Phenol degradation by fenton reaction in air injection using plasma electrolysis method

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Abstract. Phenolic compounds are pollutants which have high toxicity and could be harmful to the environment even at low concentrations. The degradation of phenolic has been conducted by various methods including photocatalytic and ozonation. However, these methods require high costs and large energy. Therefore, plasma electrolysis by the Fenton reaction may be an alternative method for phenol degradation. The purpose of this study is to determine the optimum conditions for phenol degradation by adding Fe²⁺ ions. The result shows that the most effective phenol degradation was obtained by using an optimum power of 700 watts with an air injection flow rate of 0.2 L/min and addition Fe²⁺ 20 ppm ions for 30 min experiments. Based on these conditions, the concentration of phenol in waste was reduced to 0.425 mg/L and the highest percentage of phenol degradation (99.58%) was observed. The final phenol concentrations obtained in this study met the quality standards for clean water at a concentration of 1 mg/L as well as the quality standards for drinking water treatment at a concentration of 0.5 mg/L.

1. Introduction
Phenol, also called carbolic acid or benzonal, is a white crystalline compound with a distinctive odor. This compound is usually used as an antiseptic or better known as trichlorophenol (TCP). Previous studies have shown that the effects of phenol exposure cause a decrease in fetal weight, growth retardation, and abnormal development in offspring [13,14]. Thus, it is very important to treat wastewater containing phenolic compounds prior to the final disposal. The final phenol concentrations of wastewater should meet the quality standards for clean water based on the Regulation of the Minister of the Environment (0,1 mg/L) and quality standards for the drinking water treatment process based on LH PERMEN No. 5 of 2014 (0,5 mg/L) [14]. In this study, phenol degradation was investigated by adding Fe²⁺ to produce the Fenton reaction. The Fenton reaction involves a transformation reaction between Fe²⁺ and Fe³⁺. In addition, the presence of Fe³⁺ and Fe²⁺ ions can encourage H₂O₂ that is formed due to the incorporation of fellow •OH to decompose back into •OH [9]. Some methods have been carried out for phenol degradation in organic and inorganic waste, such as oxidation [19], photocatalyst [17], ozonation [16], and adsorption [8]. However, these methods are often considered inefficient in breaking down liquid waste because the equipment is quite expensive, results in low waste degradation, and requires quite a long time [6]. Further, plasma electrolysis
technology can be an alternative method because of its high ability for phenol degradation [7]. Plasma electrolysis or Contact Glow Discharge Electrolysis (CGDE) is a sophisticated technology from conventional electrolysis in which the electrochemical process is applied a high enough voltage to both the electrodes and the electrolyte surface that surrounds it to produce plasma in solution [5].

2. Materials and methods

2.1. Material
Materials used for phenol degradation included artificial waste with a phenol concentration of 100 mg/L. The electrolyte used was 0.02 M Na₂SO₄, for the hydroxyl radical production test, 10 M H₂SO₄ and 0.01N KMnO₄ was used and for the analysis of the percentage of phenol degradation, the phenol reagent was used.

2.2. Instrumentation
Phenol degradation in artificial waste was observed using the Contact Glow Discharge Electrolysis (CGDE) plasma electrolytic reactor. The reactor is made of a 2000 mL transparent pyrex glass beaker and is covered with 10 mL acrylic glass, equipped with a cooling jacket and operating temperature range at 50-60°C. The CGDE reactor is a batch reactor consisting of two electrodes; cathode and anode. The cathode used in this study was stainless steel with a length of 17.5 cm and a diameter of 6 mm, while the anode used was tungsten (tungsten) with a length of 15 cm and a diameter of 0.5 mm and an anode depth of 15 mm which can be seen in figure 1.

Note: 1. Anode, 2. Cathode, 3. Glow Discharge, 4. Thermometer, 5. Cooling Water, 6. Gas Products and Sampling Ports, 7. Gas Products for Cathodes, 8. Stirers, 9. Baffles, 10. Quartz Glass & Air Injection, 11. Multimeters, 12. Bridge Diodes, 13. Transformers, 14. Slide Regulators, 15. MCB.

Figure 1. CGDE reactor.
2.3. Procedure
Phenol degradation testing was carried out in 3 stages. The first stage was testing the effect of air injection flow rates (0, 0.2, 0.3, 0.4, 0.6, 0.8 L/min), on various powers (500, 600, 700 watts) as seen from the percentage of degradation and energy. The second stage was looking at influence power seen from the percentage of degradation and energy. The third step was testing the effect of adding Fe\(^{2+}\) ions with variations in the air injection rate. Measurement of the concentration of the degraded phenol waste was done by measuring the absorbance before and after the plasma electrolysis process. To test the measurement of phenol concentrations, a UV-Vis spectrophotometer at a wavelength of 500 nm according to SNI 06-6989.21-2004 was used. The data read on the UV-Vis spectrophotometer was the absorbance. Therefore, a standard or calibration curve from the calibration solution was needed.

