

PHENOL DEGRADATION IN WASTEWATER WITH A CONTACT GLOW DISCHARGE ELECTROLYSIS REACTOR USING A SODIUM SULFATE

Nelson Saksono^{1*}, Ratih Tien Seratri¹, Rahma Muthia¹, Setijo Bismo¹

¹ *Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus Baru UI Depok, Depok 16424, Indonesia*

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ABSTRACT

This present study is aimed at removing phenol compounds in wastewater by using a Contact Glow Discharge Electrolysis (CGDE) reactor. To start with, the effect of voltage to direct current connections in a CGDE reactor was investigated in order to estimate several possibilities for optimum voltage for phenol degradation. Several parameters were studied for phenol treatment including the effects of voltage, electrolyte concentration, anode depth, and the presence of Fe²⁺ ions. Production of hydrogen peroxide, the percentage of phenol degradation, and energy consumption were used as main research indicators. The optimum condition was found at 700 V, in 0.03 M Na₂SO₄, and an anode depth of 5mm. The phenol degradation was valued at 40.83% after the first 15 minutes in the process, with an energy consumption of 278 kJ/mmol of phenol. Under the same conditions, with an addition of 20 mg/L of Fe²⁺ ions, the phenol degradation shot up to 92.57% and energy consumption significantly decreased to 127 kJ/mmol. The largest phenol degradation was obtained at 99.6% after 90 minutes during the experiment. The results pointed out a promising path for phenol treatment in wastewater by utilizing a CGDE reactor with recommended operating conditions which were obtained during this study.

Keywords: CGDE; Hydroxyl radical; Phenol degradation; Plasma

1. INTRODUCTION

Generally, the rapid growth of the industrial sector is accompanied with an increase in wastewater production. Industrial wastes frequently contain several organic compounds, which are harmful to humans or the environment and these subsequently cause problems, such as water pollution and skin irritations. One of those organic compounds, which currently provoke serious attention, is phenol (C₆H₅OH). Phenol is generated from the pulp industry, the polymer industry, oil and gas, organic pesticide, pharmaceutical, and other chemical industries. In certain concentration levels, phenol causes liver and kidney damage, blood pressure drop, and even fatality to humans (Slamet et al., 2005).

In 2006, BPLH Jawa Barat found that phenol was being produced by the pharmaceutical industry at a concentration of 100–150 mg/L. In fact, according to the regulations of Indonesian Environment Minister in 1995 and 2010, the threshold value as a safe indicator for phenol use in various industries is 1 mg/L. Concern about its risks and its actual impact on the environment has prompted promulgation of various methods for significant phenol degradation. The Contact Glow Discharge Electrolysis (CGDE) system has been proven to be effective to

* Corresponding author's email: nelson@che.ui.ac.id, Tel. +62-21-7863515, Fax. +62-21-7863516
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remove some of the organic compounds through hydroxyl radical attack. Some of those organic compounds are *acid orange 7* (Jin et al., 2011), ammonia (Saksono et al., 2013), *alizarin red S* (Gao et al., 2008a), etc. CGDE is a *non-Faraday* electrochemical process with a high potential difference between two electrodes and the covered electrolyte surface that leads to plasma formation (Ceccato et al., 2009). Plasma is an ionized gas which is formed by an electromagnetic attack and produces some reactive compounds, such as the hydroxyl radical (OH^\bullet) at a lower energy consumption (Saksono et al., 2014). These hydroxyl radicals would then attack and decompose phenol molecules.

To understand hydroxyl radical performance on phenol degradation, the number of hydroxyl radicals which are obtained via CGDE need to be determined. However, hydroxyl radicals have a very short lifetime in the solution, which is measured at 10^{-6} s (Gai, 2006). Consequently, hydroxyl radical concentration is difficult to measure. The presence of hydroxyl radicals could be observed through hydrogen peroxide in the solution, since hydrogen peroxide is formed by the reaction between two molecules of hydroxyl radicals (Jin et al., 2010). Hydroxyl radical productivity on phenol degradation is affected by certain variables, such as voltage, electrolyte concentration, and the depth of the anode. The addition of Fe^{2+} ions into the solution could accelerate the degradation process because of the Fe^{2+} ion's ability to decompose hydrogen peroxide into hydroxyl radicals. Besides, the addition of Fe^{3+} ions plays a specific role in enhancing phenol degradation, since the Fe^{3+} ions are able to directly react with the phenol molecules. This study aims at having an understanding of the effect of voltage, electrolyte concentrations, the depth of anode, and the presence of Fe^{2+} ions to the phenol degradation mechanism.

