decomposed using the excitation technique of a mixture of waste liquid and air in a cold plasma Dielectric Barrier Discharge (DBD) reactor. The purpose of this study was to study the degradation process of organic compounds of phenol and 2,4-DCP liquid waste into simpler compounds. Plasma technology applied to the liquid-air mixture in the DBD reactor has the ability to oxidize and degrade organic synthetic wastewater into simpler compounds with relatively faster processing times without forming new waste compounds. Plasma air (excited air) will degrade wastewater by breaking the atomic bonds of synthetic wastewater compounds at high voltages between 220 - 330 V. The performance of the degradation process of synthetic waste can be known through analysis of phenolic compounds, hydroxyl and dissolved ozone, COD, and the final product. The parameters studied in this study are air gas flow rate 2 - 2.5 L/min, waste water flow rate 52 - 100 mL/min, plasma voltage between 220 - 330 V, and volume of waste water. This study also compared the degradation process of phenol and 2,4-DCP in cold plasma DBD reactor with the degradation process in multi-injection bubble column reactor. The removal efficiency of the process achieved 57.5% for phenol and 89.55% for 2,4-DCP.

1. Introduction
Phenolic compounds, including phenol and 2,4-DCP, are among the most dangerous organic pollutants found in many industrial wastes, such as in the petroleum refining industry, pharmaceuticals, wood processing, resins, plastics, and textiles. This compound is listed in EPA US priority pollutants because of its high toxicity and difficult to degrade. Wastewater contains phenolic compounds that exceed regulatory requirements, endanger living organisms and pose a great risk to human health, causing damage to the liver, kidneys, weakening of the heartbeat, and even death [1].

Several methods have been studied to eliminate phenol, such as extraction, adsorption, membrane filtration, biological degradation, electrochemical oxidation, and photocatalytic degradation. However, most of these maintenance techniques have their own disadvantages. For example, physical adsorption has a disadvantage of adsorbent blockage and poor regeneration, biological degradation requires long maintenance and several methods cause secondary pollution [2]. Therefore, it is very important to develop effective techniques, including its simplicity and require a small process space, to remove phenolic compounds in wastewater.

AOP (Advanced Oxidation Processes) technology is a combination of several processes such as ozone, hydrogen peroxide, UV light, and several other processes to produce OH radicals. The AOP technique can be applied in various types of reactors, one of which is a bubble column reactor. This...
type of reactor has advantages because of little maintenance and low operating costs due to lack of moving parts [3]. But this type of reactor also requires relatively large space to operate.

Several studies on the degradation process of phenolic compounds have been carried out. For 2,4-DCP compounds, Zhang conducted a study on degradation of 2,4-dichlorophenol in aqueous solution by dielectric barrier discharge with effects of plasma-working gases, degradation pathways and toxicity assessment [4] and Gan conducted a study mechanism for removing 2,4-dichlorophenol via adsorption and fenton-like oxidation using iron-based nanoparticles [2].

This study presents more simple, comprehensive, compact and small space requirements, using cold plasma DBD reactors. The characteristics of the DBD reactor were evaluated for the degradation of phenolic compounds in wastewater. In this case, the application of cold plasma DBD reactors is more specifically for the application of non-thermal plasma technology based on the application of high voltage electric fields to produce very reactive short-lived ions or radicals, which are in the plasma field from the surrounding air. Active species, such as •OH, •O, •H, and H2O2 are produced during disposal and react quickly with harmful pollutants in the water due to their high reactivity. Oxidation of ozone radical and oxygen reactive species processes are the main factors for reducing pollutants in water and they usually use techniques. For this reason, the DBD reactor technology can be categorized as AOP.

2. Materials and methods

2.1 Materials
The experiments used synthetic wastewater containing 50 mg/L of phenol or 50 mg/L 2,4-Dichlorophenol. Phenol (99%) was obtained from Merck and 2,4-Dichlorophenol (99%) was obtained from Sigma-Aldrich. All solutions were prepared by using demineralized water. In addition, all the chemicals used in this work were of extra purity or analytical grade.