3. Results and discussion

3.1. The effect of air injection flowrate
The effect of air injection flow rate (0.0, 0.2, 0.3, and 0.4 L/min) on the phenol degradation was carried out to test CGDE performances. This test used 100 ppm of phenol waste, 0.02 M Na\(_2\)SO\(_4\) as an electrolyte solution, and a temperature range of 50-60°C was maintained by using cooling water circulation. During the process, 1.5 L of the solution was stirred at 2 mot motions speed for 90 min of the experiment. The sample was taken out every 0, 15, 30, 45, 60, 75, and 90 min. The amount of energy used in degrading phenol is a factor that determines the effectiveness of the process. So that the power used in this study was equated for each variation of the air injection rate so that the results of the percentage of degradation could be compared in a balanced manner. The effect of air injection flow rate on phenol degradation in various power (500, 600, and 700 watt) can be seen in figure 2.

![Figure 2. Percentage of phenol degradation with the variation of air injection flow rate at each power (Phenol 100 ppm; Na\(_2\)SO\(_4\) 0.02 M; temperature 55°C; anode depth 1.5 cm; process time 15 minutes).](image)

As can be seen in figure 2, the percentages of phenol degradation using 0, 0.2, 0.3, and 0.4 L/min of air injection at a power of 500 watts were 43.50; 61.50; 55.75; and 48.27%, respectively. The result shows that the percentage of phenol degradation increased with the addition of air injection, especially in the flow rate variation of 0.2 L/min. This trend also occurred while the power of 600 and 700 watts applied (figure 2). This was due to the higher air injection flow rate that caused instability in the
plasma or passed its optimal point, thus decreased the phenol degradation rate. However, the addition of air injection at 0.2 L/min could increase the degradation rate in comparison with and without air injection. This shows that air injection was very important to degrade phenol compounds because the addition of bubbles increased the average length of the free electron path and electron velocity so that excitation and ionization of water molecules occurred in bubbles and solution to produce more radicals [2].

The existence of plasma is strongly influenced by the stability of the air envelope produced at the electrodes. The more stable the gas casing, the better the plasma (plasma becomes brighter and more effective). To increase the stability of the gas envelope, air was injected into the plasma area thereby reducing the evaporation process and reducing energy consumption. This was due to the formation of a gas casing with the Joule Heating process which required high energy consumption. This air bubble and gas envelope could also reduce the breakdown voltage needed for the initiation process in the formation of plasma. This was caused by the dielectric strength of the gas which was smaller when compared to the liquid.[1]. The addition of air injection could make plasma fade but the rate of waste degradation continued to increase. This mechanism is in good agreement with the previous work, as depicted in figure 3 [10].

Fig. 3. Mechanism of phenol waste by air injection [10].

The injected air would form bubbles and gas envelope layers that could initiate the process of ionization and excitation of electrons more easily so that in addition to reducing energy consumption, it could also affect the formation of active species other than •OH [15]. Based on these results, it can be seen that the most effective degradation process was the use of an air injection of 0.2 L/min. This shows that the small air injection rate was able to stabilize the plasma and supply oxygen and nitrogen gas in the air added to the plasma to produce reactive species in processes other than •OH. The
following equation represents the possible mechanism reaction that might occur when air injection was applied [23].

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

\[
O^- + H_2O \rightarrow \cdot OH + \cdot OH \quad (2)
\]

\[
e + H_2O \rightarrow H^- + \cdot OH + e \quad (3)
\]

\[
\cdot OH + O_2 \rightarrow HO_2^- + O^- \quad (4)
\]

\[
2N_2 + 2H_2O + 5O_2 \rightarrow 4HNO_3^- \quad (5)
\]

Based on equation 1 to equation 5, it can be seen that the use of air injection produced other reactive species other than •OH, namely HO_2^−, •O, and HNO_3^− which could help the phenol degradation process. Phenol degradation test on the variation of power over time was carried out to determine the performance of plasma electrolysis. The variations of power used were 500, 600, and 700 watts with a concentration of 0.02 M Na_2SO_4 electrolyte solution and with a concentration of phenol waste of 100 ppm. CGDE performance testing with the effect of power on the percentage of degradation was carried out at a variation of 0.2 L/min. The air injection rate of 0.2 L/min was obtained based on variations in the air injection rate which had the highest degradation percentage compared to other air injection rates.