2. EXPERIMENTAL SETTING

In this study, phenol degradation in waste water was observed using a CGDE reactor which has been used for ammonia removal in prior experiments (Saksono et al., 2013). The CGDE reactor system is shown in **Error! Reference source not found.** The CGDE reactor was composed of 600 mL glass beaker with a wastewater volume of 400 mL. This reactor worked in a batch system that was equipped with a cooling jacket with cooling water flowing continuously through the system. The temperature in the reactor was controlled at 50–60°C since hydroxyl radicals have a maximum selectivity at that temperature level (Ranjit & Joshi, 2010). A magnetic stirrer was placed inside the reactor in order to keep the temperature distribution homogeneous.

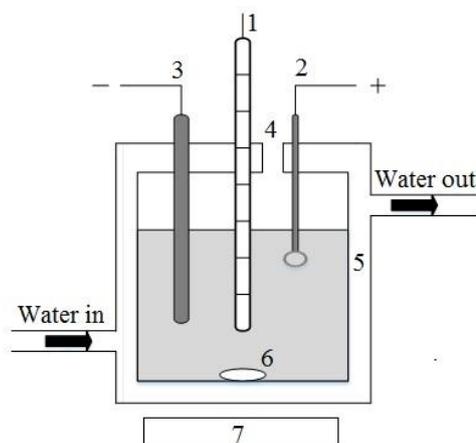


Figure 1 Schematic diagram of a Contact Glow Discharge Electrolysis reactor: 1. Thermometer; 2. Anode (Tungsten, *Wolfram*); 3. Cathode (Stainless steel); 4. Sample Port; 5. Cooling Jacket; 6. Magnetic bead; 7. Magnetic Stirrer

Sodium sulfate (Na_2SO_4) from Merck was used as an electrolyte. An 8 mm cathode made of stainless steel and 3.5 mm anode made of Tungsten (*Wolfram*) were installed in the system. The experimental activities were generally divided into two clusters: the I-V characteristics and the CGDE performance on phenol degradation.

2.1. Current-Voltage (I-V) Characteristics

Current-voltage (I-V) characteristics were obtained in order to estimate the voltage range for plasma formation. Several electrolyte concentrations were loaded into the reactor in different experimental runs. Subsequently, this voltage range was used in further studies to understand the effect of voltage on phenol degradation.

2.2. CGDE Performance on Phenol Degradation

In this cluster, the effect of voltage, electrolyte concentrations, the depth of anode, and the presence of Fe^{2+} ions to the phenol degradation mechanism were investigated. Data collection was done at 15-minute intervals throughout the 90-minute experiment. As the result indicators, several variables were identified, i.e. hydrogen peroxide concentration, phenol degradation percentage, and current averages. The current average was used to gain the value of energy consumption during the phenol degradation process. Energy consumption was calculated by using Equation 1.

$$E = \frac{\text{voltage} \times \text{current} \times \text{time}}{\text{phenol removed (mmol)}} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Current-Voltage (I-V) Characteristics

Current-Voltage I-V characteristics obtained with sodium sulfate at 0.01, 0.02, and 0.03 M concentrations, respectively are shown in Figure 1. In comparison with different concentrations of sodium sulfate, the shape of those I-V characteristics are generally identical curves. The differences between those three curves lie in the breakdown voltage and the current values. Breakdown voltage is the required voltage to generate plasma in the solution, which can be detected by a decline in the current value. At a higher concentration, breakdown voltage takes place at a smaller voltage. The greater the electrolyte concentration, the greater is the conductivity. Solutions with high conductivity result in a higher number of Joules of heat for solution vaporization so that a gas sheath is formed faster around the anode, which enhances plasma formation (Gao et al., 2008b). The breakdown voltages at various sodium sulfate concentrations are shown in Figure 1. In consideration of these breakdown voltages, a study of CGDE performance on phenol degradation was conducted in order to assess the effect of voltage in the range of 500–700 V.