2.2 Experimental installation and procedure
The experimental setting used in this study was a cold DBD plasma reactor with a continuous system. The reactor dimensions include volume, height, and diameter, respectively 0.15 L, 40 cm and 22 mm. Figure 1 shows a schematic diagram of the experimental settings for this study. This research begins with a reactor start-up test to ensure that plasma generating systems can be operated without significant complexity of problems. The reactor leak test was carried out initially by flowing distilled water and air feed from the compressor to the reactor. If there is a leak, replace the glue that is more uniform, or install rubber, and prevent other water leaks from flowing and inject air from the compressor through the reactor. After making sure there are no leaks (in the reactor), then the physical plasma test is carried out in the next step. The next step is to look at the phenomenon of plasma formation. This phenomenon is characterized by purple light in the plasma release area (along the reactor).
Tests in the form of hydrodynamics, quantification of hydroxyl radicals and dissolved ozone are carried out thereafter. Water and air are used in hydrodynamic tests to prevent possible further reactions. Hydroxyl radical analysis was carried out by permanganometric titration method. Some experimental parameters such as wastewater flow rate and airflow rate were evaluated in this study. The waste water flow rate is 52 mL/min, 65 mL/min, 80 mL/min and 100 mL/min, the air flow rate is 2 L/min and 2.5 L/min. The operating conditions were the initial concentrations of phenol and 2,4-dichlorophenol ± 50 mg/L, the initial pH of 12 wastewater, and the duration of the process was 90 minutes with sampling at 0, 15, 30, 45, 60 and 90 minutes. Phenol and 2,4-DCP are shown in figure 2.

The best operating conditions are obtained when the final concentration of phenol and 2,4-DCP reaches the lowest value at the end of the processing time, which means the highest percentage of degradation. Phenol and 2,4-DCP concentrations were determined using the 4-aminoantipyrine method. The aminoantipirin method begins by diluted the sample to be tested and then added the ammonia solution to the sample bottle. The next step was to added 4-aminoantipyirin and K₃Fe(CN)₆ to the sample bottle. The sample was then tested on a spectrophotometer.

3. Results and discussion

3.1. Hydroxyl radical quantification test
Quantification analysis of hydroxyl radicals was carried out by permanganometric titration method. Aquadest is used as a substitute for phenolic compounds to measure hydroxyl radicals. Because no compounds can be oxidized, it is assumed that the hydroxyl radicals formed will react with each other and form H₂O₂ with the following reaction [5]:

\[ \text{OH}^\cdot + \text{OH}^\cdot \rightarrow \text{H}_2\text{O}_2 \] (1)
The oxidation of $\text{H}_2\text{O}_2$ by $\text{KMnO}_4$ follows the following reduction-oxidation principal and formed in the reaction below:

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

Comparative analysis was carried out under the optimal operating conditions for each reactor, while the initial pH of wastewater used was 12. The initial pH solution adjusted to 12 with addition of NaOH 4 M. The alkaline condition (pH=12) chosen as the initial value because in alkaline conditions, ozone are easily decomposed to form hydroxyl radicals, thus improving the removal efficiency of phenol [6]. Based on figure 3 (a), the formation of hydroxyl radicals in the bubble column reactor was higher than that of the DBD reactor. This phenomenon can occur because ozone injection is carried out in a bubble column reactor. Ozone injection produces ozone species into bubble column reactors, where ozone decomposes into hydroxyl radicals and thus results in relatively higher hydroxyl radical production [7]. In addition, differences in the volume of water between the two reactors are thought to affect hydroxyl radical production. Higher volumes of water cause higher hydroxyl radical production. In the bubble column reactor the volume of water used is 20 L while in the DBD reactor the volume is only 1500 mL.

In this analysis, the effect of plasmatron input (Electronic Neon Sign Transformer) on hydroxyl radical production was also evaluated. Voltage variations are carried out with measured values of 220 V, 240 V, 260 V, 280 V, 300 V and 330 V. Figure 3 (b) shows that the production of hydroxyl radicals is higher with increasing electricity voltage. The phenomenon of higher hydroxyl radical production is shown by higher $\text{H}_2\text{O}_2$ formed in solution. With a higher electricity voltage, the higher current and charge that flows into the DBD system. This also causes a higher electric field between the two electrodes. A high enough electric field can accelerate electrons, molecules, or ions and their will enter into non-elastic collisions, and finally the number of molecules increase and will be ionized, radicalized [8]. As a result, in this condition ionization, excitation, the dissociation process can continue. Molecules from the air are also radicalized so chemical reactions must be increased and produce higher active species, including hydroxyl radicals. Figure 3 (b). also shows that $\text{H}_2\text{O}_2$ production increases with increasing processing time. It can be concluded that there is an accumulation of $\text{H}_2\text{O}_2$ production over time. Increasing the concentration of $\text{H}_2\text{O}_2$ compounds occurs because OH radicals form in large quantities and are very reactive, interacting with each other to form $\text{H}_2\text{O}_2$. 