3.2. Power variation of phenol degradation

Figure 4 shows that the use of 600 watts power could increase 8.65% of phenol degradation in the first 15 min. However, the phenol degradation increased significantly (16.12%) in the first 15 min while applying 700 watts power. Previous research reported that the plasma produced at 500 watts and 600 watts of power was smaller than the plasma produced at 700 watts of power.

![Figure 4. Percentage of power variation degradation (Phenol 100 ppm; Na_2SO_4 0.02 M; temperature 55°C; anode depth 1.5 cm; air injection flow rate 0.2 L/min, Fe^{2+} 20 ppm ions).](image)

Based on figure 4, with a plasma produced at 700 watts or more, more OH will be generated. This was because the increase in power was affected by the increase in voltage. The increase in voltage applied to the system could increase the production of H_2O_2 in solution. At a large potential difference,
the energy given to the ions to move carried electrons toward the larger anode, and electrons capable of jumping through the envelope of gas became larger. The collision of electrons with the gas envelope was what caused the formation of •OH and H$_2$O$^+$ gas ions. This H$_2$O$^+$ gas ion was used to decompose water molecules (H$_2$O) into •OH which played a role in degrading waste. This mechanism can be seen in equations 6 and 7 [4].

\[
\begin{align*}
\text{H}_2\text{O}_{\text{gas}} + e^- & \rightarrow \text{H}_2\text{O}^+_{\text{gas}} \tag{6} \\
\text{H}_2\text{O}^+_{\text{gas}} + \text{H}_2\text{O} & \rightarrow \cdot\text{OH} + \text{H}_3\text{O}^+ \tag{7}
\end{align*}
\]

Thus the greater the voltage the more intensive plasma produced and the more formation of H$_2$O$_2$. In addition, figure 4 shows that in a longer electrolysis process, the degradation rate of phenols tended to be sloping in the last 60 to 90 min. It indicated that the interaction between •OH and phenol waste occurred quickly at the beginning of the experiment, but the concentration of phenol waste began to run out in the last 60 and 90 min so that •OH tended to degrade intermediate compounds (organic) produced from the previous process.

3.3. The effect of Fe$^{2+}$ ions addition phenol degradation

The absence and presence of Fe$^{2+}$ ions in the wastewater were also investigated and carried out with a phenol concentration of 100 ppm, with optimum power of 700 watts, a maintained operating temperature of around 50-60°C, anode depth of 1.5 cm, Na$_2$SO$_4$ 0.02 M, and the volume of the waste solution of 1.5 L. In this study, variations in air injection flow rate (0 L/min; 0.2 L/min; 0.3 L/min; and 0.4 L/min) was used to obtain the optimum flow rate with the addition of Fe$^{2+}$ ions. The study was carried out for 90 min of the experiment and the samples were taken out every 15 min.

![Figure 5](image)

**Figure 5.** Comparison of phenol degradation without addition of Fe$^{2+}$ Ion (●) and with addition of Fe$^{2+}$ Ion (▲) 20 mg/L (air injection flow rate 0.2 L/min and power 700 watts).

The Fenton reaction involves a transformation reaction between Fe$^{2+}$ ions and Fe$^{3+}$ ions. It can be seen in equations 8 to equation 12, the presence of Fe$^{2+}$ and Fe$^{3+}$ ions could encourage H$_2$O$_2$ formed by combining fellow •OH to decompose into •OH and could catalyze H$_2$O$_2$ to produce more •OH [9].

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH} & k=76 \text{ M}^{-1}\text{s}^{-1} \tag{8} \\
\cdot\text{OH} + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} & k=4.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \tag{9} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2\cdot + \text{H}^+ & k=0.01 \text{ M}^{-1}\text{s}^{-1} \tag{10} \\
\text{HO}_2\cdot + \text{H}_2\text{O} & \rightarrow \cdot\text{OH} + \text{H}_2\text{O} + \text{O}_2 & k=3 \text{ M}^{-1}\text{s}^{-1} \tag{11}
\end{align*}
\]
Fe$^{3+}$ + •H $\rightarrow$ Fe$^{2+}$ + H$^+$  \hspace{1cm} k=2 \times 10^6 \text{M}^{-1}\text{s}^{-1} \hspace{1cm} (12)

This study used the addition of Fe$^{3+}$ ions because the rate constant of Fe$^{2+}$ ions with H$_2$O$_2$ (76 M$^{-1}$s$^{-1}$) was almost four times greater than Fe$^{3+}$ ions with H$_2$O$_2$ (0.01 M$^{-1}$s$^{-1}$) and the oxidative ability of HO$_2$• (3 M$^{-1}$s$^{-1}$) was lower than •OH (4.3 x 108 M$^{-1}$s$^{-1}$). The addition of Fe$^{2+}$ ions to the system could have a catalytic effect on the degradation of organic compounds and increased the efficiency of its degradation [20,21]. It can be seen that more Fe$^{2+}$ ions were formed in the CGDE process and the newly formed Fe$^{2+}$ ions reacted with H$_2$O$_2$ in solution to produce more •OH. Water molecules in the liquid phase were decomposed by positive ions entering from the plasma into •OH and •H atoms by the CGDE method. OH and H could react with phenols, which led to a decrease in the concentration of phenol compounds (degradation). The mechanism can be seen in equation 13 and equation 14.