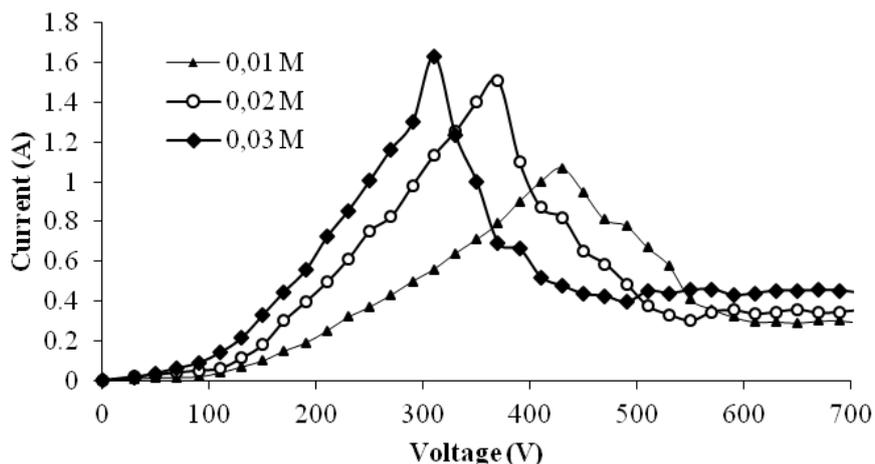


Figure 1 I-V characteristics

3.2. CGDE Performance on Phenol Degradation

3.2.1. Voltage effect

As mentioned previously, the voltage ranges from 500–700 V. The voltage effect was observed in an electrolyte solution of 0.02 M of sodium sulfate with an anode depth of 5mm.

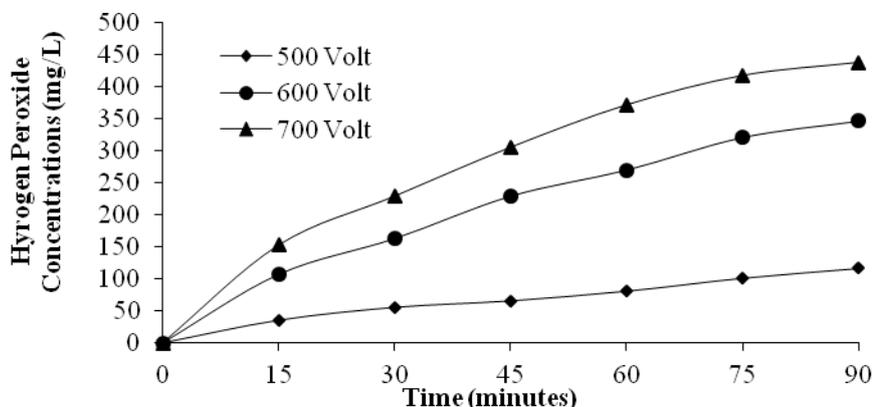


Figure 2 Hydrogen peroxide production in the study of voltage effect 0.02 M of Na₂SO₄ and an anode depth of 5mm

Figure 2 shows hydrogen peroxide concentrations which were found in different experiments. By increasing the duration of the experiment, larger concentrations of hydrogen peroxide at various voltages were gained. As the higher voltage was applied, more hydrogen peroxide was produced. By using a higher voltage, ions gain higher energy levels to move to the anode side. As its kinetic energy is higher, the chance of excitation and decomposition of gas molecules near the anode would be greater. As a consequence, a large amount of hydroxyl radical was created. The mechanism for the hydroxyl radical formation is shown in Equations 2 and 3:



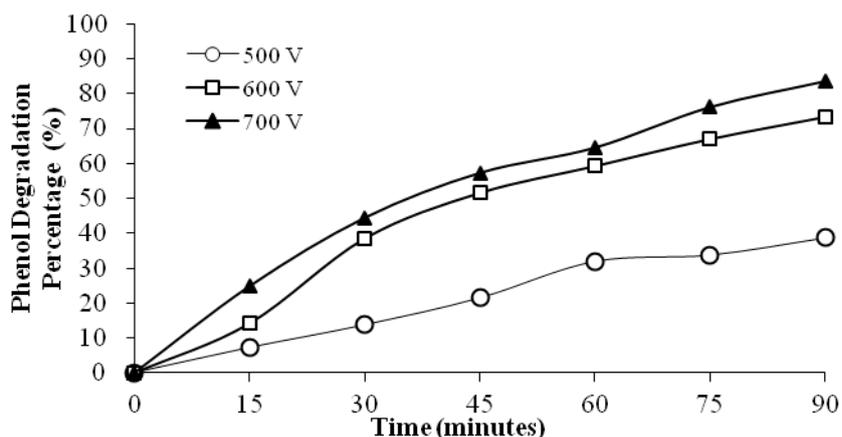


Figure 3 Phenol degradation percentage in the study of voltage effect, 0.02 M of Na_2SO_4 and an anode depth of 5mm