![Figure 3. (a) Concentration of OH radicals in DBD reactor and bubble column reactor (b) Concentration of OH radicals in DBD reactor with variation of voltage](image-url)
3.2. Dissolved ozone test
Dissolved ozone concentration in water were determined by using a spectrophotometer. Sample must be reacted with potassium sulfate and boric acid solution before measured by spectrophotometer. In this analysis, input voltage was not significantly affect the dissolved ozone concentration.

![Figure 4. Concentration of dissolved ozone in water](image)

**Figure 4.** Concentration of dissolved ozone in water

Comparison of dissolved ozone in DBD reactor and bubble column reactor with air as source is showed in figure 4. The concentration of dissolved ozone in DBD reactor is higher than the bubble column reactor. This is caused by bubble column reactor, which used ex situ ozone injection system, has shorter life time. The ozone dissolved in water of bubble column reactor reacts with water molecules and more easily break down into oxygen, compared to DBD reactor, with the following reaction:

$$O (g) + HO + 2e \rightarrow O_2 (g) + 2OH^{-} \text{ (aq)}$$

(3)

3.3. The effect of air flow rate on degradation percentage
The effect of air flow rate to percentage of degradation is evaluated with variations of 2 L/min and 2.5 L/min. The operating conditions used were the initial concentration of phenol and 2,4-dichlorophenol ± 50 mg/L, wastewater flow rate of 85 mL/min, volume of wastewater 500 mL, the initial pH of wastewater 12 and the degradation process for 90 minutes.

| Air Flow Rate | Phenol Degradation | 2,4-Dichlorophenol Degradation |
|---------------|---------------------|-------------------------------|
| 2 L/min       | 54.5 %              | 89.55 %                       |
| 2.5 L/min     | 57.5 %              | 88.56 %                       |

Based on table 2, the highest degradation of phenol was obtained at 2.5 L/min. This result showed that the higher air flow rate will increase the percentage of compound degradation. The increasing percentage contributed due to higher more active species produced during discharge plasma process. However, the highest degradation of 2,4-dichlorophenol was obtained at 2 L/min. Yet, the concentration between different air flow rate has small difference. It can be conclude that the air flow rate was not significantly affect the percentage of 2,4-dichlorophenol degradation.

The decrease of phenol concentration with air flow rate of 2.5 L/min and 2,4-dichlorophenol with air flow rate of 2 L/min can be seen in figure 5 (a). The concentration of phenol and 2,4-dichlorophenol was decreased with time. This decreased concentrations indicate there were degradation process by active species and ozonation in DBD plasma reactor from time to time.
The effect of wastewater flow rate on degradation percentage

The effect of wastewater flow rate to percentage of degradation is evaluated with variations of 52 mL/min, 65 mL/min, 85 mL/min, and 100 mL/min. The operating conditions used were the initial concentration of phenol and 2,4-dichlorophenol ± 50 mg/L, air flow rate of 2.5 L/min, volume of wastewater 500 mL, the initial pH of wastewater 12 and the degradation process for 90 minutes.

**Table 3. The effect of wastewater flow rate on degradation percentage**

| Wastewater Flow Rate | Phenol Degradation | 2,4-Dichlorophenol Degradation |
|----------------------|--------------------|-------------------------------|
| 52 mL/min            | 54.5%              | 82.59%                        |
| 65 mL/min            | 57.5%              | 89.55%                        |
| 85 mL/min            | 41.5%              | 88.56%                        |

Based on Table 3 and Figure 5 (b), the highest degradation of phenol was obtained at 85 mL/min and 2,4-dichlorophenol was obtained at 65 mL/min. The increasing of wastewater flow rate will be decreased the percentage of degradation wastewater, its because the residence time of wastewater inside reactor was shorter. The contact time between wastewater and ozone will be increased due to the longer wastewater stayed in reactor. The degradation of wastewater will be increased along with increasing contact time. This decreased concentrations indicate there were degradation process by active species and ozonation in DBD plasma reactor from time to time.

3.5. **Comparison of phenol and 2,4-dichlorophenol under optimum condition**

The optimum condition was obtained with wastewater flow rate 85 mL/min, air flow rate 2.5 L/min, using ozonator. After 90 minutes process under optimum condition, degradation of phenol and 2,4-dichlorophenol were reached 57.5% and 89.5%, respectively. Based on Fig. 3 (a), the concentration of phenol and 2,4-dichlorophenol were decreased along the increasing degradation time. This decreased concentration indicated there were degradation process in dielectric barrier discharge reactor. During 90 minutes of degradation, phenol concentration was reduced from 50.00 mg/L to 21.25 mg/L, while 2,4-dichlorophenol concentration was reduced from 50.00 mg/L to 5.25 mg/L. During the first 15 minutes of degradation, the concentration of both compounds was reduced significantly. At early process time, the wastewater contain high concentration of organic (phenol or 2,4-dichlorophenol) molecules, which led to higher possibility of direct interaction between organic molecules and OH radicals.