C$_6$H$_5$OH + •OH $\rightarrow$ C$_6$H$_5$(OH)$_2$ \hspace{1cm} k=1,2 \times 10^{10} \text{M}^{-1}\text{s}^{-1} \hspace{1cm} (13)

C$_6$H$_5$OH + •H $\rightarrow$ C$_6$H$_5$OH \hspace{1cm} k=4,2 \times 10^9 \text{M}^{-1}\text{s}^{-1} \hspace{1cm} (14)

From equations 13 and 14, it can be seen that •OH reacted more quickly than •H with phenol, so that •OH played an important role in degrading phenol compounds. However, the effectiveness of •OH in degrading organic waste in the CGDE reactor needed to be increased because the production of •OH was quite high but the interaction between •OH and organic waste was still not effective enough so that at the end of the reaction, •OH in the form of H$_2$O$_2$ in the reactor was still much left. This caused the CGDE process to become ineffective since it required a relatively long time to obtain better degradation results, especially for complex organic waste. Surely this condition would cause high energy consumption of the process. To minimize energy use, the effectiveness of the waste degradation process by the CGDE method can be increased by the addition of Fe$^{2+}$ ions through the Fenton reaction [22].

The rate of degradation of phenols by the addition of Fe$^{2+}$ ions was very high compared to without the addition of Fe$^{2+}$ ions in the first 30 and 15 min where a significant slope occurred. It indicated that the role of Fe$^{2+}$ for •OH recombination to increase degradation rate appeared at the beginning of the CGDE process. Phenol degradation was a rapid reaction which only required 30 min by the addition of 20 mg/L of Fe$^{2+}$ ions. Figure 5 shows that phenol degradation of 92% occurred in the first 15 minutes of the process. The remainder degraded slowly, taking about half an hour to achieve a greater oxidation efficiency of 99%. There are several reasons for this phenol oxidation rate behavior, but generally, this is thought to be related to the dynamics of hydroxyl radical generation. Thus, it was proposed that initially, the Fe$^{2+}$ ion reacted rapidly with H$_2$O$_2$, producing a large amount of hydroxyl radicals which caused the aromatic ring to break quickly [3]. But after that, as the reaction continued, the Fe$^{2+}$ ion was continuously regenerated and reacted again, so that the rate of regeneration kept the production of radicals in the solution proportional to the actual production of H$_2$O$_2$ [24]. In the amount of products tested, the reduction in the phenol oxidation rate might be due to the decreased iron activity, because Fe$^{3+}$ ions were formed and reacted with other intermediate compounds [12]. This is consistent with [20] research results which state that •OH produced from the GDP process attacks phenol to form para- and ortho dihydroxycyclohexadienyl radicals, and then dihydroxycyclohexadienyl radicals convert Fe$^{3+}$ ions to Fe$^{2+}$ ions (figure 6).

The newly formed Fe$^{2+}$ ion reacted with H$_2$O$_2$ to produce more •OH to increase phenol degradation. In addition, the presence of Fe$^{3+}$ ions accelerated the degradation process to react directly with phenol intermediate products. Para and ortho dihydroxycyclohexadienyl radicals result from the release of the dihydroxycyclohexadienyl radical hydrogen atom, reacted again with Fe$^{3+}$ ions to form benzoquinone. Benzoquinone attacks OH and Fe$^{3+}$ ions to form carboxylic acids to form CO$_2$ and H$_2$O [9,20,21].
4. Conclusion
Phenol degradation in artificial waste contained 100 ppm of phenol and the use of air injection with a flow rate of 0.2 L/min could increase the percentage of phenol degradation by 17.05%. The optimum condition for phenol degradation was obtained by using 700 watts of power with an air injection flow rate of 0.2 L/min. The addition of 20 ppm of Fe$^{2+}$ ion increased the phenol degradation up to 99.58% in the first 30 min by using 700 watts power and 0.2 L/min of air injection. Further, the highest phenol degradation (99.89%) was obtained for a total of 90 min of the experiment.

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