Figure 3 points out percentage of phenol degradation at various voltages. In general, phenol degradations for all values of voltage have the same trend with hydrogen peroxide production which indicates that phenol degradation occurs through the attack of hydroxyl radical. At 500 V, phenol degradation is relatively smaller compared to two other higher voltages. Allegedly, normal electrolysis still occurred at this applied voltage so that hydroxyl radical production was lower.

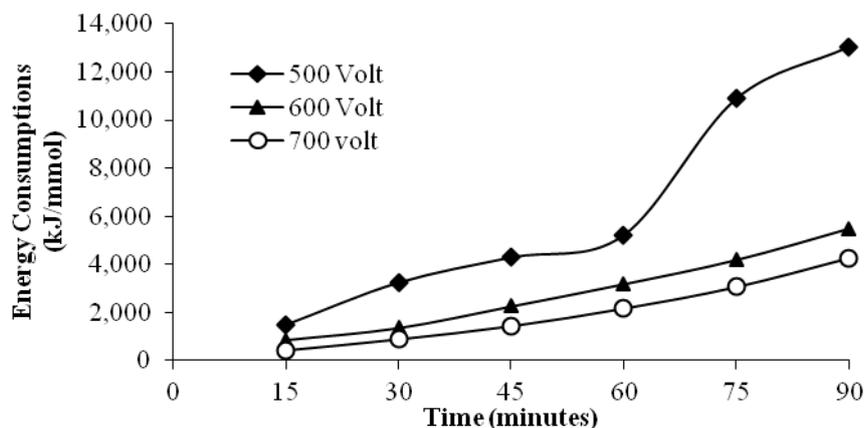


Figure 4 Energy consumption in the study of effect of voltage, at 0.02 M Na_2SO_4 and an anode depth of 5mm

Figure 4 shows the energy consumption required for phenol degradation at various voltages. Since more hydroxyl radicals were found at the higher voltages, collisions between those radicals and phenol compounds became more intensive. Therefore, less energy was needed at 700 V. Among those three different voltages (500V, 600V, 700V), the largest energy consumption took place at 500 V. Furthermore, at 500 V, energy consumption shot up after 60 minutes. In that state, phenol concentration increased in the solution, whereas only a small amount of hydroxyl radicals was produced. Hence, the energy consumption was higher.

3.2.2. Effect of electrolyte concentration

In this section, the effect of electrolyte concentration will be discussed. From the previous experiments of the voltage effect, 700 V was found to be better in terms of the rate of phenol degradation and energy consumption. Therefore, 700 V was selected as the operating condition

in this study. Various electrolyte concentrations were loaded into the reactor, i.e. 0.01 M, 0.02 M, and 0.03 M, respectively of sodium sulfate, with an anode depth of 5mm

Figure 5 shows hydrogen peroxide production based on the effect of electrolyte concentrations. As a more concentrated electrolyte solution was added into the reaction, the hydrogen peroxide produced was larger. At a higher concentration, a large amount of ions, acting as the electron carrier, was found in the solution. As more electrons flew in the solution, the possibility of electron excitation was greater. Hence, plasma was formed and more hydroxyl radicals were produced (Gao et al., 2004). This leads to a higher percentage of phenol degradation as shown in Figure 6. When the higher sodium sulfate concentration was loaded into the reactor, the phenol degradation percentage was higher.

3.2.3. Effect of anode depth

In this section, the effect of anode depth on CGDE performance for phenol degradation will be discussed. Figure 7 shows hydrogen peroxide production with different anode depths, relative to the duration of the experiments. As the deeper anode was dipped into the solution, a larger amount of hydrogen peroxide was produced. With such a large contact area within the electrolyte solution, electrons flew freely to the anode. Therefore, electrons excitation and hydrogen peroxide were more intense. With an anode depth of 10 mm, hydrogen peroxide was produced rapidly; yet, there was no indication of any significant incremental increase over a prolonged time period. Most possibly, when hydrogen peroxide in the solution was accumulated in the reactor, the peroxide was converted into oxygen (O₂) via reactions as shown in Equations 4, 5 and 6 (Jin et al., 2011).