However after 15 minutes process, the degradation has no notable difference. It indicated OH radicals as strongest oxidant yet has non-selective characteristic, attack other substance (beside phenol
or 2,4-dichlorophenol) in water, since the organic substance has decreased. The degradation of 2,4-dichlorophenol is faster than phenol as simple phenolic compounds. This attributes due to chloro atom which has high electronegativity and strong electrons also lower energy to break the bonds for dechloronation of 2,4-dichlorophenol. Additionally, 2,4-dichlorophenol has a larger molecular structure than phenol. Ozone as one of active species reacts quicker with a larger molecular structures that contains double bonds, activated aromatic groups or amines. Hence degradation of phenol needs longer time than degradation of 2,4-dichlorophenol.

3.6. Comparison of phenol and 2,4-dichlorophenol in DBD plasma reactor with bubble column reactor

The degradation process of phenol and 2,4-dichlorophenol in the DBD plasma reactor has also been carried out in the bubble column reactor. The operating conditions of the DHF plasma reactor are air flow rate 2.5 L/min, wastewater treatment 85 mL/min, pH 12, and 60 minute reaction time. The bubble column reactor operating conditions are air flow rate 12 L/min, wastewater treatment 405 mL/min, pH 12, 60 minute reaction time, and multi ozon injection system.

| Time (min) | DBD Plasma Reactor | Bubble Column Reactor | DBD Plasma Reactor | Bubble Column Reactor |
|------------|---------------------|-----------------------|---------------------|-----------------------|
| 0          | 0.00%               | 0.00%                 | 0.00%               | 0.00%                 |
| 15         | 47.50%              | 81.58%                | 83.08%              | 84.18%                |
| 30         | 52.50%              | 95.30%                | 83.58%              | 97.36%                |
| 45         | 53.50%              | 99.25%                | 84.08%              | 98.44%                |
| 60         | 54.50%              | 99.49%                | 88.56%              | 99.83%                |

Based on table 4 after 60 minutes at optimal conditions, the phenol composition in the new DBD plasma reactor has largest percentage degraded to 54.4% while in the bubble column the phenol reactor has been degraded as much as 99.49%. The difference in the percentage of degradation is the content of ozone in the bubble column reactor is much higher than in the DBD plasma reactor. The ozone comes from a multi-ozone injection system. In addition to this, the bubble column reactor also has a multi ozone injection system so that the presence of ozone is greater than the DBD plasma reactor.

The degradation process of 2,4-dichlorophenol after 60 minutes in the DBD plasma reactor has been degraded to 88.56% while in the 2,4-dichlorophenol reactor column it has been degraded as much as 99.83%. The difference in the degradation percentage of 2,4-dichlorophenol compound in the DBD plasma reactor and bubble column reactor is not too large. It can be concluded that 2,4-dichlorophenol is degraded in the DBD plasma reactor and in the bubble column reactor. The difference in the degradation percentage of phenol and 2,4-dichlorophenol is very large because 2,4-dichlorophenol is more easily degraded than phenol because 2,4-dichlorophenol has a molecular structure greater than phenol and ozone reacts faster with a larger molecular structure. 2,4-dichlorophenol has high electronegativity, so electrophilic activating hydroxyl radicals attack the Chloro atom. The chlorine atom then becomes hydrochloric acid.

4. Conclusions

In view of the results obtained, the conclusion is as follows:

- Degradation process of wastewater in DBD plasma reactor for 90 minutes at pH = 12 for phenol was degrade 54.5% and 2,4-dichlorophenol was degrade 88.56%.
- 2,4-Dichlorophenol were easier to degrade than phenol because of 2,4-dichlorophenol has a larger molecular structure than phenol and ozone reacts faster with a larger molecular structure.
- Degradation processes were affected by air flow rate, ozone injection system, input ozonator voltage, wastewater volume, and wastewater flow rate.
- The optimum condition of the treatment process was obtained when air flow rate for phenol and 2,4-dichlorophenol was 2.5 L/min, using ozone multi injection system, and flow rate of wastewater 85 mL/min.

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