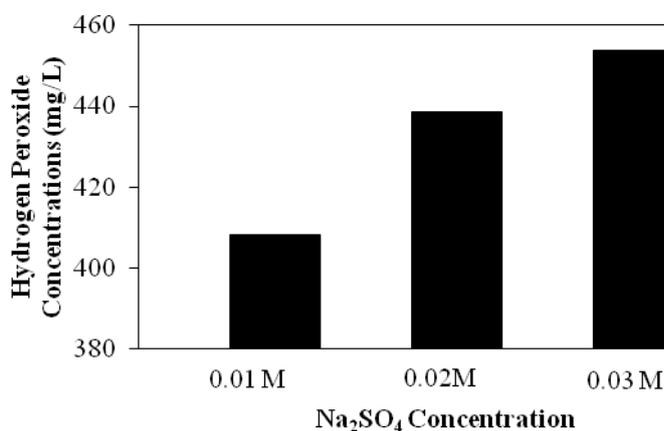
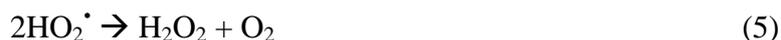


Figure 5 Hydrogen peroxide production in the study of the effect of electrolyte concentration, 700 V and an anode depth of 5mm

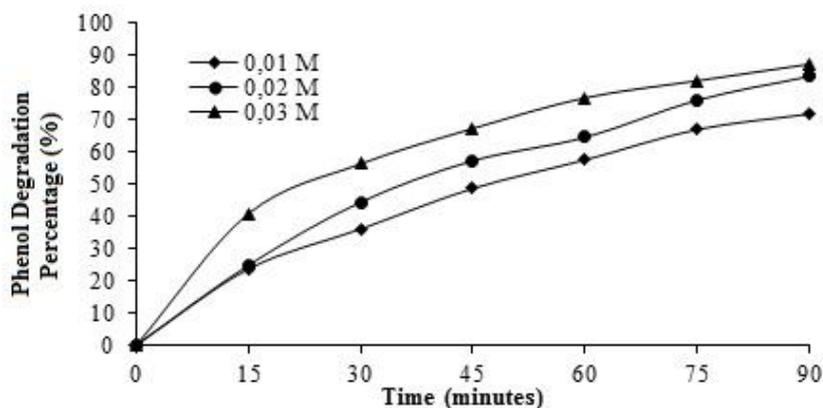


Figure 6 Phenol degradation percentage in the study of the effect of electrolyte concentration, 700 V and an anode depth of 5 mm

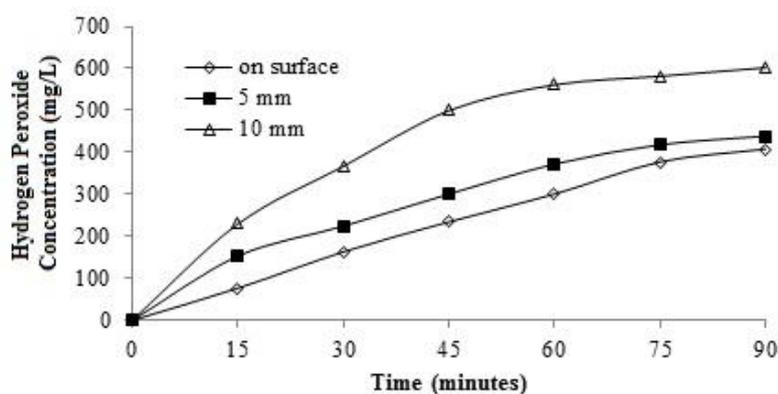


Figure 7 Hydrogen peroxide production in the study of the effect of anode depth, 0.03 M of Na_2SO_4 and 700 V

Figure 8 shows the phenol degradation percentage with a direct correlation in relation to the depth of anode. In line with the trend of hydrogen peroxide production, the phenol degradation percentage rises with the increase in anode depth. The highest percentage (93.69%) was achieved after 90 minutes with an anode depth of 10 mm, with an energy consumption rate of 718.5 kJ/mmol.

The movement of electrons in the liquid zone affected an increase in the current rate, which was easier than in the gas zone. The formation of the gas sheath is the beginning of plasma formation due to Joule heating levels (Gai, 2006; Jin et al., 2010; Saksono et al., 2013). With the deeper anode position, most of the energy was used for creating a continuous gas sheath, but the presence of hydrostatic pressure hindered gas stability. As a result, the electric current could flow easily to the anode, thus improving the conductivity. A smaller volume of energy was used for gas formation, due to position of anode that was close to the solution surface. Consequently, the plasma was formed and stabilized quickly due to the lower influence of hydrostatic pressure. The plasma stability can resist electrons effectively. Based on these phenomena, the anode position on the surface produces a lower energy consumption rate per mmol of phenol degraded than the anode depths of 5 mm and 10 mm, respectively (Figure 9).

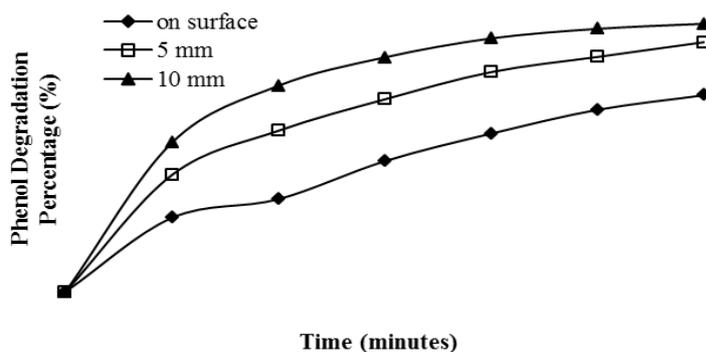


Figure 8 Phenol degradation percentage in the study of the anode depth effect with 0.03 M of Na_2SO_4 and 700 V

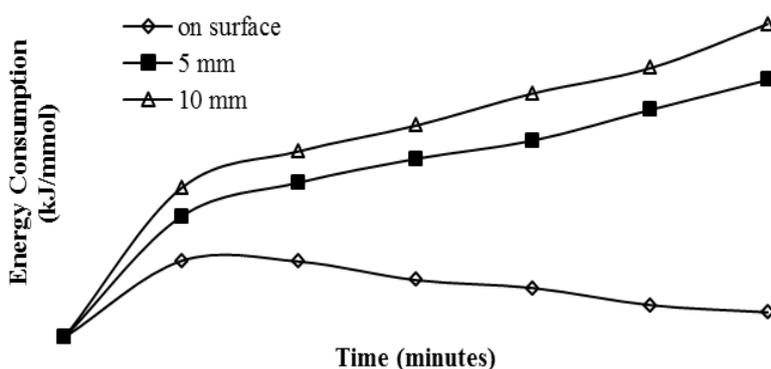


Figure 9 Energy consumption in the study of the anode depth effect of 0.03 M with Na_2SO_4 and 700 V

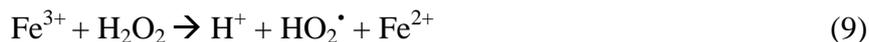
Despite resulting in a more significant rate of phenol degradation, the anode depth of 10 mm could not be recommended as the optimum parameter, since it caused damage to the anode connection. This condition triggers difficulty in temperature control and requires a higher rate of energy consumption. The anode depth of 5 mm is considered to be the best, with phenol degradation of 87.27% and the energy consumption of 590.2 kJ/mmol after 90 minutes.

3.2.4. Effect of Fe^{2+} presence

In this section, the effect of the presence of Fe^{2+} in the reactor will be discussed. A measure of 20 mg/L of Fe^{2+} ions, which was obtained from FeSO_4 salt, was added to the system. The electrolyte solution used 0.03 M of sodium sulfate. 700 V was determined as the operating condition.

Figure 101 shows the phenol degradation percentage in the study of the effect of Fe^{2+} presence. With the addition of Fe^{2+} ions, phenol degradation reached 92.57% after 15 minutes. This value was much higher than the degradation without the Fe^{2+} addition, which was 40.83% after 15 minutes. After 90 minutes, the phenol degradation percentage with and without addition of Fe^{2+} ions was 99.59% and 87.27%, respectively. The higher phenol degradation percentage with the presence of Fe^{2+} ions was obtained through the decomposition of hydrogen peroxide into hydroxyl radicals via Equations 7, 8, 9 and 10 (Gao et al., 2006):





With the presence of an excess hydroxyl radical, phenol was converted to a phenoxy radical and then it formed a dihydroxycyclohexadienyl radical. Furthermore, those radicals reacted with hydroxyl radicals, eventually to produce CO_2 and H_2O . Fe^{3+} ions could directly react with para- and ortho-hydroquinone, which are composed of phenol and its intermediate products. Orto-hydroquinone reacted with Fe^{3+} ions and formed benzoquinone as shown in Equation 11 (Wang & Jiang, 2009).

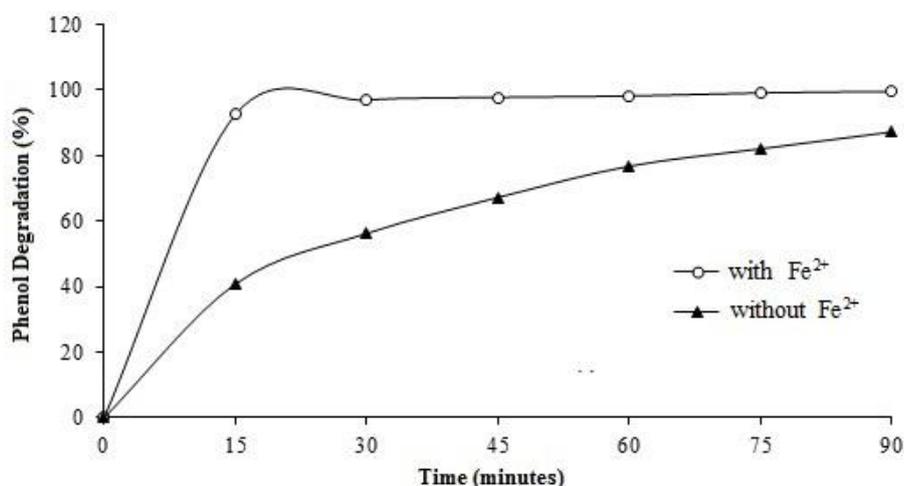
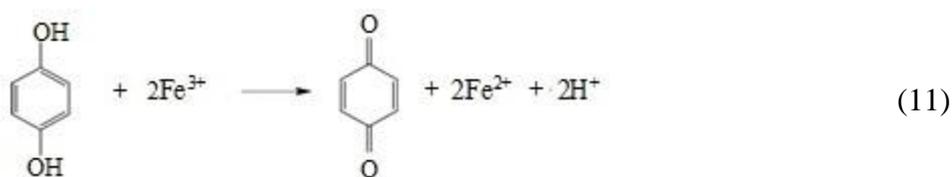


Figure 101 Phenol degradation percentage in the study of the effect of Fe^{2+} presence, 0.03 M of Na_2SO_4 , 700 V, and an anode depth of 5mm

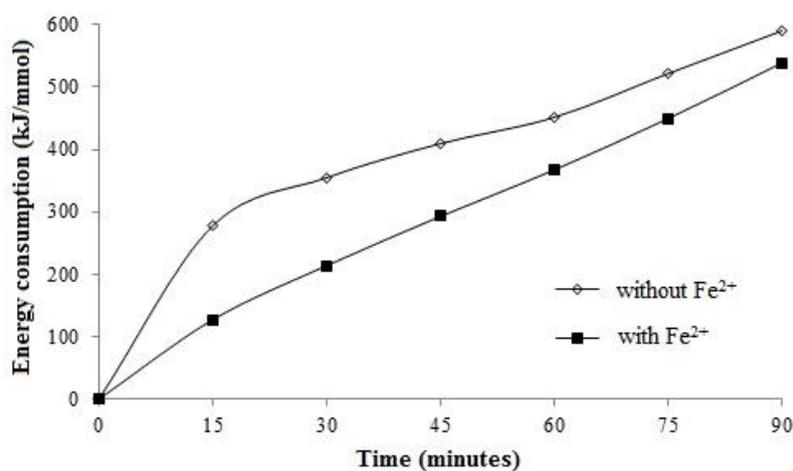


Figure 12 Energy consumption in the study of the effect of Fe^{2+} presence, 0.03 M of Na_2SO_4 , 700 V, and an anode depth of 5mm

4. CONCLUSION

This study has been successful in assessing the effect of voltage, electrolyte concentrations, the depth of anode, and the presence of Fe^{2+} ions to phenol degradation in wastewater by using a Contact Glow Discharge Electrolysis (CGDE) reactor. Phenol degradation was found to be higher when higher voltage rates, electrolyte concentration, and depth of anode were applied. The addition of Fe^{2+} ions has been proven to be effective to enhance the degradation process. The largest phenol degradation was achieved at 99.6% after 90 minutes of experimentation at 700 V, with 0.03 M of sodium sulfate as an electrolyte solution, with an anode depth of 5mm, and with the addition of 20 mg/L of Fe^{2+} ions.

5. ACKNOWLEDGEMENT

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6. REFERENCES

- Ceccato, P., Mention, E.P., Cavitation, I.D.E., Milieu, E.N., Condense, F., De, L.A.P., Queen, G., 2009. *Microplasmas De Cavitation En Milieu Fluide Condense: Filamentary Plasma Discharge Inside Water : Initiation and Propagation of a Plasma in a Dense Medium*. Paris
- Gai, K., 2006. Aqueous Diphenyl Degradation Induced by Plasma with Glow Discharge Electrolysis. *Journal of the Chinese Chemical Society*, Volume 53, pp. 627–632
- Gao, J., Yu, Y., Lu, Q., Yang, W., Li, Y., Pu, L., 2004. Plasma Degradation of 1-Naphthylamine by Glow-discharge Electrolysis. *Pakistan Journal of Biological Sciences*, Volume 7(10), pp. 1715–1720
- Gao, J., Yu, J., Li, Y., He, X., Bo, L., Pu, L., Yang, Z., 2006. Decoloration of Aqueous Brilliant Green by using Glow Discharge Electrolysis. *Journal of Hazardous Materials*, Volume 137, pp. 431–436
- Gao, J., Yu, J., Lu, Q., He, X., Yang, W., Li, Y., Yang, Z., 2008a. Decoloration of Alizarin Red S in Aqueous Solution by Glow Discharge Electrolysis. *Dyes and Pigments*, Volume 76(1), pp. 47–52
- Gao, J., Wang, A., Fu, Y., Wu, J., Ma, D., Guo, X., Li, Y., Yang, W., 2008b. Analysis of Energetic Species Caused by Contact Glow Discharge Electrolysis in Aqueous Solution. *Plasma Science and Technology*, Volume 10(1), pp. 30–38
- Jin, X., Bai, H., Wang, F., Wang, X., Wang, X., Ren, H., 2011. Plasma Degradation of Acid Orange 7 with Contact Glow Discharge Electrolysis. *IEEE Transactions on Plasma Science*, Volume 39(4), pp. 1099–1103
- Jin, X., Wang, X., Yue, J., Cai, Y., Zhang, H., 2010. *Electrochimica Acta* The effect of Electrolyte Constituents on Contact Glow Discharge Electrolysis. *Electrochimica Acta*, Volume 56(2), pp. 925–928
- Ranjit, M.S., Joshi, S., 2010. *Polymer Surface Modification using Novel Underwater Plasma (UWP) Technique*. BAM-Dissertationsreihe 59, Berlin
- Saksono, N., Adiwidodo, B.P., Karamah, E.F., Kartohardjono, S., 2013. Contact Glow Discharge Electrolysis System for Treatment of Wastewater Containing Ammonia. *Journal of Environmental Science and Technology*, Volume 6(1), pp. 41–49
- Saksono, N., Nugraha, I., Gozan, M., Bismo, S., 2014. Plasma Formation Energy and Hydroxyl Production on Contact Glow Discharge Electrolysis. *International Journal of Arts & Sciences*, Volume 07(03), pp. 71–77
- Saksono, N., Seratri, R.T., Muthia, R., Bismo, S., 2015. Phenol Degradation in Waste Water with Contact Glow Discharge Electrolysis (CGDE) System by using Sodium Sulfat

- Solution Conference: *The 14th International Conference on Qir (Quality in Research)*, 11-13 August 2015, Mataram, Lombok, Indonesia
- Slamet, Arbianti, R., Daryanto, 2005. Pengolahan Limbah Organik (Fenol) dan Logam Berat (Cr^{6+} atau Pt^{4+}) Secara Simultan Dengan Fotokatalis TiO_2 , ZnO-TiO_2 , dan CdS-TiO_2 . *Makara Teknologi*, Volume 9(2), pp. 66–71
- Wang, L., Jiang, X., 2009. Unusual Catalytic Effects of Iron Salts on Phenol Degradation by Glow Discharge Plasma in Aqueous Solution. *Journal of Hazardous Materials*, Volume 161(2–3), pp. 926–932